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REPORT

The Royal Society of Canada Expert Panel:

The Behaviour and Environmental Impacts of Crude Oil Released into Aqueous Environments

Fall 2015

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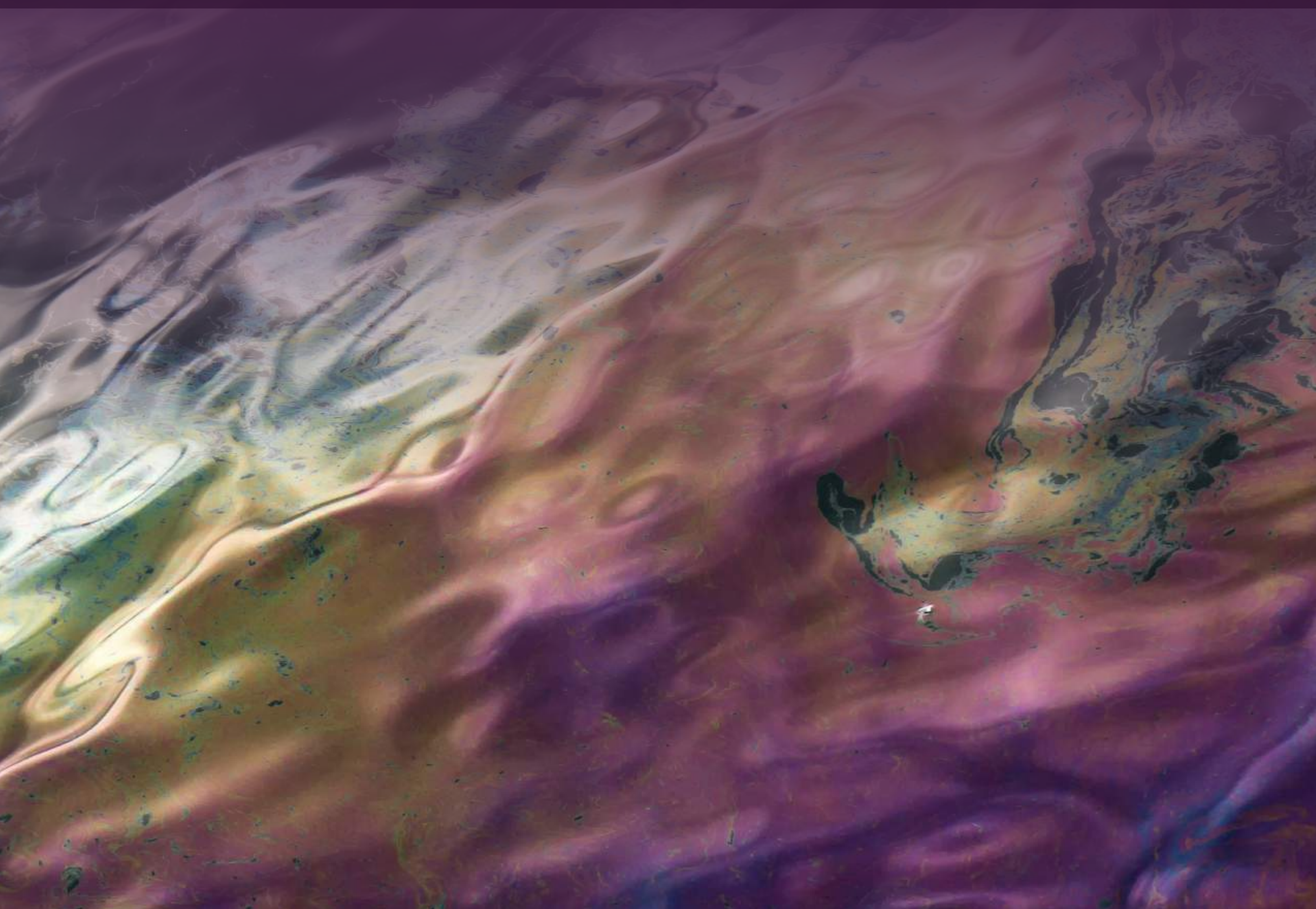

Behaviour and Environmental Impacts of Crude Oil Released into Aqueous Environments

An Expert Panel Report prepared at the request of
the Royal Society of Canada
for the Canadian Energy Pipeline Association
and the Canadian Association of Petroleum Producers

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The Royal Society of Canada Expert Panels

The Expert Panels of the Royal Society of Canada (RSC) are central to the society since its mission includes a charge to *"…advance knowledge, encourage integrated interdisciplinary understandings and address issues that are critical to Canadians"*.

RSC Expert Panels provide independent, timely and authoritative insights and advice to governments, industry, non-governmental organizations, and citizens. Topics for expert panels are selected, in part, on the benefit they are likely to receive from a critical assessment of existing knowledge from a wide range of disciplinary and sectorial perspectives. While the Society does not shy away from controversial topics, it does insist that there must be room for critical, balanced, scientific analysis that makes it possible to achieve a consensus document from a diverse group of experts. Topics where differences in opinion are based on belief systems that are not founded in informed science are not be appropriate for an RSC Expert Panel.

Not surprisingly, RSC Expert Panels are often commissioned (and funded) by organizations that may have a strong interest in the conclusions of the report. However, for a variety of reasons, they not only want to receive a report that is independent, balanced and objective, but they want that report to be seen to be so by other stakeholders.

To ensure that this is the case, the RSC Committee on Expert Panels has developed a rigorous set of procedures[1] that guide their work. These procedures include:

1. **Defining the Terms of Reference (TOR):** Other than writing a cheque, this is the only part of the Expert Panel process where the commissioning organization has significant input. The RSC 'Committee on Expert Panels' works with the funder to develop draft TOR describing the charge to the panel, ensuring that it is neither too narrow, nor too broad, and, in particular, that it does not direct the panel towards a pre-determined conclusion. Before the TOR are approved, they are discussed with experts from the relevant stakeholder communities and, if appropriate, modifications are made before final approval by the funder and the RSC.
2. **Selection of Panel members.** Panel selection is the responsibility of the Committee on Expert Panels and its Oversight Committee, and does not consult with the commissioning organization. Explicit effort is made to ensure diversity of both expertise and perspectives (bias) in the subject area. Prospective panelists are interviewed and complete 'conflict of interest declarations' before being selected. Panelists are not reimbursed for the considerable time and effort that they contribute to the work of RSC Expert Panels.
3. **Deliberations of the Panel and Report Preparation.** Panel deliberations are 'in Camera', with the exception of planned public hearings that are open to all. The panelists decide on the content of their submitted report and write it themselves. They are identified as the authors of the report (not the RSC), since RSC Expert Panels are reports to the RSC not from the RSC to the sponsor.
4. **Selection of Reviewers.** Selection of a Peer Review Monitor and the Peer Reviewers is also the responsibility of the Committee on Expert Panels and its Oversight Committee. The monitor manages the Peer Review process and is selected to ensure they have sufficient expertise to be comfortable in the content area, but have no conflict of interest or perception of bias. The peer review monitor works with the Panel Chair to ensure that all feedback from reviewers is carefully assessed and that appropriate revisions are made.
5. **Public Release of the Report.** The report is released to the media and public (on the RSC website[2]). No opportunity is given to the commissioning organization to request modifications of the report or its recommendations. However, the commissioning organization does receive a copy

[1] *See http://www.rsc.ca/en/expert-panels/information-about-expert-panels*
[2] *http://www.rsc.ca/en/expert-panels/rsc-reports*

of the report a few days before it is released so they have an opportunity to prepare responses to its content by the time the report is publically released.

6. **Ownership of the report.** The report belongs to the RSC. However, the RSC typically gives written permission to the panelists / authors to rework the document and submit portions of it to academic journals or other publications if they wish to do so.

Organizations or individuals interested in discussing opportunities for the RSC to carry out an Expert Panel on a topic of interest to them should contact the Chair of the Committee on Expert Panels at epsec@rsc-src.ca.

Preface

Canadians are among the highest per capita consumers of oil in the world, equivalent to about 25 barrels—or about 4000 litres—of oil per person per year.

Canada is also one of the world's only developed economies that produces more oil than it demands for domestic consumption, currently about 1.5 times more (about 6000 L/person/yr). In recent years, the rate of oil production has been increasing by about 5% per year, primarily through the growth of Alberta's oil sands.

To meet both domestic and international demand, the oil must be moved by pipeline, rail, tanker trucks or ship from where it is recovered to where it will be refined and ultimately used. In recent years, the energy industries have been developing plans and seeking permission to expand or modify their transportation networks, especially those involving pipelines. Keystone XL, Northern Gateway, Trans-Mountain, Line 9 Reversal and Canada East are names of pipeline projects that have regularly been a regular feature in the news.

Hot-button topics at the forefront of those concerned with these pipeline projects include questions about the consequences of accidental spills of crude oil into aquatic ecosystems. *Do we have sufficient knowledge about how crude oils behave when released into fresh waters, estuaries or oceans to develop effective strategies for spill preparedness, spill response and remediation? What are the gaps in knowledge and how should research insights inform policies, regulations and practices in this area?*

Among the conditions for the approval of the Gateway project, the National Energy Board required the applicants to establish '*a research program regarding the behavior and cleanup (including recovery) of heavy oils spilled in freshwater and marine aquatic environments' (Condition 169).*[3] In mid 2014, the Royal Society of Canada's (RSCs) Committee on Expert Panels was approached about carrying out an independent, arm's length assessment of the state of the science in this area.

Since the prospective funders of this panel (Canadian Energy Pipeline Association (CEPA) and the Canadian Association of Petroleum Producers (CAPP)) might be perceived to have a strong interest in the outcome of the work, the Committee on Expert Panels was especially rigorous in following its procedures (see previous pages) to ensure an independent, balanced and objective report.

CEPA and CAPP suggested the initial Terms of Reference, and were receptive to changes in those terms following RSC preliminary consultation with diverse experts. Neither CEPA nor CAPP (or their membership) had any input into the selection of panelists or reviewers, or into the recommendations of this panel.

The RSC thanks CEPA and CAPP for their support of this project and appreciates their professional approach that let us go about our work without interference of any kind.

We wish to thank the Panel Chair, Dr. Ken Lee and his fellow panelists (listed on the next page) for volunteering their time and expertise to prepare this report. This comprehensive and high quality report did not emerge without exceptional effort. Thank you!

We also want to thank the Peer Review Monitor, Dr. Robie Macdonald, FRSC and eight expert reviewers (listed on the next page), who provided extensive comments, criticisms and suggestions on the first draft of this report. The additions and clarifications that resulted from their feedback significantly added to the quality of the document.

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[3] *Report of the Joint Review Panel for the Enbridge Northern Gateway Project (Dec 19, 2013) Conditions 169, 170, and 193* *http://gatewaypanel.review-examen.gc.ca/clf-nsi/hm-eng.html*

Finally, a special thank you to Russel MacDonald from the RSC office in Ottawa and Lisa Isaacman from Bonnyville who provided administrative and editorial support for the work of the panel and to the members of the Committee on Expert Panels and its Oversight Committee that were involved in selecting the panelists and reviewers.

David B Layzell, PhD, FRSC
Chair, Committee on Expert Panels

Graham Bell, PhD, FRSC
President, Royal Society of Canada

RSC Committee on Expert Panels (2014-15)

David B. Layzell, PhD, FRSC. (Chair) Professor and Director, Canadian Energy Systems Analysis Research (CESAR) Initiative, University of Calgary, Calgary, Alberta

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John P. Smol, OC, PhD, FRSC (Member-at-Large) Canada Research Chair in Environmental Change, Department of Biology, Queen's University, Kingston, Ontario

Panel Members

Dr. Kenneth Lee (Chair) is the Director of Oceans and Atmosphere , Commonwealth Scientific and Industrial Research Organisation (CSIRO) in Perth, Australia. This research group provides large-scale multidisciplinary science to support the management and sustainable development of Australia's marine and atmospheric resources. The founding Executive Director of the Centre for Offshore Oil, Gas and Energy Research (COOGER), Department of Fisheries and Oceans, Canada, he received the "Prix d'Excellence" for exemplary contributions in science (Fisheries and Oceans Canada) and the Government of Canada's "Federal Partners in Technology Transfer - Leadership Award" for technology transfer from a federal laboratory to the private sector.

Dr. Michel Boufadel is Professor of Environmental Engineering and Director of the Center for Natural Resources Development and Protection at the New Jersey Institute of Technology. He is a Professional Engineer in Pennsylvania and New Jersey, a Board Certified Professional Engineer, and a Fellow in the American Society of Civil Engineers.

Dr. Bing Chen is the leader of the Northern Region Persistent Organic Pollution Control (NRPOP) Laboratory, Associate Professor of Civil Engineering with the Faculty of Engineering and Applied Science, and Chair of the Environmental Systems Engineering & Management Program at the Memorial University of Newfoundland, St. John's, NL, Canada.

Dr. Julia Foght is Professor Emerita at the University of Alberta, where she was a Professor of Petroleum Microbiology in the Department of Biological Sciences from 1994 to 2014. Julia received the Petro-Canada Young Innovators Award in 2001, a McCalla Professorship in 2011 from the University of Alberta, and in 2014 the Alberta Science & Technology Foundation (ASTech) award in Innovation in Oil Sands Research.

Dr. Peter V. Hodson is an ecotoxicologist and Professor Emeritus with Biology and the School of Environmental Studies at Queen's University, and a Past President of the Society of Environmental Toxicology and Chemistry. He began his career with Fisheries and Oceans and his research contributed to the development of Great Lakes Water Quality Objectives under the 1972 Canada-US Great Lakes Water Quality Agreement and to the development of Federal Environmental Effects Monitoring Programs for the pulp and paper sector. Since 1995, he has focused on the toxicity of petroleum hydrocarbons to fish embryonic development and the role of contaminants in the decline of American eel abundance in Lake Ontario.

Dr. Stella Swanson is an aquatic ecologist and risk assessment specialist with Swanson Environmental Strategies that she operates out of Calgary, AB and Fernie, BC. Her 30-year career has included management of the Aquatic Biology Group at the Saskatchewan Research Council, and consulting positions with SENTAR Consultants (now Stantec) and Golder Associates Ltd. (where she attained the position of Principal).

Dr. Albert D. Venosa is the former Director of the Land Remediation and Pollution Control Division (LRPCD), one of the five divisions within the National Risk Management Research Laboratory (NRMRL), Cincinnati, OH, in the United States Environmental Protection Agency's (U.S. EPA's) Office of Research and Development. As an environmental scientist and microbiologist, he managed EPA's oil spill research program from 1990 until 2014, during which time he became an expert in bioremediation and dispersant research and other response technologies. Prior to that, he led U.S. EPA's national program on wastewater disinfection research for 13 years. He is now retired after 45 years of government service.

Support of the Work of the Panel

We are grateful to the following individuals:

Christopher Stone, (Calgary, Alberta) for his assistance in compiling references and identifying prospective panellists and reviewers.

Lisa Isaacman, (Bonnyville, Alberta) for her administrative work with the panel and editorial work on the report

Russel MacDonald, (Officer, Expert Panels & the College, the Royal Society of Canada, Ottawa, Ontario) for his assistance in managing the funds, helping with logistics, taking notes and producing the final report.

Peter Christie (Science Writer, Kingston, Ontario) for his assistance with some critical sections of the report.

Peer Reviewers

The Royal Society of Canada would like to acknowledge and sincerely thank the Peer Review Monitor and eight peer reviewers who provided valuable, detailed input into the first draft of this report. The following reviewers have permitted the RSC to release their names:

Dr. Robie Macdonald, FRSC, (*Peer Review Monitor)* Fisheries and Oceans Canada, Victoria, British Columbia

Dr. Ronald Atlas, Department of Biology, University of Louisville, Louisville, Kentucky

Dr. Tracy Collier, Science Director, Puget Sound Partnership, Bainbridge Island, Washington

Dr. Merv Fingas, Independent Consultant, Edmonton, Alberta

Dr. Jeffrey Hutchings, FRSC, Department of Biology, Dalhousie University, Nova Scotia

Dr. Don Mackay, OC, Department of Chemistry, Trent University, Peterborough, Ontario

Dr. Jacqueline Michel, Research Planning, Inc., Columbia, South Carolina

Dr. Jeffrey Short, JWS Consulting, Juneau, Alaska

The peer reviewers provided many very constructive comments, but they were not asked to endorse the conclusions or recommendations, nor did they see the final draft of the report before it was released. The identification of reviewers is done to recognize them for their valuable contributions and does not imply that they endorse the report or agree with its content. Responsibility for the final content of this report rests entirely with the Panel.

TABLE OF CONTENTS

LIST OF ACRONYMS

ACR: acute-chronic ratio
ADEC: Alaska's Department of Environmental Conservation
AER: Alberta Energy Regulator; Alberta Government agency
AhR: aryl hydrocarbon receptor.
AMOP: Arctic and Marine Oilspill Program; an international technical forum held in Canada since 1978
ANS: Alaska North Slope crude oil
API: American Petroleum Institute
AMRA: Arctic Marine Risk Assessment
ASMB: Alberta Sweet Mixed Blend
ASTM: formerly the American Society for Testing and Materials; an international organization that publishes consensus technical standards and analytical methods
AUV: autonomous underwater vehicle
BaP: Benzo(a)pyrene, a 5-ringed PAH
BAT: best available technology
bbl: barrel; a unit of volume that varies between countries and for different products. A barrel of crude oil is equivalent to 159 litres.
BSEE: Bureau of Safety and Environmental Enforcement, U.S. Department of the Interior
BOEM: Bureau of Ocean Energy Management, U.S. Department of the Interior
BSD: blue sac disease
BTEX: benzene, toluene, ethylbenzene and xylene isomers: monoaromatic hydrocarbons commonly present in petroleum, particularly in light crude oils and diluents
CAPP: Canadian Association of Petroleum Producers
CEPA: Canadian Energy Pipeline Association
CEWAF: chemically-enhanced water-accommodated fraction of oil
CNRL: Canadian Natural Resources Ltd.; an oil sands mining company
CROSERF: Chemical Response to Oil Spills Ecological Effects Research Forum
DFO: Department of Fisheries and Oceans (Canada)
DWH: Deepwater Horizon; subsurface blowout of very light crude oil in the Gulf of Mexico in 2010
EBSA: Ecologically and Biologically Significant Areas
EC50: median effective concentration
ECRC-SIMEC: Eastern Canada Response Corporation, certified by Transport Canada to respond to oil spills from tankers and oil-handling facilities in the Great Lakes, Quebec and Atlantic regions.
EDCF: effects-driven-chemical-fractionation
EEM: environmental effects monitoring
EEPP: Energy East Pipeline Project
EIA: environmental impact assessment
ERA: ecological risk assessment
ERCB: Energy Resources Conservation Board (Alberta), now replaced by AER
ESI: environmental sensitivity index
EVOS: *Exxon Valdez* Oil Spill; spill of Alaska North Slope crude oil into Prince William Sound in 1989
FID: flame ionization detector
GC: gas chromatography
HEWAF: high energy water-accommodated fraction of oil

HFO: heavy fuel oil, e.g., Bunker C
HLB: Hydrophilic-lipophilic balance
HMW: high molecular weight
HPLC: high performance liquid chromatography
IFO: intermediate fuel oil, e.g., IFO 180
ISB: *in situ* burning (of oil on water)
ITOPF: International Tanker Owners Pollution Federation; a not-for-profit marine ship pollution response advisory body
K_{ow}: octanol-water partition coefficient
LC50: median lethal concentration
LMW: low molecular weight
MC-252: Macondo crude oil
MESA: Medium South American crude oil
MoA: Mode of action
MOA: Mechanism of action
MMW: medium molecular weight
MNA: monitored natural attenuation
MS: mass spectrometry
NAS: National Academy of Sciences (United States)
NAs: naphthenic acids
NEB: National Energy Board (Canada)
NEBA: net environmental benefits analysis
NGP: Northern Gateway Pipeline
NOAA: National Oceanographic and Atmospheric Administration, U.S. Department of the Interior
NRC: National Research Council (in both Canada and the United States)
NTSB: National Transportation Safety Board (United States)
OHCB: obligate hydrocarbonoclastic bacteria
OMA: oil-mineral aggregate
OPA: oil-particle aggregate
PAH: polycyclic aromatic hydrocarbon
PBCO: Prudhoe Bay Crude Oil
PHMSA: U.S. Pipeline and Hazardous Materials Safety Administration
ppm: parts-per-million; a unit of concentration; e.g., mg/L or mg/kg.
ppt: parts-per-thousand; a unit of concentration; e.g., g/L or g/kg.
PTO: pole treating oil
RO: response organization
ROS: reactive oxygen species
ROV: remotely operated vehicle
SAGD: steam-assisted gravity drainage
SAR: synthetic aperture radar
SARA: an acronym for the four major chemical classes of petroleum constituents: saturates, aromatics, resins and asphaltenes
SCAT: shoreline cleanup and assessment technique
SCO: synthetic crude oil

SSD: species sensitivity distributions
TAN: total acid number
TCRA: Transport Canada Risk Assessment
TLM: target lipid model
TMPEP: Trans Mountain Pipeline Expansion Project
TPAH: total polycyclic aromatic hydrocarbon
TPH: total petroleum hydrocarbon
TSB: Transportation Safety Board of Canada
TSPS: Tanker Safety Panel Secretariat, Transport Canada
TU: toxic unit
UCM: unresolved complex mixture
UME: unusual mortality event
VEC: valued ecosystem component
U.S. EPA: United States Environmental Protection Agency
USGS: U.S. Geological Survey
VOCs: volatile organic compounds
WAF: water-accommodated fraction of oil
WCMRC: Western Canada Marine Response Corporation
WSF: water-soluble fraction of oil

Glossary of Terms

Acute-chronic ratio: the ratio of the acute and chronic toxicity values for a given compound, usually the average of the ratios for a variety of species; used to estimate the chronic toxicity of a compound or a mixture of compounds, from the measured or modeled acute toxicity when no chronic toxicity data are available.

Alberta Sweet Mixed Blend: a major blend of light crude oil exported from Alberta; also used by Environment Canada as a reference for laboratory tests.

Annual Exceedance Probability: the chance or probability of a natural hazard event (usually a rainfall or flooding event) occurring annually and is usually expressed as a percentage. Bigger rainfall events occur (are exceeded) less often and will therefore have a lesser annual probability.

Aromatics: class of hydrocarbons comprising one or more benzene ring structures having alternating double bonds; may have one or more alkyl side chains in various positions, but no heteroatoms.

Aryl hydrocarbon receptor: a cellular protein that binds planar or plate-like polycyclic aromatic compounds with a shape and dimensions that resemble 2,3,7,8 tetrachorodibenzo(p)dioxin.

Asphaltenes: class of petroleum compounds of high molecular weight and complexity; defined as the oil fraction that precipitates in low molecular weight *n*-alkanes (e.g., C5-C7) but is soluble in toluene.

Bioaccumulation (or bioconcentration): the tendency of substances to accumulate in the body of organisms; the net uptake from their diet, respiration or transfer across skin and loss due to excretion or metabolism. The bioaccumulation factor (BAF) or bioconcentration factor (BCF) is the ratio of concentrations in tissue to concentrations in a source, i.e., water or diet.

Bioavailability (or biological availability): compound that is in a physical or chemical form that can be assimilated by a living organism; also, the proportion of a chemical in an environmental compartment (e.g., water) that can be taken up by an organism.

Biodegradation: a natural process of microbial transformation of chemicals, such as oil under aerobic or anaerobic conditions; oil biodegradation usually requires nutrients, such as nitrogen and phosphorus; transformation may be complete, producing water, carbon dioxide and/or methane, or incomplete, producing partially-oxidized chemicals.

Biomagnification: a food chain or food web phenomenon whereby a substance or element increases in concentration at successive trophic levels; occurs when a substance is persistent and is accumulated from the diet faster than it is lost due to excretion or metabolism.

Biomarkers: a term used in two different ways, depending upon discipline. In petroleum chemistry, a biomarker is a relic chemical relating its presence to the original biological source (microbial, plant or animal); biomarkers are usually poorly or non-biodegradable and so persist in the oil, enabling their use as internal standards in petroleum analysis. In environmental toxicology, a biomarker is a biochemical process, product or cellular response that indicates the organism's exposure to a pollutant and/or the toxic effects of the pollutant.

Bioremediation: an intervention strategy to enhance biodegradation of spilled oil (or other contaminants), ranging from no remedial action other than monitoring (**natural attenuation**) to nutrient addition (**biostimulation**) to inoculation with competent microbial communities (**bioaugmentation**).

Bitumen: heaviest class of petroleum, having high viscosity and density; widely considered to represent the residue from lighter oils that have undergone biodegradation over geological time.

Blue sac disease: a disease syndrome of fish embryos caused by a variety of environmental stresses, including exposure to PAH and to alkyl PAH.

C_n: a molecule, such as a hydrocarbon, having *n* carbon atoms.

Chemically-enhanced water-accommodated fraction of oil (CEWAF): a solution of hydrocarbons and a suspension of oil droplets created when a chemical dispersant is added to oil and water with stirring. See also WAF and HEWAF.

Conventional crude oil: commonly defined as liquid petroleum that flows in the reservoir and in pipelines and is recovered from traditional oil wells using established methods, including primary recovery and water flooding (e.g., condensates, light and medium crude oils), versus unconventional crude oils.

Crude oil: synonymous with petroleum; a naturally-occurring and typically liquid complex mixture of thousands of different hydrocarbon and non-hydrocarbon molecules.

CYP1A: a member of the cytochrome P_{450} family of proteins; an enzyme of vertebrates, including fish, birds and mammals, that catalyzes the addition of oxygen to double bonds as a first step in the metabolism and excretion of PAHs.

cyp1a: the gene that codes for CYP1A proteins.

Dilbit: bitumen diluted with a lighter petroleum class, such as condensate or naphtha, typically 70% bitumen and 30% diluent; also see Synbit.

Dispersion: suspension of oil droplets in water accomplished by natural wind and wave action, production of biological materials (biosurfactants) and/or chemical dispersant formulations.

Dispersant: a chemical or mixture of chemicals applied, for example, to an oil spill to disperse the oil phase into small droplets in the water phase.

EC50: the concentration of a substance that causes sublethal effects on the median or 50^{th} percentile organism tested within a specified exposure time (e.g., 14 d EC50)

Effects-driven-chemical-fractionation (EDCF): the step-wise fractionation, toxicity testing and chemical analysis of complex mixtures of compounds to isolate and identify the constituents responsible for the toxic effects of the whole mixture.

Ecological risk assessment: process for analyzing and evaluating the possibility of adverse ecological effects caused by environmental pollutants.

Emulsification: formation of water droplets in an oil matrix (water-in-oil) or conversely oil droplets in a water matrix (oil-in-water) achieved by the action of agitation, such as wind and wave activity; can be unstable, separating into oil and water phases again soon after formation, or stable for months or years (e.g., 'chocolate mousse', a water-in-oil emulsion).

Environmental impact assessment: the process of measuring or estimating the environmental effects of pollutants, such as oil spills, relative to conditions at a reference site or to a time prior to a spill.

Evaporation: the physical loss of low molecular weight components of an oil to the atmosphere by volatilization.

Flame ionization detector (FID): used with analytical instruments like gas chromatographs to detect components of petroleum by combustion ionization, hence GC-FID

Fracking: see hydraulic fracturing.

Gas chromatography (GC): an analytical method used to characterize petroleum components; GC is combined with different detection methods, hence GC-FID, GC-MS, etc.

HEWAF: A solution of hydrocarbons and a suspension of oil droplets created when oil and water are mixed by high energy agitation. See also WAF and CEWAF.

Heteroatom: in petroleum, an atom such as nitrogen, sulfur and/or oxygen that is part of a hydrocarbon skeleton, such as found in the Resins fraction of crude oils

High molecular weight (HMW): relative term referring to the molecular mass of chemicals; in oil, asphaltenes would be typical of HMW compounds.

High performance liquid chromatography (HPLC): an analytical method for separating chemicals in solution.

Hydrocarbon: a chemical that is composed of only carbon and hydrogen; chemicals containing heteroatoms, such as nitrogen, sulfur and/or oxygen, are not hydrocarbons, even though they may petroleum constituents.

Hydraulic fracturing: also known as fracking'; an unconventional method for recovering liquid petroleum from shale oil deposits that otherwise would not release the gas and/or fluid in the reservoir.

Hydrogen sulfide (H_2S): a toxic, flammable and corrosive gas sometimes associated with petroleum.

Hydrophilic-lipophilic balance (HLB): a measure of the properties of dispersants and surface-active agents at the interface of polar and non-polar liquids, such as oil and water. The higher the surfactant HLB value, the more hydrophilic (water-loving) it is.

Hyporheic flow: the perculating flow of water through the sand, gravel, sediment and other permeable soils under and beside the streambed.

Intermediate fuel oil: the heaviest commercial class of refined petroleum diluted with a lighter refined product, commonly burned in furnaces, boilers or ship engines; e.g., IFO 180.

Isomers: chemicals that have the same molecular formula (i.e., elemental composition) but different structures; may also have different properties, including water solubility, biodegradability and toxicity.

K_{ow}: the partition coefficient describing the equilibrium concentration ratio of a dissolved chemical in octanol versus in water, in a two-phase system at a specific temperature; used in prediction of toxicity.

LC50: the concentration of a substance toxic to the median or 50^{th} percentile organism tested within a specified exposure time (e.g., 96 h LC50).

Lacustrine: relating to lakes.

Low molecular weight: relative terms referring to the molecular mass of chemicals; in oil, monoaromatics and aliphatics up to C_{10} would be typical of these compounds.

Mass spectrometry: an analytical method used for detailed characterization of petroleum components, often in combination with GC, hence GC-MS.

Mechanism of action (MOA): describes a functional or anatomical change at the molecular level.

Medium molecular weight: relative terms referring to the molecular mass of chemicals; in oil, 3 to 6-ringed PAH and aliphatics up to C_{20} would be typical of MMW compounds.

Mineralization: complete oxidation of a compound (e.g., hydrocarbon) to carbon dioxide and water; may be accomplished by a single species of organism or by a community of microbes.

Mode of action (MoA): describes a functional or anatomical change at the cellular level, resulting from the exposure of a living organism to a substance.

Monitored natural attenuation: a remediation strategy in which there is no intervention but the site is monitored using various parameters.

Monoaromatics: aromatic hydrocarbons having only a single benzene ring; may also have one or more alkyl side chains.

Naphthenic acids: a class of polar petroleum compounds that contributes to aquatic toxicity and to petroleum infrastructure corrosion by contributing to TAN.

Natural attenuation: remediation of a contaminated site by natural processes alone, without human intervention; also see monitored natural attenuation.

Obligate hydrocarbonoclastic bacteria: bacteria that have adapted to use hydrocarbons as their sole source of carbon and energy for growth and metabolism.

Oil-mineral aggregate (OMA): floc containing oil adhering to mineral particle, which may float, sink or re-suspend in a water column; a process initially referred to as clay-oil flocculation.

Oil-particle aggregate (OPA): more general term than OMA, describing oil adhering to particles that may be inorganic (minerals) and/or organic, including microbial cells.

Partitioning: the diffusion of compounds between two immiscible liquid phases, including water and oil droplets and water and lipid membranes.

Petroleum: synonymous with crude oil; a naturally-occurring complex mixture of thousands of different hydrocarbon and non-hydrocarbon molecules.

Photooxidation: oxidation due to the influence of photic energy, usually from UV light.

Photo-enhanced toxicity: increased toxicity due to photooxidation *in vivo.*

Polycyclic aromatic hydrocarbons: (PAHs) a subclass of aromatic hydrocarbons having two or more fused benzene rings; may also have one or more alkyl side chains, generating large suites of isomers; some are considered ‘priority pollutants’ because of their toxicity and/or potential carcinogenicity.

Reactive oxygen species (ROS): a group of chemicals that can cause cellular damage due to their high reactivity; are released during reactions that add oxygen to double bonds. In turn, ROS can react with double bonds in lipids, proteins and nucleic acids to change their structure and function.

Resins: a solubility class of poorly characterized, polar petroleum compounds in which each molecule contains one or more atoms of nitrogen, sulphur and/or oxygen in a hydrocarbon skeleton.

Riparian: related to being situated on or dwelling on the bank of a river or other body of water, such as a lake or tidewater.

Riverine: relating to lakes.

SAGD (steam-assisted gravity drainage): an unconventional *in situ* method to produce bitumen from deep oil sands deposits without surface mining operations.

Saturates: class of hydrocarbons that may be straight-chain, branched-chain or cyclic, in which all carbon atoms have single bonds to either carbon or hydrogen.

Shale oil: also known as ‘tight oil’ (but not to be confused with ‘oil shale’); liquid petroleum that is produced from shale oil reservoirs, typically by hydraulic fracturing methods.

Sour crude: petroleum that has a >1% total sulfur content that may be present as hydrogen sulfide and/or as organic forms of sulfur in a hydrocarbon backbone.

Species sensitivity distributions (SSD): compare the cumulative proportion of species (percentile) affected by a chemical to a toxicity endpoint measured for each species (e.g., 96 h LC50); SSD model assumes that species sensitivity is randomly distributed.

Sweet crude: petroleum with low total sulphur content, variously defined as <0.5% or <1% sulphur.

Synbit: bitumen diluted with synthetic crude oil, typically at 1:1 ratio.

Synthetic crude oil: a partially-refined fraction of bitumen; may be used as a diluent to make dilbit for transport.

Target lipid model: estimates the aqueous concentration of organic compounds, or mixtures of organic compounds, that cause toxicity by narcosis.

Total acid number (TAN): a measure of the acidity determined by the amount of potassium hydroxide in milligrams that is needed to neutralize the acids (typically naphthenic acids) in one gram of oil; used by refineries as an indicator of potential corrosion and scale production.

Total petroleum hydrocarbons (TPHs): the total mass of all hydrocarbons in an oil or environmental sample, including the volatile and extractable (non-volatile) hydrocarbons; may be further defined by stating the analytical method used, e.g., GC-detectable TPH or TPH-F (TPH measured by fluorescence), which vary in their rigour.

Total polycyclic aromatic hydrocarbons (TPAHs): including alkyl-PAHs and parent (unsubstituted) PAHs; the sum of all concentrations of PAHs measured by GC-MS.

Toxic unit (TU): ratio between the concentration of a compound in water and a toxic endpoint (e.g., 96 h LC50).

Unconventional crude oils: petroleum that does not flow readily in the reservoir and/or must be produced by using unconventional methods, such as surface mining of shallow bitumen deposits, steam-assisted gravity drainage (SAGD) for *in situ* extraction of deep bitumen deposits, cyclic steam injection for heavy oils, or horizontal drilling with hydraulic fracturing for recovery of light shale oils.

Unresolved complex mixture (UCM): petroleum constituents that are not resolved by conventional GC and appear as a ‘hump’ in the gas chromatogram; comprises many hundreds or thousands of unresolved isomers.

Unusual mortality event (UME): term coined by NOAA to describe a greater-than-usual rate of mortality of marine mammals.

Volatile organic compounds (VOCs): chemicals having high vapour pressure at room temperature (and corresponding low boiling point) that therefore tend to evaporate or sublimate into the air; for example, BTEX.

Water-accommodated fraction of oil (WAF): hydrocarbons that will partition from oil to water during gentle stirring or mixing; may contain droplets, in contrast to water-soluble fractions (WSF).

Water-soluble fraction of oil (WSF): aqueous solution of hydrocarbons that partition from oil; does not include droplet or particulate oil. See also CEWAF and HEWAF.

Weathering: a suite of changes in spilled oil composition and properties brought about by a variety of environmental processes including spreading, evaporation, photooxidation, dissolution, emulsification and biodegradation, among others.

EXECUTIVE SUMMARY

A panel of leading experts on oil chemistry, behaviour and toxicity reviewed the current science relevant to potential oil spills into Canadian marine waters, lakes, waterways and wetlands. The review, which examined spill impacts and oil spill responses for the full spectrum of crude oil types (including bitumen, diluted bitumen and other unconventional oils), is among the most comprehensive of its kind. It surveyed scientific literature, key reports and selected oil spill case studies, including tanker spills, an ocean rig blowout, pipeline spills and train derailments. The Panel also consulted industry, government and environmental stakeholders across the country.

The Panel found that the dozens of crude oil types transported in Canada exist along a chemical continuum, from light oils to bitumen and heavy fuels, and the unique properties of each of these oil types (their chemical 'fingerprints') determine how readily spilled oil spreads, sinks, disperses, impacts aquatic organisms, including wildlife, and what proportion ultimately degrades in the environment. Despite the importance of oil type, the Panel concluded that the overall impact of an oil spill, including the effectiveness of an oil spill response, depends mainly on the environment and conditions (weather, waves, etc.) where the spill takes place and the time lost before remedial operations.

The Panel recommends that this critical research should concentrate on seven general high-priority research needs:

High-Priority Research Needs Identified by the Expert Panel

1. *Research is needed to better understand the environmental impact of spilled crude oil in high-risk and poorly understood areas, such as Arctic waters, the deep ocean and shores or inland rivers and wetlands.*
2. *Research is needed to increase the understanding of effects of oil spills on aquatic life and wildlife at the population, community and ecosystem levels.*
3. *A national, priority-directed program of baseline research and monitoring is needed to develop an understanding of the environmental and ecological characteristics of areas that may be affected by oil spills in the future and to identify any unique sensitivity to oil effects.*
4. *A program of controlled field research is needed to better understand spill behaviour and effects across a spectrum of crude oil types in different ecosystems and conditions.*
5. *Research is needed to investigate the efficacy of spill responses and to take full advantage of 'spills of opportunity'.*
6. *Research is needed to improve spill prevention and develop/apply response decision support systems to ensure sound response decisions and effectiveness.*
7. *Research is needed to update and refine risk assessment protocols for oil spills in Canada.*

Timeframes for conduct of the recommended studies are provided by the Panel. This executive summary highlights these central conclusions and other priority research questions identified in the report chapters.

What happens when crude oil spills into oceans, into lakes or into the waterways that wind through our forests, fields and towns? Canada produces some three million barrels of oil every day, importing hundreds of thousands more, and all of it travels somewhere. In this lake-and-river-rich country with the world's longest coastline, crossing water is inevitable when oil is transported. Whether in vast tankers traversing the sea or in pipelines, trucks and trains passing countless rivers, lakes and wetlands, oil is on the move. Some is drilled directly from the seabed where offshore rigs perch above ocean waves.

Meanwhile, accidents happen. Headline-grabbing calamities, such as the Deepwater Horizon blowout in the Gulf of Mexico in 2010, the *Exxon Valdez* spill off Alaska in 1989 and the *Arrow* spill off the coast of Nova Scotia in 1970, are periodic reminders that oil spills can shock the environment, the economy and the communities affected by them—at least in the short-term. Water is fouled. Wildlife is tarred. Fisheries and other industries struggle to recover.

The good news is that transporting oil at sea is safer than it has ever been. According to the International Tanker Owners Pollution Federation, large tanker spills occurred almost 14 times more often during the 1970s on average than they do today. Undersea blowouts during oil production and exploration are also rare (although Canadian offshore exploration and drilling is expected to increase). Less known is how much oil spilled from pipelines, trains and trucks reaches our lakes, rivers and wetlands (where oil can become trapped and remain concentrated causing more harm or creating more concern because towns and cities are nearby). However, while big oil spills from grounded tankers, oil rigs, pipeline ruptures or train wrecks are guaranteed newsmakers, in truth most of the oil-related chemicals that make it into our oceans arrive from natural seepage, routine tanker maintenance and runoff from land.

Even so, the potential impact of spills into Canadian waters during the transport of oil can be profound.

The Royal Society of Canada Expert Panel report addresses this impact. Its purpose is to better understand what we know and, perhaps more importantly, what we need to find out. Chief among the report's aims is to provide a roadmap to research questions concerning how crude oils, including diluted bitumen and other unconventional oils, behave and how they affect ecosystems and communities after spilling into the changeable and weather-affected environments of Canada's vast marine and inland waters.

The Expert Panel has highlighted hundreds of conclusions and identified a long list of research needs in its extensive report. This executive summary highlights only the most pressing of these research priorities. Answers to these research questions are considered by the Panel to be essential for equipping policy makers, oil industry decision makers, oil spill responders and other Canadians with critical tools to better anticipate spills and their consequences and to better protect Canada's marine and inland waters from the adverse effects of spilled oil. The Panel has consolidated seven general, high-priority research needs (see the box above) in this executive summary from hundreds of research priorities identified in the report chapters. The rationale for these research needs, and more detailed descriptions, can be found within the report itself.

CHAPTER 1: INTRODUCTION

The Royal Society of Canada (RSC) Expert Panel was established in response to a request from the Canadian Energy Pipeline Association (CEPA) and the Canadian Association of Petroleum Producers (CAPP). The request was the result of a widespread recognition within industry, governments and elsewhere that Canadians should know what to expect in the event of an accidental spill, and that those who move oil and respond to spills have the information they need to protect our environment, economy and communities across the country.

The Panel, composed of international experts on oil chemistry, behaviour and toxicity, reviewed the current science relevant to crude oils spilled into Canadian marine waters, lakes, waterways and wetlands. (Spills of gasoline, diesel and other refined fuels were not considered.) The Panel relied on scientific literature, key reports and selected oil spill case studies, including well-known tanker spills (e.g., the *Arrow* spill in 1970 and the *Exxon Valdez* spill in 1989), the Deepwater Horizon spill of 2010, pipeline spill ruptures and train derailments.

The Panel's work also involved extensive consultations with key industry, government and environmental stakeholders across the country. These included representatives from CEPA and CAPP, government agencies in Canada (Environment Canada, Natural Resources Canada, Fisheries and Oceans Canada, Alberta Innovates) and the United States (the National Oceanographic and Atmospheric Administration), private sector consultants, oil spill response agencies (e.g., the Eastern Canada Response Corporation), non-government organizations (e.g., Greenpeace), as well as other academics and interested individuals. Formal consultations included public forums involving open, online access held in Calgary in February 2015 and in Halifax in April 2015. A third Panel meeting in June 2015 included informal discussions with attendees at the 38th international Arctic and Marine Oilspill Program (AMOP) technical conference in Vancouver.

These consultations and the scientific review examined spill impacts and oil spill responses for the full spectrum of oil types, from ultra-light condensates and light oils to bitumen, diluted bitumen and heavy fuels. Many of the largest knowledge gaps were found to be associated with the chemical composition and environmental behaviour of emerging petroleum types, including diluted bitumens and other unconventional oils.

CHAPTER 2: CHEMICAL COMPOSITION, PROPERTIES AND BEHAVIOUR OF SPILLED OILS

While many Canadians think of the oil travelling by pipeline, train, truck or tanker as much the same, the crude oil crossing the country or plying its offshore waters each day represents dozens of different types. This may seem trivial to some, but if the oil spills into water, the type of oil involved can make a world of difference: How much damage it does, how easy it is to cleanup and how readily the oil degrades in the environment.

Each of the oil types transported in Canada is a complex mixture of thousands of chemicals. While these different types can be thought as existing along a kind of chemical continuum (from ultra-light oil condensates and light oils to heavy crude oils and the thick bitumen commonly associated with Canada's oil sands), each has its unique 'chemical' fingerprint.

The Panel found that this chemical fingerprint is a key predictor of not only the physical properties of the oil (e.g., how heavy or thick it is), but also its behaviour in the environment (e.g., how it spreads, sinks or disperses in water), its toxic effects on aquatic organisms and humans, and its susceptibility to degradation by 'weathering' (i.e., changes to the oil caused by the sun, waves, weather conditions and microorganisms in the environment). How the fingerprint of each spilled oil type changes in the environment is an important tool for spill responders for monitoring cleanup efforts and setting cleanup goals.

Although the Panel found the chemical composition and behaviour of many oil types have been well-studied, more research is needed to better understand the chemistry, properties and spill behaviour of newer, less-familiar oils, such bitumen, diluted bitumen blends and other unconventional oils.

CHAPTER 3: EFFECT OF ENVIRONMENT ON THE FATE AND BEHAVIOUR OF OIL

The unique features of the environment where an oil spill takes place are at least as important as the type of oil in determining effects on aquatic ecosystems.

Saltwater straits, freshwater lakes, running rivers and dense wetlands are home to distinctive combinations of physical characteristics, water and sediment chemistry and natural communities of microorganisms that can transform oil as it spills and spreads. Microorganisms, for example, degrade various hydrocarbons found in different oil types to varying degrees, and their impact is often an important part of oil spill cleanup strategies. Sunlight, wind, waves and weather conditions can physically and chemically transform a spill. Temperature, dissolved oxygen, nutrient supply, salinity and pH also alter the composition and behaviour of contaminating oil. These changes to the chemistry of oil are crucial factors affecting how spilled oil spreads, affects aquatic organisms and people or lingers in the environment.

Indeed, the Panel found that, despite the importance of oil type, the overall impact of an oil spill, including the effectiveness of an oil spill response, depends mainly on the environmental characteristics, the conditions where the spill takes place and the speed of response

The impact on spilled oil of the characteristics and conditions of a spill site has been carefully studied in some environments, but knowledge gaps remain. In particular, research is needed to better understand what happens to oil spilled into the cold, icy, yet ecologically sensitive waters of the Arctic, where interest in oil exploration, production and shipping is on the rise. Similarly, little is known about the fate of oil and its impact in permafrost areas or in marine environments covered in ice. Microorganisms that break down oil are considered less active when temperatures are near freezing, but this relationship may not be as clear as we think and further study is needed.

High-Priority Research Need #1

Research is needed to better understand the environmental impact of spilled crude oil in high-risk and poorly understood areas, such as Arctic waters, the deep ocean and shores or inland rivers and wetlands.

i. Research is needed to assess the complex interactions among physical, chemical and biological factors unique to Arctic conditions (e.g., extreme cold temperatures, permafrost ecosystems, snow and ice) and different types of spilled crude oil. *(Timeframe: Within 5 years)*
ii. Research is needed to assess the fate and behaviour of oil spilled into freshwater ecosystems, especially in northern bogs, fens and areas of permafrost. *(Timeframe: Within 5 years)*
iii. Research is needed to evaluate risks associated with the shipment of fuel oil to communities in the Arctic. *(Timeframe: Within 5 years)*
iv. Research is needed to assess the risks of deep sea blowouts in the Beaufort Sea and in areas of the Atlantic coast that support commercial and subsistence fisheries, including research into the behaviour of oil on the surface with and without ice and the effects of subsurface oil plumes, residual oil deposited on deep sea sediments, oil stranded along shorelines and in backwater, marshy areas, and the impact of dispersant additions. *(Timeframe: 5-10 years)*
v. Research is needed to assess the risks of pipelines in Arctic freshwater environments, with an emphasis on the Mackenzie River. *(Timeframe: 5-10 years)*
vi. Research is needed to investigate the fate of unrecovered oil in rivers where it can interact with ice, substrates, woody debris, bed sediments, groundwater and engineered structures. *(Timeframe: 5-10 years)*

CHAPTER 4: OIL TOXICITY AND ECOLOGICAL EFFECTS

Oil spills can have significant consequences for aquatic ecosystems. These effects can be both short-lived and long-lasting. In the days following a spill, floating oil smothers mollusks, plants and other species at the shoreline. Oil on birds and mammals destroys their thermal insulation and buoyancy. Some chemical components of spilled oil dissolve in water and kill fish and other aquatic creatures (before they typically break down quickly and disappear). Other chemicals, such as polycylic aromatic hydrocarbons (PAHs), can persist in the water and cause chronic health effects for aquatic species that show up months or years later.

Light oils contain more compounds that are acutely toxic to aquatic organisms than medium or heavy oils. On the other hand, heavy oils contain more of the chronically toxic alkyl PAHs. The Panel could not conclude that diluted bitumens present a greater or lesser health risk to most species than other oils because there are too few data available on toxicity. However, there may be greater risk to bottom- and sediment-dwelling organisms due to the tendency for diluted bitumens to sink in fresh water under certain conditions.

The characteristics of the oil spill location and its environment determine how spilled oil affects aquatic biota. Oil spills into fresh water, for example, are generally smaller than marine spills, but they may have a greater relative impact because the oil can't be diluted and degraded by the large volumes of water available at sea. Inland shorelines and sediments are more likely to become fouled, and less time is available to contain a freshwater oil spill before it contaminates sensitive habitats.

It is not only the spills themselves that threaten ecosystems, but oil spill cleanup can be damaging as well. Physical cleanup (e.g., removing oiled vegetation or tarred shoreline) destroys habitat and can cause erosion or the buildup of silt. Habitat damage reduces the abundance and productivity of native species and fosters invasive species. Using chemicals to disperse spilled oil often means surface oil is transferred to subsurface water at concentrations that can be toxic to aquatic life (especially to fish embryos). More research is needed on spill cleanup methods that limit habitat damage and the threats to wildlife.

Oil spill impacts on aquatic ecosystems are difficult to measure. In many cases, information about the ecology of a site before a spill occurs (i.e., baseline data) is scarce or missing altogether. Baseline monitoring is typically the responsibility of provincial and federal government departments as part of environmental and natural resource management. Coordination and collaboration is needed between the oil industry and these government agencies to ensure that monitoring addresses the needs for data to assess the distribution and effects of spilled oil in ecosystems most at risks of spills.

Assessment of oil spill impacts on 'ecosystem services' should be considered. Ecosystem services are the benefits provided by ecosystems to humans that contribute to making human life both possible and fulfilling. Further research is also required to better understand how the toxicity of spilled oil is affected by its interaction with the environment in which it was spilled.

High-Priority Research Need #2

Research is needed to increase the understanding of effects of oil spills on aquatic organisms, populations, communities and ecosystems.

i. Research is needed to investigate the cumulative and interactive effects of co-exposure to oil and other human-induced and natural environmental stressors, such as industrial and municipal pollution, extreme temperatures, salinity, low oxygen concentrations and elevated concentrations of suspended sediments. *(Timeframe: 5-10 years)*

ii. Research is needed on the effects of spilled oil on populations and community structure of aquatic biota. *(Timeframe: 5-10 years)*

iii. Research is needed to understand the indirect effects of oil spills on ecological processes, such as interactions within and among trophic levels in aquatic food chains. *(Timeframe: 10+ years)*

iv. A program of research is needed on the resilience of aquatic ecosystems affected by oil spills, particularly at sites of past spills and in ecosystems unique to northern Canada (e.g., bogs, fens, etc.) at a high risk of oil exposure. *(Timeframe: 10+ years)*

v. Research is needed to investigate the socioeconomic impacts of oil spills as a first step in implementing an ecosystem services approach to oil spill impact assessments *(Timeframe: 10+ years)*

CHAPTER 5: MODELING OIL SPILLS IN WATER

Knowing what to expect and how to respond when oil spills into an ocean, lake or river is no mean feat. The complex chemistry of each oil type makes it difficult to predict how the oil will act and change when it meets the equally complex water chemistry, ecology and conditions at the particular site where a spill takes place. For this predictive work, scientific models are invaluable tools.

Scientific modeling creates conceptual or mathematical representations of complex real-world phenomena that can't be readily observed. Scientific models of oil spills use what we know from experiments, previous spills and other information to approximate what happens when oil of a particular type spills in particular circumstances. Scientists are constantly adding information and refining these models to improve their accuracy for predicting spill consequences and for understanding the best spill responses.

Early models of oil behaviour and transport relied heavily on experimental observations. Since the early 1980s, advances in oil spill modeling focused mainly on oil dispersion (the formation of oil droplets), the formation of oil particle aggregates, emulsification, evaporation and the general transport of oil in open water as well as in other types of ecosystems. More recently, researchers have developed more advanced numerical models of these various processes to better predict oil's behaviour and changes in situations where no direct measurements can be made, such as in deep water or in the Arctic.

The Panel found that while scientific modeling has made many advances in predicting how the environment can influence spilled oil and its behaviour (through dispersion, biodegradation, dissolution, etc.), more research is needed to improve models of oil-in-ice effects, oil dispersion by waves, oil droplet formation from blowouts, the formation of oil particle aggregates and the biodegradation of oil droplets under various environmental conditions (such as temperature, salinity, nutrient availability, light and chemical dispersants).

High-Priority Research Need #3

A national, priority-directed program of baseline research and monitoring is needed to develop an understanding of the ecological characteristics of areas that may be affected by oil spills in the future.

i. Research is needed to collect and evaluate baseline information from high-risk, poorly understood areas, such as the Arctic and other less-studied Canadian environments. *(Timeframe: Within 5 years)*
ii. Research is needed to understand the current status of sensitive and highly-valued species and vulnerable habitats for specific, pre-defined locations in Canada representing a range of human disturbance, from relatively undisturbed to highly disturbed. *(Timeframe: Within 5 years)*
iii. Research is needed to create ecosystem sensitivity maps, prioritized according to recent relative risk assessments, the intensity of current and potential future human use, the relative sensitivity of ecosystems and geographic gaps (e.g., in large areas of inland Canada). *(Timeframe: Within 5 years)*
iv. Research is needed to understand the natural variability of population and community metrics (e.g., abundance, diversity, productivity) across physical and chemical gradients as well as across time (seasonal and annual). *(Timeframe: Within 5 –10 years)*
v. Research is needed to identify other anthropogenic stressors that could influence the effects of oil spills. *(Timeframe: Within 5–10 years)*

CHAPTER 6: A REVIEW OF SPILL RESPONSE OPTIONS

Just as types of crude oil are far from uniform and the environments and conditions where spills occur are many, effectively responding to oil spills is complicated. Decisions about what response is best and the likelihood of success depend not only on the oil type, environment and weather conditions, but also on technical and logistical factors (such as the responders' knowledge and skills, the availability of personnel and equipment, time constraints, regulatory approvals, health and safety criteria, etc.), as well as financial concerns (such as the cost and economic impacts of the spill). Other considerations include the level of community engagement.

There are three main categories of oil spill responses. The first simply relies on natural processes to disperse and degrade spilled oil. For instance, naturally occurring microorganisms can remove or break down some of the hydrocarbons and other chemicals in the oil (called 'natural attenuation'). Evaporation can also help remove volatile and lighter weight components of spilled oil, while exposure to sunlight and oxygen causes the natural photooxidation of some of the oil's aromatic compounds. The second type of response involves physically containing and removing spilled oil, often using booms and skimmers on the water or washing and scraping at shore. Thick slicks of oil can also be burned at a spill site. The third response type uses biological and chemical methods. This can involve methodologies to enhance the growth of oil-degrading microbes and/or plants on contaminated sites (phytoremediation) or the application of chemical dispersants that break up oil slicks into small droplets that become diluted into the water column where they are eventually also biodegraded.

Choosing the best response or combination of responses depends on the unique circumstances of each spill. Among these are weather, wave height, ice conditions, daylight and ecological factors, including the risk to fish, invertebrates and other wildlife. Technical and economic factors also play a role, as well as the inherent effectiveness of the response strategy being considered.

The Panel found that most of what is known about oil spill response technologies has been developed through laboratory work and case studies. A better understanding of appropriate spill responses in the Arctic and in snow and ice conditions is vital. The Panel recommends carefully controlled field studies to help close this knowledge gap (without significant negative impact on the environment). Research is also needed to better understand less familiar response methods, such as anaerobic biodegradation in sediments, and emerging technologies (e.g., bioventing, air sparging, etc.) for aiding in the cleanup of anaerobic or anoxic sea floor and lake bottom environments contaminated by sunken oil. What happens to chemically-dispersed oil in both the deep sea and on its surface also needs to be studied using controlled empirical experiments.

High-Priority Research Need #4

A program of controlled field research is needed to better understand spill behaviour and effects across a spectrum of crude oil types in different ecosystems and conditions.

i. Controlled field experiments on oil spills (sanctioned by the federal government through a new permitting system) with rigorous statistical designs are needed at a variety of sites representing different coastal marine and freshwater ecosystems and conditions. *(Timeframe: Within 5 years and beyond)*
ii. Research is needed at the site of previous oil spills in Canada to increase our understanding of the effects of spilled oil over the long-term and of the extent of natural cleanup. *(Timeframe: Within 5 years)*

High-Priority Research Need #5

Research is needed to investigate the efficacy of spill responses and to take full advantage of 'spills of opportunity'.

i. Research is needed to help develop effective oil spill response measures tailored to the Arctic, including studies that explore the interactions of oil with permafrost and ice or that examine the microbial degradation of oil at low temperatures. *(Timeframe: Within 5 years and beyond)*
ii. Advanced planning and contingency funds are needed to support research on the fate, behaviour and effects of real-world oil spills as they occur ('spills of opportunity') in the short, medium and long-term, including studies of the relative effectiveness of response measures. *(Timeframe: Within 5 years)*
iii. Indigenous peoples from all parts of Canada need to be involved the development of research protocols, in oil spill preparedness, cleanup and remediation/restoration, including involvement in the investigations of 'spills of opportunity'. *(Timeframe: Within 5 years)*
iv. Research is needed (along with the engagement of Indigenous peoples and other stakeholders and economic analysis) to address the long-standing remediation question "how clean is clean?" *(Timeframe: 5-10 years)*
v. Research is needed to develop and improve methods for remediation, reclamation or restoration of damaged marine and freshwater habitats following oil spills. *(Timeframe: 5-10 years)*
vi. Research is needed on the efficacy and environmental impacts of conventional and new oil spill remediation options, particularly in Arctic and freshwater ecosystems. *(Timeframe: 5-10 years)*

CHAPTER 7: PREVENTION AND RESPONSE DECISION MAKING

The best way to protect aquatic environments from the sometimes devastating impacts of spilled oil is to prevent spills from happening in the first place. That is, reducing the likelihood of accidental spills is always more effective than managing the risks (to the environment or to the economy) after a spill has occurred. This principle is particularly true in the sensitive ecosystems where spills can cause catastrophic or irreversible consequences, such as in the Arctic where industrial activities (e.g., offshore oil and gas, mining), urban growth and climate-related changes to navigation routes are expected to increase tanker traffic in the years ahead.

All oil spill strategies emphasize prevention as the prior emergency management activity. Effective prevention combines an understanding of the science and technologies associated with oil operations and potential oil spills with a clear understanding of the environment and conditions in which these activities are taking place. For example, properly designed pipelines or tankers can be built to withstand anticipated conditions (waves, wind, ice, etc.) that increase spill risk. Similarly, established procedures, proper inspection and maintenance of equipment and training for extreme and adverse circumstances help reduce the chances of a spill.

High-Priority Research Need #6

Research is needed to improve spill prevention and develop/apply response decision support systems to ensure sound response decisions and effectiveness.

i. A national guidance program for post-spill monitoring is needed to collect reliable, adequate, credible and consistent information on the fate and effects of oil in the environment. This program should be developed based upon consultations among industry, government, Indigenous organizations, and community stakeholders. (Timeframe: Within 5 years)
ii. Research is needed to develop methods to support the monitoring of oil-spill impacts and the fate of released oil. (Timeframe: 5-10 years)
iii. Research is needed to develop methods for the derivation of comprehensive mass balances for spilled and recovered oil. (Timeframe: 5-10 years)
iv. Research is needed to develop modeling methods to simulate and optimize individual and collective cleanup processes (e.g., booming, *in situ* burning, skimming, dispersion and bioremediation) for supporting response decision-making. (Timeframe: Within 5 years)
v. Research is urgently required on development and demonstration of oil spill response decision support systems, which can dynamically and interactively integrate monitoring and early warning, spill modeling, vulnerability/risk analysis, response process simulation/control, system optimization and visualization. (Timeframe: Within 5 years)
vi. Research investment is needed on trial tests and field validation of new prevention and decision-making methods to demonstrate feasibility, increase confidence for implementation and improve response capabilities. (Timeframe: Within 5 years)
vii. Research is needed to better quantify modeling uncertainties, evaluate their propagation and mitigate their impacts on spill response decision-making. (Timeframe: 5+ years)
viii. Further research and development are desired on environmental forensics, remote sensing and *in situ* measurement, early warning and diagnosis, and biological monitoring to improve spill prevention and decision-making. (Timeframe: 5+ years)
ix. Special attention of the above research should be given to some emerging issues (e.g., diluted bitumen, aging/subsea pipelines, railcars and the Arctic) to enhance effectiveness and confidence of prevention and response strategies and decisions. (Timeframe: Within 5 years)

Prevention policies and measures are often best informed by the timely monitoring and analysis of the causes and outcomes of spills when they do occur. Importantly, knowing the characteristics and ecological features of an environment before a spill occurs is central to understanding how it has been affected. Developing baseline data in areas where oil is transported should be an important priority for research.

Indeed, despite the best prevention efforts, spills happen, and then making sound and timely decisions about how to respond is a critical second line of defense. The Panel found that management strategies should be in place to identify the lead decision-making agencies in the case of a spill and to present clearly the steps to contain potential damage to human health, businesses and the environment. Decisions concerning what to do following an oil spill can occasionally mean weighing the potential benefits of a response against its possible harm or against the pros and cons of another approach altogether. Net environmental benefit analysis (NEBA) provides a helpful framework and has been widely used for supporting these decisions. The review also disclosed the limited research efforts in simulating, predicting and optimizing cleanup processes (e.g., *in situ* burning, skimming and dispersion) individually and collectively and evaluating their effects on response decisions. Inadequate decision support is one of the major challenges that limit the efficiency of current response practices. Due to limited attention and investment, existing decision support systems are rare and lack dynamic and interactive support from other modeling tools (risk analysis, spill modeling, NEBA, process simulation, etc.) and field validation. In addition, uncertainty is a major hindrance to improving efficiency and confidence of decision-making. These are especially true for the Arctic waters where the window of opportunity is significantly short. The Panel also noticed that advances in monitoring and information technologies such as remote sensing, geographic information systems, artificial intelligence and visualization have provided a set of cost-effective and powerful tools that can play a more important role in better addressing complexity and dynamics of spills and supporting sound response making and operations.

High-Priority Research Need #7

Research and work are needed to update, refine and focus risk assessments of oil spills in Canada.

i. Follow-up relative risk assessments are needed to build upon the Transport Canada assessments of marine spills, focusing on high-sensitivity areas. *(Timeframe: Within 5 years)*
ii. Research is needed to update and refine risk assessment methods to include such things as credible spill scenarios, analyses of seasonal differences in fate, transport and effects of oil (particularly for spills in winter) and the prediction of chronic toxicity. *(Timeframe: Within 5 years)*
iii. A comprehensive national database is needed to track the fate, behaviour and effects of various types of oil spilled and the efficacy of current and emerging oil spill countermeasures over a range of environmental conditions. *(Timeframe: 5-10 years)*
iv. Research is needed to expand species sensitivity distributions (SSDs) for acute and chronic toxicity of oil to aquatic biota. SSDs should be expressed as measured concentrations of total petroleum hydrocarbons and total polycyclic aromatic hydrocarbons. *(Timeframe: 5-10 years)*
v. Research is needed to extend models of chronic toxicity to a wider array of species and environmental (temperature, salinity, etc.) and life history variables. *(Timeframe: 10+ years)*

CHAPTER 8: RISKS FROM OIL SPILLS

Learning from history is important to understanding what's known about the risks posed by potential oil spills in Canada and, most significantly, what needs further study. The Panel reviewed the circumstances and outcomes for selected oil spill cases involving tanker accidents (e.g., the *Arrow* spill in 1970 and the *Exxon Valdez* spill in 1989), a major ocean-rig blowout (i.e., the Deepwater Horizon Gulf of Mexico spill in 2010), pipeline spills and train derailments that occurred in marine and fresh water in Canada and the United States over the past few decades.

Chief among the Panel's conclusions is that each case was unique in the combination of different physical, chemical and biological factors at the spill location, as well as in the cleanup and recovery measures used in the wake of each accident. These varied combinations of factors were critical for either increasing or decreasing the overall impact for each spill.

Delays in responding to the spilled oil affected the outcome of all case studies examined. Indeed, despite the obvious importance of weather, remote location and technological challenges facing each accident, human error (individuals and organizations) played a dominant role in affecting the impact of the spills across all case studies. Absent or inadequate planning, limited data analysis, inadequate training, poor communication, insufficient personnel and equipment, poor or no information sharing, and lapses in regulatory oversight were common to most, if not all, spill case studies.

From its case study review, the Panel found that the ability of aquatic ecosystems to recover from the shock of an oil spill may be influenced by the presence of other longer-term environmental stresses (e.g., habitat degradation caused by urban development, fishing pressure or water pollution from sewage discharges or agriculture). In most cases, the lack of pre-spill baseline data (i.e., information about the natural environment and ecology of each area) hampered efforts to predict or monitor the long-term effects of the oil spills on populations and communities of aquatic life. Similarly, monitoring following spills was not conducted according to any standard or consistent national protocols. The Panel's review of risk assessments of oil spills in Canada revealed a number of challenges, notably the lack of readily accessible data for use in the assessments and the need for increased sophistication of both exposure and effects analyses. In many cases, even if data were accessible, they were extremely limited, particularly for the Arctic and large portions of inland rivers, lakes and wetlands. The Panel found that the assumptions used in the risk assessments sometimes were overly optimistic given the experience gained from oil spill case studies. This was especially true for the spill response times assumed in the assessments.

CHAPTER 9: CONCLUSIONS

Crude oil spills are infrequent in Canada's coastal or inland waters. But the consequences of these spills into sensitive waterbodies can be profound. They can significantly affect not only the environment but also the economy of affected areas as well as human health and safety.

Canada's offshore oil and gas industry, meanwhile, is expected to grow. The production and transport of unconventional oils, such as diluted bitumens and Bakken crude oil, are likely to increase. Spills of these oils from offshore platforms, pipelines, tankers, rail, and other sources will continue to pose risks to Canadian aquatic environments and the communities that rely on them.

The Royal Society of Canada expert Panel prepared this report—based on a review of the science and consultations with key stakeholders—to better understand what is behind these risks. Among the Panel's many conclusions is a long list of research needs, including seven key research areas that should become top research priorities.

In particular, the Panel recommends that research needs to identify where most oil spills occur and why (e.g., pipeline spills into wetlands are more common than these spills into rivers; oil from truck spills are more likely to enter storm sewers before reaching rivers; etc.). Researchers need to examine past spill response records, current risk management processes and regulations to identify their weaknesses. Other critical knowledge gaps include developing a better understanding of environmental sensitivities that affect the impact of spilled oil. More research is also needed to understand how the type of oil, its source, the environment and the level of preparedness of spill responders combines to influence spilled oil's fate and effects.

These research gaps are significant. The data needed to assess oil spill risks in Canada are often either absent or widely scattered among government agency, industry and academic sources. Information needed to reliably assess the environmental sensitivity of areas at risk from oil spills is also very limited for large portions of Canada. Input of traditional knowledge from Indigenous peoples and other interested parties is needed.

Examples that demonstrate the need for more research are numerous. Many are documented in the Panel report. While scientific advances have significantly reduced the threat of oil spills in Canadian waters over the past few decades, much about the fate and effects of oil spills remains poorly understood.

To meet the research and oil spill-response needs identified in the expert report, the Panel recommends the conduct of coordinated multi-disciplinary research programs between industry, government and academia to further study the effects of oil spills on various marine and freshwater ecosystems, including wetlands. The program should also include Indigenous people for the provision of traditional knowledge and expertise. The science from these studies will provide a much needed database on the interaction and effects of spilled oil with its surrounding environment that will support science-based decision-making following future spill incidents to protect our aquatic environment and its living resources.

CHAPTER 1: INTRODUCTION

Abstract

This chapter describes the rationale and mandate for a Royal Society of Canada Expert Panel established to provide a scientific review of our current knowledge and understanding of the behaviour and environmental impacts of a range of crude oils, including diluted bitumen, which may be accidentally released into Canadian marine or freshwater ecosystems.

To provide context for its evaluation of the risks associated with spills, an overview of global and Canadian information is provided on the probable causes and predicted frequency and size of crude oil spills into marine or fresh waters from exploration, production and transport operations. The global frequency of large spills (>700 tonnes) from oil tankers has decreased significantly in the past four decades and, fortunately, large spills due to tanker incidents in Canadian marine waters have been rare. Return periods (i.e., time between spills of a given volume) in Canada range between about 40 and 240 years (depending on spill volume); however, these return periods may not provide a reliable basis for predicting future occurrences in circumstances where the frequency and/or volumes of shipments are increasing. Diffuse sources, such as natural seeps and runoff from land-based sources, account for the majority of petroleum hydrocarbon inputs to oceans. Thus, while continued efforts to reduce tanker spills are necessary, attention should also focus on sources such as urban runoff and recreational boating because the spills are chronic and often occur in sensitive ecosystems. While freshwater spills associated with land-based extraction of crude oils (including the extraction of bitumen) and the transport of petroleum hydrocarbons (by pipeline, rail tankers and trucks) are expected to be at much smaller volumes than their marine counterparts, they may cause significant damage because of their higher probability to occur within populated areas and the proximity to water bodies lacking the dilution and dispersion capacity typically found within the marine environment.

Notwithstanding the apparent relative infrequency of crude oil spills into aqueous environments in Canada, the consequences of spills into sensitive marine and freshwater systems can be substantial, both with respect to impacts on human health, safety and the environment and with respect to economic impacts. Therefore, a primary focus of this Report is on the consequences of spills, no matter how low the probability may be. This focus is commensurate with the key questions posed by the sponsors and stakeholders.

1.1 Sponsors and Mandate of the Panel

The Expert Panel was established by the Royal Society of Canada (RSC) in response to a request from the Canadian Energy Pipeline Association (CEPA) and the Canadian Association of Petroleum Producers (CAPP) who recognized the need for a scientific review of our current knowledge and understanding of the behaviour and environmental impacts of a range of crude oils, including diluted bitumens, accidentally released into Canadian marine or freshwater ecosystems. The Panel was asked to address the following questions [with additional context added by the panel]:

1. How do the various types of crude oils compare in the way they behave when mixed with surface fresh, brackish or sea waters under a range of environmental conditions or when chemically treated for spill remediation?
2. How do the various crude oils compare in their [chemical composition] and toxicity to organisms in aquatic ecosystems?
3. What should be done to ensure optimal microbial activity for rapid remediation of aquatic systems impacted by a spill [and how do microbial processes affect crude oils in aquatic ecosystems, thereby modifying their physical and chemical properties, persistence and toxicity]?

4. Is the research [and oil spill response] community able to relate, with reliable predictions, the chemical and physical [and biological] properties of crudes to their behaviour, [persistence], toxicity and ability to be remediated in water and sediments?
5. How should these scientific insights be used to inform optimal strategies and regulatory requirements for spill preparedness, spill response and environmental remediation?
6. Given the current state of the science, what are the priorities for research investments?

1.2 Scope of the Panel's Review

The Panel considered accidental releases of conventional and unconventional light, medium and heavy crude oils, including diluted bitumens. The Panel evaluated reports on the environmental behaviours of these oils and the effectiveness of current and emerging oil spill response models and technologies available for use in the event of accidental releases. Releases of biofuels or refined petroleum products (e.g., gasoline, diesel, aviation fuel, heating oil, etc.) were determined to be outside of the scope of this Report by the project stakeholders, although spills of Bunker C and IFO (intermediate fuel oil) were included for comparison.

> The terms 'conventional' and 'unconventional' oils are related to the techniques used to extract them from reservoirs, not to their chemical composition. Conventional oils include liquid crudes that flow in the reservoir and in pipelines. Such oils (e.g., condensates, light and medium crude oils) are recovered from traditional oil wells using established methods like primary recovery and waterflooding. Unconventional oils are produced using unconventional methods, such as surface mining of shallow oil sands, steam-assisted gravity drainage of bitumen (SAGD) and horizontal drilling with hydrofracturing ('fracking') for recovery of light shale oils ('tight oils').

The scope of this Report was intentionally focused on the accidental release of crude oils at the exploration and production source or as they are transported to refineries. Thus, the transport of crude oil by pipeline, ship, rail and truck was considered both with respect to the probability of accidental releases and consequences in the aqueous environment. Unplanned releases from offshore platforms, including subsurface blowouts, were included in light of the recent Deepwater Horizon (DWH) blowout and the expected growth of Canada's offshore oil and gas industry. The Panel focused on the Canadian environment; however, it reviewed and considered the applicability of case studies from the United States and other countries. Case studies were selected to represent different types of crude oil spilled into either marine or freshwater systems. Efforts were also made to find case studies applicable to cold climates.

This Expert Panel Report is not expected to provide exhaustive overview of previous oil spill research and case studies that have been cited in numerous existing reviews. While this information is clearly considered in the response to the above questions, emphasis has been placed on the expertise and experience of the individual Panel members to identify the most relevant and current literature in scientific journals and academic, government and consultant reports on current policies and practices in oil spill prevention and response, including the assessment of environmental impacts and remediation. The Panel recognizes the existence of numerous review articles related to recent oil spill events and the large amount of important research currently being conducted (e.g., research on diluted bitumen, and studies related to Natural Resources Damage Assessment following the DWH spill in the Gulf of Mexico). The conclusions and recommendations are based on a consideration of the large body of literature available up to the date of writing.

1.3 Consultation with Stakeholders

The Panel consulted with representatives of CEPA and CAPP, government agencies in Canada (Environment Canada, Natural Resources Canada, Fisheries and Oceans Canada, Alberta Innovates) and the U.S. (National Oceanographic and Atmospheric Administration [NOAA]), private sector consultants, first responders (e.g., Eastern Canada Response Corporation [ECRC-SIMEC]), non-government organizations (e.g., Greenpeace), as well as individuals (e.g., academics). The formal consultations included public forums with open online access that were hosted by the Panel in February (Calgary, AB) and April (Halifax, NS), 2015 that involved presentations, as well as question and answer sessions. A third Panel meeting in June, 2015 included informal discussions with attendees at the 38th international Arctic and Marine Oilspill Program (AMOP) technical conference that included a dedicated session on diluted bitumens.

Several stakeholders emphasized that the Panel's work could be used as supporting information for government and industry policy and practice regarding spill prevention and emergency response. Some stakeholders were interested in receiving relevant information regarding transportation routing (e.g., to avoid or minimize risk to highly sensitive environments or species). Considerable interest was expressed in gaining an understanding of the relative risks associated with the transportation and handling of different types of crude oil. Some stakeholders wanted to know about the best available and emerging technologies for spill cleanup, as well as monitoring requirements to track the effectiveness of cleanup.

Stakeholders expected the Panel to take a comparative approach in order to better understand the relative impacts of conventional crude oils and diluted bitumen. The results of the comparisons among crude oil types (and impacts in different marine and freshwater ecosystems) would then be useful when making decisions regarding preparedness and appropriate spill response procedures.

The stakeholders requested that the Panel clearly summarize what is known and not known about the key issues and make recommendations for actions and further research. Particular interest was expressed in the performance of different cleanup technologies and the long-term effects of spills.

1.4 Context for Oil Spills in Canada

The Panel delivers the following brief overview of information on the causes, frequency and size of crude oil spills into marine or fresh waters in Canada to provide context for its evaluation of the risks associated with spills.

1.4.1 Spills from Oil Tankers in Marine Waters

Although this report considers the full range of Canadian aquatic ecosystems, most of the research, response and media attention throughout the decades has focused on marine oil spills, particularly large-scale accidents involving oil tanker vessels. The largest spill due to an oil tanker accident was the *Atlantic Empress* in 1979 off the island of Tobago in the West Indies, where 287,000 tonnes of oil were released after a collision with another vessel, followed by fire and an explosion that sank the tanker. No impact studies were carried out, so it is not known what quantity of oil burned or sank, but only minor shore pollution was reported on nearby islands (ITOPF 2015a). The *Amoco Cadiz* grounding off the coast of Brittany in 1978 resulted in the release of 223,000 tonnes of light Iranian and Arabian crude oil and 4,000 tonnes of bunker fuel into heavy seas—causing the formation of an emulsion that increased the volume of pollutant by up to five-fold. Numerous shoreline types were affected and much of the oil became buried in sediments and entrapped in salt marshes and estuaries (ITOPF 2015b). The spill of 37,000 tonnes of Alaska North Slope crude oil into Prince William Sound, AK, from the *Exxon Valdez* in 1989 was small in comparison, but led to the mortality of thousands of seabirds and marine mammals, a significant reduction in population of many intertidal and subtidal organisms, and reports of long-term environmental impacts (Spies et al. 1996).

Fortunately, large spills due to tanker incidents in Canadian marine waters have been rare. In terms of national involvement, one of the largest spills was in 1988 when the tanker *Odyssey* loaded with over 132,000 tonnes of North Sea Brent crude oil broke into two and sank 700 miles (~1,100 km) off the coast of Nova Scotia beyond Canada's Exclusive Economic Zone[1] (ITOPF 2015c). Fire started on the stern section as it sank and the surrounding oil caught fire. Due to rough weather, the Canadian Coast Guard was only able to come within about 2 km of the vessel while it was on fire. No shoreline effects occurred because of the distance of the spill from the coastline. Another well-known tanker accident off the Canadian coast occurred in 1970 when the *Arrow*, hauling 9,500 tonnes of Bunker C fuel oil from Aruba to Nova Scotia, encountered severe weather and gale force winds near Port Hawkesbury, NS, at the entrance to Chedabucto Bay. The tanker ran aground on Cerberus Rock spilling most of the fuel oil cargo and contaminating 75 miles of shoreline with residues of thick black sludge, which can still be found (Lee et al. 2003; Owens et al. 2008). Within the scientific community, the *Arrow* spill was unique because a section of the affected shoreline (Black Duck Cove) was intentionally left 'untreated' to enable scientific assessment of natural recovery processes.

The frequency of large spills (>700 tonnes) from oil tankers has decreased significantly in the past four decades. According to data from the International Tanker Owners Pollution Federation (ITOPF 2015d), an average of 1.8 large spills per year occurred internationally in the period 2010-2014 compared to an average of 24.5 large spills per year between 1970 and 1979. One large spill was recorded in 2014 - the sinking of a tanker in the South China Sea loaded with a cargo of about 3,000 tonnes of bitumen. The U.S. Department of the Interior's Bureau of Ocean Energy Management (BOEM) and Bureau of Safety and Environmental Enforcement (BSEE) produced a comprehensive summary report on the occurrence rates for offshore oil spills from U.S. Outer Continental Shelf (OCS) Platform and Pipeline Spill Data (1964 - 2010), Worldwide Tanker Spill Data (1974 - 2008), and Barge Spill Data for U.S. waters (1974 - 2008) (Anderson et al. 2012). According to this report, the rate of offshore oil spills in the U.S. has been declining since 1994, due mostly to major regulatory changes in the early 1990s (arising from the *Exxon Valdez* spill) that substantially eliminated the use of single-hull tankers by requiring double hulls or their equivalent. In 2013, a report by the Canadian Tanker Safety Panel Secretariat (TSPS) published two tables produced by GENIVAR, a professional services firm, showing the risk calculations for the probability and potential impacts of ship-source oil spills in Canada (Table 1.1) and internationally (Table 1.2). The significant figures in these two tables are from those reported by the data sources. The return periods (i.e., time between spills of a given volume) presented in these tables may not be a reliable basis for predicting future occurrences in circumstances where the frequency and/or volumes of shipments are increasing (e.g., along the southern British Columbia coastline if the proposed TransMountain Pipeline Expansion Project, with associated tanker traffic, is approved).

Table 1.1 Spill frequency estimates for ship-source spills occurring in Canada, calculated using only previous Canadian spill occurrences. *Data from TSPS (2013)*

	Return period, years [a]			
Spill volume, m^3	**10-100**	**100-1,000**	**1,000-10,000**	**> 10,000**
Crude oil	– [b]	–	–	–
Refined Cargo oil	1.7	10.0	–	–
Bunker oil	0.5	1.7	–	–
Total	**0.4**	**1.4**	**–**	**–**

[a] *estimated average number of years between spills*
[b] *probability could not be estimated due to the lack of spills in Canada in this category in the previous 10 years, indicating that the probability of a spill in this size range and category is remote.*

[1] *The exclusive economic zone (EEZ) is an area of the sea adjacent to and beyond the territorial sea, extending out to 200 nautical miles from the baseline. Within the EEZ, a coastal state has sovereign and jurisdictional rights over exploration and management (e.g., scientific research and protection of the marine environment) and economic exploitation of living and non-living resources in the waters above the seabed, in the seabed and beneath the seabed.*

Table 1.2 Spill frequency estimates for ship-source oil spills in Canada, based on international and Canadian data. *Data from TSPS (2013)*

	Return period, years [a]			
Volume, m^3	**10-100**	**100-1,000**	**1,000-10,000**	**> 10,000**
Crude oil	46.4	69.2	51.6	242.3
Refined Cargo oil	1.7	10.0	42.2	– [b]
Bunker oil	0.5	1.7	154.8	–
Total	**0.4**	**1.4**	**20.2**	**242.3 [c]**

[a] *estimated average number of years between spills*
[b] *probability could not be estimated due to the lack of spills in the previous 10 years in this category, indicating that the probability of a spill in this size range and category is remote*
[c] *i.e., a crude oil spill of >10,000 tonnes in Canadian waters is predicted to occur once every 242 years, based on the occurrence of only two such spills worldwide in the past 10 years, both from single-hulled vessels (the Tasman Spirit spill of ~30,000 tonnes in 2003 in Pakistan, and the Hebei Spirit spill of ~10,500 tonnes in 2007 in South Korea).*

In addition to the estimates above, ITOPF (2014) published actual oil tanker spill statistics, which show a declining trend in the number of tanker spills greater than 700 tonnes from 1970-2014 (**Figure 1.1**).

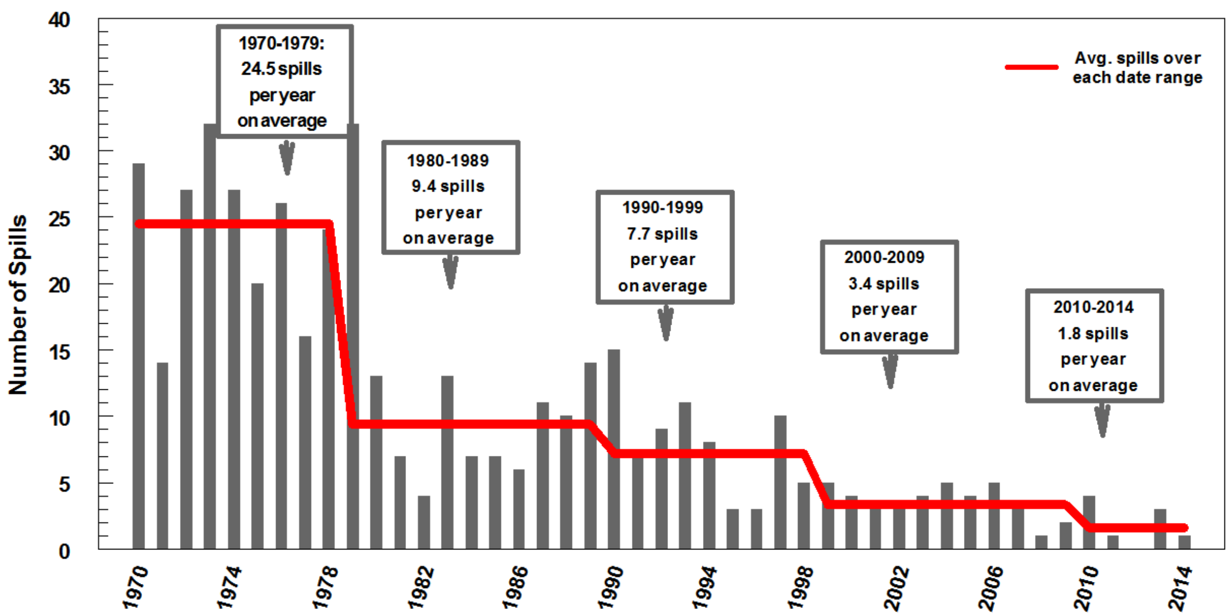


Figure 1.1 Number of large oil tanker spills (>700 tonnes) occurring worldwide from 1970 to 2014 (grey bars), and average number of spills per decade (red line). *Adapted from ITOPF (2014)*

The 1989 *Exxon Valdez* incident increased public and political awareness about the risks involved in the storage and transportation of oil and oil products. This awareness resulted in changes to regulations, including: the enactment of the 1990 *Oil Pollution Act* by the U.S. Congress, which regulates spills in the United States; regulations within Canada under the *Canada Shipping Act* (2001) (http://laws-lois.justice.gc.ca/eng/acts/s-9/), which regulates tankers; and the *Canada Arctic Waters Pollution Prevention Act* (1985, most recently amended in 2014) (http://laws-lois.justice.gc.ca/eng/acts/A-12/), which includes regulations regarding the design of Arctic class ships.

1.4.2 Accidental Releases from Offshore Oil and Gas Exploration and Production

Spills, blowouts and malfunctions may occur during any offshore oil and gas exploration activity. As defined by the U.S. NOAA, a blowout occurs when operators of a drilling rig are unable to control the flow of oil, gas or other fluids from the well, causing it to be released into the underground formation, marine environment and/or atmosphere. Until recently, the risk of blowouts was considered low in the oil exploration and development industry and thus of minor concern. For example, from 1979 to 1998, 19,821 wells were drilled within the Gulf of Mexico, with only 118 wells resulting in uncontrolled flows or blowouts - a 0.6% occurrence rate (API 2009). The reported blowouts were not considered a significant source of hydrocarbon releases to the environment due to effective blowout prevention (BOP) systems and the fact that they often sealed naturally and ceased flowing within a matter of hours or days. In 2004, the Canada Nova Scotia Offshore Petroleum Board (CNSOPB) predicted a 1-in-1800 chance per year of having any sort of deep water blowout off the continental shelf during exploratory drilling, with the probability of shallow water gas blowouts without a release of oil having a three- to four-fold higher probability of occurrence (Hurley and Ellis 2004). However, the DWH blowout in the Gulf of Mexico, which resulted in the continuous discharge of petroleum gas and crude oil into surrounding waters (4.2 million bbl [~600,000 m^3] over an 87 day period) and impacts on the Gulf shoreline and salt marshes, has changed the world's perception of the environmental risk associated with blowouts, with accompanying changes in regulatory requirements. For example, Canada's National Energy Board (NEB) is mandating same-season relief well capability or equivalent for the Arctic because the tracking and cleanup of oil spills under ice are major challenges in terms of response.

Only one major oil well blowout has occurred in Canadian offshore waters - the 1984 Uniake G-72 gas and condensate well off Sable Island approximately 150 nautical miles (~275 km) from Halifax, NS (Boudreau et al. 1999). In 2004, due to equipment failure, about 170 tonnes of crude oil was accidentally released from the Terra Nova production, storage and offloading platform on the Grand Banks, about 340 km east-southeast of St. John's, NL. The primary risk was to seabirds present in relatively high densities in the area of the spill. It was estimated that about 10,000 seabirds were killed by the spill (Wilhelm et al. 2007) as the oil slick was dispersed by natural physical processes.

Diffuse sources (natural seeps and runoff from land-based sources) account for the majority of petroleum hydrocarbon inputs to oceans (NRC 2003). The total input of petroleum into the sea worldwide from all sources over the period 1990-1999 was estimated by the NRC as approximately1.3 million tonnes per year. Natural petroleum seeps and runoff from land-based sources contributed 46% and 11% of petroleum hydrocarbon inputs, respectively. Tank vessel spills contributed about 8% of total inputs, while operational discharges (e.g., bilge discharges and cargo washings) contributed about 3% of inputs. Furthermore, most spills from tank vessels are relatively small. Data from the ITOPF on oil tanker spills show that of nearly 10,000 incidents, 81% resulted in releases of less than 7 tonnes (ITOPF 2015d). More recent comparisons of relative contributions of petroleum hydrocarbons to the world's oceans confirm earlier conclusions (**Figure 1.2**).

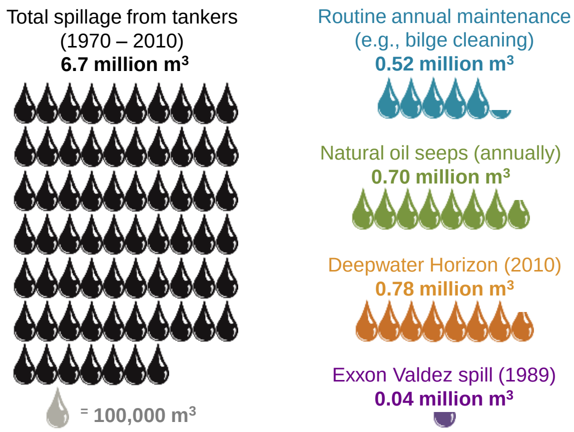


Figure 1.2 Volumes of oil released to marine waters from natural sources and spills. *Data from NRC (2003); Mackenzie (2011)*

Examination of the proportion of oil released into North American coastal and offshore marine waters from natural and human activities reveals that natural seeps and land-based sources accounted for an even greater proportion of inputs (NRC 2003) (**Figure 1.3**). The NRC estimated total inputs to North American waters were 260,000 tonnes per year over the period 1990-1999, with natural seeps contributing 61% of total inputs. Extraction of petroleum contributed about 1% of total inputs, largely from produced waters. Transportation of petroleum, including pipeline, tank vessel and coastal facility spills, accounted for 3.5% of inputs. The category "Consumption of Petroleum" included land-based river and runoff, recreational marine vessels, operational discharges and jettisoned aircraft fuel; these accounted for 32% of total inputs. The NRC noted that urban runoff and recreational boating require attention because the spills are chronic and often occur in sensitive ecosystems.

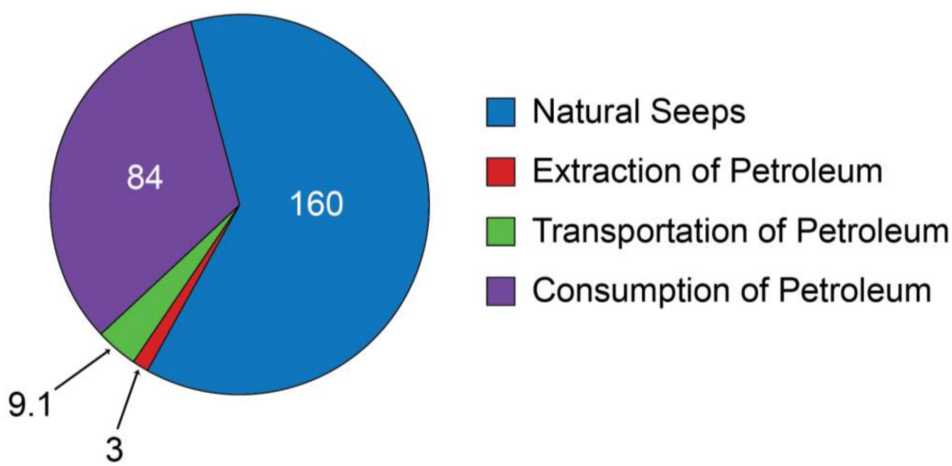


Figure 1.3 Average annual releases of oil (in kilotonnes) into North American marine waters from various sources (1990-1999). *Data from NRC (2003)*

1.4.3 Inland Freshwater Spills

Compared to marine oil spills, inland oil spills have received less attention, but freshwater spills are common, with more than 2,000 oil spills, on average, taking place each year in the inland waters of the continental United States (Owens et al. 1993). Although freshwater spills tend to be smaller volumes than their marine counterparts, they can have a greater potential to pose risks to the environment because of the greater likelihood that they occur within populated areas close to waterbodies with much less dilution and dispersion capacity, and involve shorelines that are often immediately adjacent to or directly impacted by the spill.

There are several recent examples of the substantial impacts of spills into inland waters. The spill of about 1,500 tonnes of Bunker C heavy fuel oil into Wabamun Lake, AB, in 2005 (due to a train derailment) resulted in residents being advised to avoid all use of lake and well water, and in impacts to habitat for numerous aquatic organisms and waterfowl (Thormann and Bayley 2008; Martin et al. 2014). The release of 26,000 bbl (1 bbl = 3,100 tonnes) of dilbit into Talmadge Creek, a tributary of the Kalamazoo River near Marshall, MI, in July 2010, resulted in the largest inland oil spill and one of the costliest spills in U.S. history. Another major, high visibility inland spill occurred in March 2013, when an Exxon-Mobil pipeline carrying Canadian Wabasca heavy crude from the Athabasca oil sands ruptured in Mayflower, AR, releasing 5,000 to 7,000 bbl (600 to 880 tonnes) of oil mixed with water into a residential neighbourhood. The oil eventually flowed through storm drains into Lake Conway, a recreational fishing lake.

Data on spills into fresh water in Canada were available primarily from the Transportation Safety Board of Canada (TSB), the NEB, the Alberta Energy Regulator (AER), and the AER's predecessor, the Energy Resources Conservation Board (ERCB). Data from the other major oil producing province, Saskatchewan, were also of interest to the Panel. However, the hundreds of spill reports in the Government of Saskatchewan Petroleum and Natural Gas Spill Report Directory (Government of Saskatchewan 2015) were not filed in a manner amenable to searching by keyword in order to focus on volume, type of spill or receiving environment. The only search criterion was spill location. Therefore, an efficient and effective review of the number and consequence of spills in Saskatchewan was not possible.

1.4.4 Spills from Pipelines

The volumes of releases of crude oil from pipeline accidents are usually small and releases are rarely into waterbodies. The TSB reported that over the 2004-2013 period, 14 pipeline accidents resulting in releases of crude oil occurred in Canada; eight of these releases were less than 1 m^3 (<1 tonne), two were between 1 and 25 m^3, three were between 26 and 1,000 m^3, and one release was over 1,000 m^3 (TSB 2013b). The AER reported that the number of crude oil pipeline incidents per 1,000 km of pipe ranged from 1.5 to 3.1 during the period 1990-2000 and from 1.0 to 1.9 during the period 2001-2012 (AER 2013). The AER stated that the stable spill frequencies in recent years may indicate that current practices may not result in further improvements; rather, new technologies or management strategies would be required to achieve significant spill reductions.

Although the incidence of crude oil releases from pipelines into fresh water have been relatively rare, spills entering rivers or wetlands have caught the public's attention due to the potential ecological damage on sensitive sites. Some of these spills are summarized in **Table 1.3** to provide context regarding volume, the type of receiving environment and environmental effects (if noted by the investigators).

Table 1.3 Examples of recent larger-volume pipeline spills in Alberta

Date and Location	Volume and type of spilled oil	Type of Receiving Environment	Environmental Effects	Reference
January 2001, Enbridge pipeline at Hardisty, AB	3,800 m^3 crude oil	Permanent slough	3,760 m^3 recovered; no effects noted	TSB (2001)
April 2011, Plains Midstream pipeline near First Nations Community of Little Buffalo, AB	4,500 m^3 crude oil	Beaver ponds and muskeg	Beaver, amphibian, bird and small mammal mortalities; reclamation required including re-vegetation	ERCB (2013)
May 2012, Pace Oil and Gas pipeline near Rainbow Lake, AB	800 m^3 crude oil	Wetlands	No wildlife or aquatic life mortalities noted; remediation efforts reported as being effective with vegetative regrowth noted	AER (2014a)
June 2012, Plains Midstream pipeline near Sundre, AB	460 m^3 crude oil	Red Deer River	Effects on water supplies of two communities and on recreational uses; effects on wildlife, soils and riparian vegetation	AER (2014b)
July 2015, Nexen Energy pipeline at its Long Lake operations, AB	5,000 m^3 bitumen emulsion	Muskeg adjacent to the pipeline right-of-way	Duck and frog mortalities; concerns focus on effects of high-salinity process water in the spilled oil: water emulsion	AER news release https://www.aer.ca/compliance-and-enforcement/nexen-long-lake

1.4.5 *Other Releases from Production Sources into Fresh Water*

Crude oil releases to fresh water at production sources can be due to blowouts or "flow-to-surface" incidents associated with hydraulic fracturing ("fracking") or with *in situ* oil sands production facilities. Well blowouts can involve releases of oil, produced water, frac fluids and/or gases. A review of investigation reports by the AER and previously the ERCB showed that the main consequences were to workers and public safety due to fire, explosion and toxic gases (particularly hydrogen sulphide gas). Effects on soils and vegetation in the immediate vicinity were also noted. Only one case was found (for the period 2006-2015) where release to a waterbody was noted; in this case, wellbore fluids (produced water and diesel fuel) entered an unnamed watercourse about 100 m from the well (ERCB 2011). The volumes and/or consequence of the release to the watercourse were not discussed.

A documented release of crude oil to a surface waterbody due to a fracking incident was not found in the record of reports released by the AER or ERCB. The ERCB investigated one incident that resulted in a 'misting' of released fluids on trees and soils; however, no release into water was noted (ERCB 2012).

The release was caused by hydraulic fracturing operations affecting a nearby producing oil well, resulting in a release of frac and formation fluids, produced water and natural gas.

The use of high-pressure steam to release bitumen from oil sands formations *in situ* can result in release of oil to the surface environment. For example, a series of four bitumen releases occurred at the Canadian Natural Resources Ltd (CNRL) Primrose high-pressure cyclic steam stimulation operations near Cold Lake, AB, from 2013-2014. The events were related to the use of high-pressure steam in a situation where vertical hydraulically-induced fractures could propagate, the cementing of wellbores was inadequate, and natural fractures and faults contributed additional pathways to the surface (Independent Panel Review 2014). Estimates of the total volume released ranged from about 1,200 to 1,900 m^3 (volume reports varied between CNRL, AER and third-party reviewers). Beaver, migratory bird, amphibian and small mammal mortalities occurred within the affected wetland complexes. A 20-ha portion of a lake had to be drained to remove bitumen and re-filled. The AER prohibited future high-pressure steaming at specific CNRL Primrose locations. CNRL reduced steam volumes and implemented enhanced monitoring and response to any further bitumen releases pending a final report from the AER.

1.4.6 Spills Due to Train Derailments

The recent increase in transport of crude oil by rail has resulted in an accompanying increase in rail-related spills. The TSB's most recent report on railway occurrences stated that over the 2004-2014 period, an increase in accidents involving release of crude oil was concurrent with an increase in shipments of crude oil by rail, from 500 car loads in 2009 to 160,000 car loads in 2013 (TSB 2015a). Five rail accidents resulted in the release of crude oil in 2013, including the Lac Mégantic derailment (see below). One accident involved a release of crude oil in 2014.

According to the U.S. Pipeline and Hazardous Materials Safety Administration (PHMSA), the United States has also experienced an increase in train-related oil spills. Between 1975 and 2009, no reported oil spills occurred during eight of those years, and spills of just one gallon or less were reported in five other years. However, more recently, data compiled by PHMSA reported a total of 3,700 tonnes of crude oil spilled from rail cars in 2013, greater than the 2,600 tonnes reported during the previous 37 years combined. A significant portion of the increased crude-by-rail transportation can be related to shale oil production in North Dakota, which has greatly expanded its output since the discovery of a new oil field in 2006 (the Parshall Oil Field producing from the Bakken and Three Forks Formations in the Williston Basin) (LeFever 2008)

Bakken crude oil produced in North Dakota was involved in three crude-by-rail spills during 2013, including the derailment in Lac-Mégantic, QC, on July 6, where a subsequent explosion and fire killed 47 people. An estimated 100 m^3 of spilled crude oil entered Mégantic Lake and the Chaudière River via surface flow, underground infiltration and sewer systems (TSB 2014b). In November 2013, derailment of 26 tank cars in Aliceville, AL, resulted in the release of nearly 2,400 tonnes of Bakken crude oil; the U.S. National Transportation Safety Board (NTSB) noted that the crude oil was released into a wetland (NTSB 2014). The third major spill occurred on December 30 near Casselton, ND, where several tank cars ruptured when a crude oil unit train derailed after striking another derailed freight train, spilling an estimated 1,300 tonnes of crude oil (NTSB 2013). A post-accident fire created dense, toxic smoke that forced a temporary evacuation of the town (NTSB 2014). The NTSB preliminary report did not note any release to surface waterbodies from the Casselton spill, and the online NTSB docket did not include any references to reports regarding effects on waterbodies (NTSB 2015).

As reported in the public media, releases of crude oil due to rail accidents continued in 2015. In several cases, the oil caught fire and towns were evacuated. Most spills occurred on land rather than in aquatic environments, but one entered a river. Examples during the first six months of 2015 include the following:

- 16 February – Canada – A Canadian National Railway (CN) freight train transporting crude oil derailed 80 km south of Timmins, ON. Of the 100 cars in the train, 29 derailed and seven crude oil tank cars caught fire. No injuries occurred and the burning oil was contained to the area (Mangione 2015).
- 16 February – U.S. – A CSX freight train hauling 109 tank cars of Bakken crude oil derailed near Mount Carbon, WV. At least seven crude oil tank cars caught fire, forcing the evacuation of about 200 people, one injury and no deaths (Van Pelt 2015). About 685 m^3 of crude oil were subsequently recovered by CSX and about 9,070 tonnes of soil were removed and shipped for disposal (Raby 2015).
- 5 March – U.S. – A BNSF oil train derailed in a rural area near Galena, IL. Of the 105 cars being transported, 21 containing Bakken formation crude oil left the track and caught fire. No injuries were reported. The U.S. EPA reported that sampling of surface water did not detect any oil in the Mississippi or Galena Rivers (EPA 2015).
- 7 March – Canada – A CN freight train derailed near Gogama, in northern Ontario. Forty of the 100 cars derailed, with five entering the Makami River and seven carrying crude oil catching fire and burning for several days (TSB 2015b). Cleanup crews deployed booms to soak up floating oil, as well as vacuum trucks to recover oil residues in the river. Thousands of tonnes of oily snow were removed. A drinking water advisory issued for Minisinakwa Lake was lifted on June 10, 2015, after analyses confirmed that hydrocarbon concentrations did not pose a risk to human health (Gillis 2015).
- 6 May – U.S. – A BNSF train derailed near Heimdal, ND, which ignited a crude oil fire in six tanker cars and forced the evacuation of approximately 40 nearby residents. No injuries or fatalities were reported (Riordan Seville et al. 2015).

1.4.7 Spills Due to Truck Transport Accidents

The total volume of crude oil transported by truck in Canada is an order of magnitude smaller than transport by pipeline, but the number of incidents per million m^3 of crude transported is four-fold greater (**Table 1.4**). The rate of incidents per volume transported was lowest for rail transportation. This disparity remained consistent in 2014, when only one crude-by-rail spill occurred while transporting a total volume of 9,339,576 m^3 of oil (significant figures are those reported by the data sources), an incident rate of 0.11 per million m^3 (data from National Energy Board [2015] and TSB [2015a]) versus a thirteen-fold greater rate for oil transport by truck in 2011 (**Table 1.4**).

Table 1.4 Number of accidents, volume shipped and accident rate by mode of crude oil transport [a,b] *. Data from Young (2014)*

Year	Mode	Number of Accidents	Volume Shipped (m^3)	Rate (per million m^3)
2011	Truck	45	31,459,085	1.43
2011	Pipeline	259	736,285,714	0.35
2012	Rail	1	3,908,266	0.26

a, Volume data from Statistics Canada and Transport Canada; accident numbers from Transport Canada for rail and truck and from provincial governments and NEB for pipeline. Volumes were estimated using crude oil density of 0.9 kg/l. There were no in-transit rail accidents in 2011; therefore, 2012 data were used for comparison. Pipeline volume includes some diluent.
b. The number of significant figures in the table are those reported by Young (2014)

Data from the U.S. indicate a similar pattern. The volume of oil spilled per distance transported has been greatest for tanker trucks among all modes of transport since 1996 (**Figure 1.4**). However, this metric has decreased over the same time period for all spills from all modes of transportation, including oil spills from trucks.

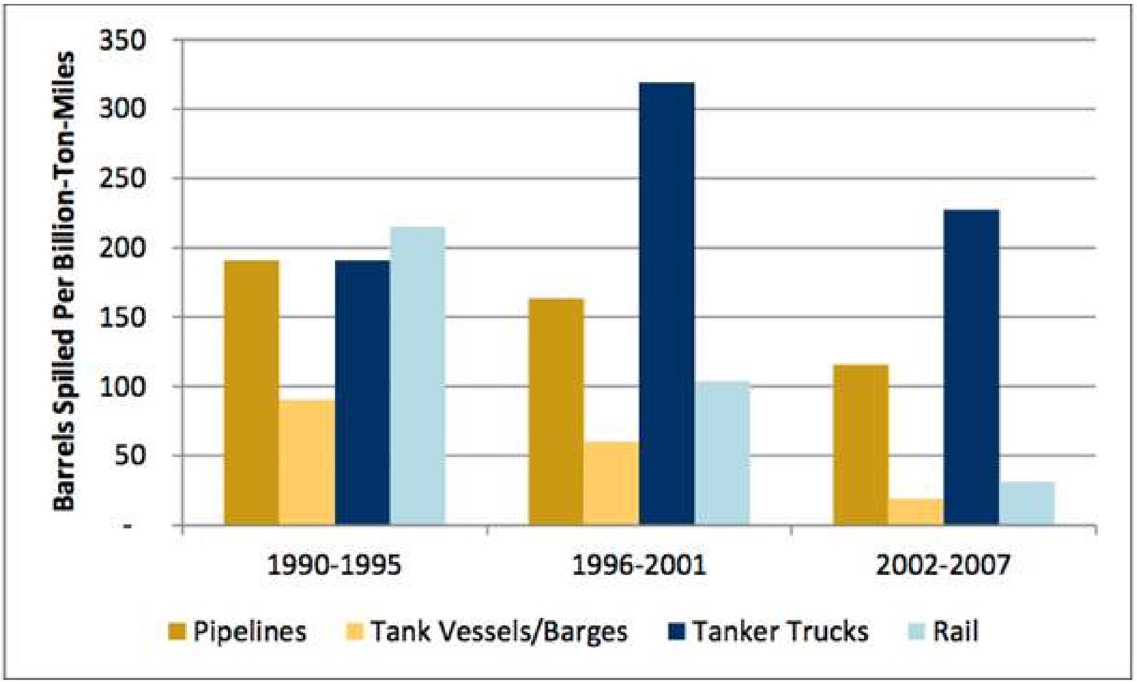


Figure 1.4 Average volumes of crude oil and petroleum product spilled per distance transported by all modes in the United States. *Notes: Pipelines include onshore and offshore pipelines. The time periods were chosen based on the available annual data for both spill volume and ton-miles. The values for each time period are averages of annual data for each six-year period. Source: Frittalli et al. (2014)*

Although the incident rate is highest for truck transport, the average spill volume per incident is much smaller and mainly on land. Unlike other modes of transport, trucks are primarily used to transport oil for relatively short distances. However, a recent increase in truck oil shipments has occurred, which is not reflected in the historic data shown in Figure 1.4. Shipment of oil by truck from shale formations in North Dakota and oil sands in Canada to U.S. refineries increased by 38% between 2011 and 2012 (Christopherson and Dave 2014). Risks to public health and safety from a tanker truck spill would be greater in the event of a fire and explosion if the spill occurred close to inhabited areas, and risks to the environment would be greater if the spill was released directly into waterbodies. For example, in 2013 a tanker truck carrying 35 m^3 of jet fuel tipped over into Lemon Creek, BC (a tributary of the Slocan River) resulting in an evacuation order affecting about 1,500 people, a “do not drink” water order that lasted a week, some fish and bird mortalities, and effects on water and sediment quality (CBC 2013; Executive Flight Centre 2014). While this incident did not involve crude oil, it illustrates the effects of hydrocarbon spills directly into waterbodies. A release of crude oil would be expected to have longer-term impacts due to the persistence of the non-volatile components of the spill in water, sediments and biota.

1.4.8 Summary of Crude Oil Spills in Canada

Spills of crude oil into marine or freshwater systems in Canada from oil production facilities, tankers, pipelines, rail and truck transport are infrequent, and the probability of spills decreases with increasing spill size (**Table 1.5).** However, as pointed out by SL Ross Environmental Research (2014), while statistics for spills into the marine environment are readily available in Canada, statistics for inland spills into fresh water are not. The difficulty in locating inland spill data produced the “nd” results for rail and road incidents in Table 1.5. The Panel’s review confirmed the difficulty of obtaining clear and reliable data on crude oil spills into fresh water. For example, the information presented in the sections above on spills from production facilities, rail and truck transport had to be gleaned from details within statistical reports on all incidents, whether involving oil transport or not (e.g., the TSB [2015] report on railway occurrences), by laborious searching through individual investigation reports (e.g., individual TSB or AER reports) and/or from media reports. Even when reports were available on spill incidence and volume (e.g., the AER [2013] report on pipeline performance), spills of crude oil were not always distinguished from refined product spills; instead, statistics were presented on "hydrocarbon liquids".

Table 1.5 Annual frequency of oil spills in Canada by source and volume. *Source: SL Ross Environmental Research (2014)*

Source	**Spill Volume (m^3)**					
	<1	**1-10**	**10-100**	**100-1,000**	**1,000-10,000**	**> 10,000**
Offshore exploration and production[a]	20.9	1.7	0.4	0	0	0
Vessel Spills[b]						
Crude	nd[d]	nd	0.02	0.01	0.19	0.004
Refined	nd	nd	0.60	0.10	0.024	0.00
Fuel	nd	nd	1.90	0.60	0.01	0.00
Total	nd	nd	2.52	0.71	0.05	0.004
Pipelines[c]						
Release into	0.56	0	0.20	0	0	0
Total	0.75	3.8	1.89	0.94	0	0
Rail	nd	nd	nd	nd	nd	nd
Road	nd	nd	nd	nd	nd	nd

[a]. *2004 to 2013. Canada-Nova Scotia Offshore Petroleum Board (http://www.cnsopb.ns.ca/environment/incident-reporting) and http://www.cnsopb.ns.ca/environment/incident-reporting*
[b]. *WSP Canada Inc. (2014).*
[c]. *2008 to April 2013. https://www.neb-one.gc.ca/sftnvrnmnt/sft/dshbrd/index-eng.html*
[d]. *nd, no data; information was not publically available or was not immediately accessible.*

Notwithstanding the apparent relative infrequency of crude oil spills into aqueous environments in Canada, the consequences of spills into sensitive waterbodies can be substantial, both with respect to impacts on human health, safety and the environment and with respect to economic impacts. Therefore, a primary focus of this Report is on the consequences of spills, no matter how low the probability may be. This focus is commensurate with the key questions posed by the sponsors and stakeholders.

1.5 Organization of This Report

The relationships among the chapters of this report and the key questions posed by the sponsors and stakeholders are illustrated in **Table 1.6**. There is overlap in the subject matter among the chapters but the Panel strove to avoid duplication. In some cases, topics are discussed from a different perspective, or in more or less detail, depending upon the primary focus of the chapter. Chapter 8 considers all of the major topics within a risk framework and uses case studies to examine the importance of physical, chemical and biological factors, as well as cleanup and recovery measures in determining short-term and long-term risk of spills. The final chapter (Chapter 9) presents the Panel's recommendations.

Table 1.6 Relationship between chapters and key questions

Chapter	**Question 1:** Behaviour of Crude Oil Types	**Question 2:** Chemical Composition and Toxicity of Crude Oil Types	**Question 3:** Microbial Processes Affecting Crude Oil Toxicity and Characteristics	**Question 4:** Relationship Among Crude Oil Behaviour, Toxicity, Characteristics and Remediation	**Question 5:** Research Priorities	**Question 6:** Spill Prevention, Preparedness and Response
2: Composition, Properties and Behaviour	X	X	X		X	
3: Effects of Environment on Oil Fate and Behaviour			X	X	X	
4: Toxicity and Ecological Relevance		X	X	X	X	X
5: Modeling Spill Behaviour				X	X	
6: Spill Response Options					X	X
7: Prevention and Response Decision Making					X	X
8: Risks from Oil Spills	X	X	X	X	X	X

CHAPTER 2: CHEMICAL COMPOSITION, PROPERTIES AND BEHAVIOUR OF SPILLED OILS

Abstract

The chemical composition of petroleum[1] is of utmost importance for understanding oil spills in aquatic environments because the chemistry of the oil dictates its physical properties (e.g., density and viscosity), behaviour (e.g., spreading, sinking, dispersion), biological impacts (e.g., toxicity, susceptibility to biodegradation) and ultimate fate in the environment. Thus, petroleum chemistry is important to oil spill responders for predicting hazards, such as fire and explosion, and for selecting suitable cleanup and remediation approaches. It is also important to regulators for forensic purposes, monitoring and determining acceptable endpoints for spill remediation.

The petroleum hydrocarbons transported within Canada range from ultra-light condensates and light oils to heavy oils and bitumens, as well as blends like diluted bitumens and heavy fuel oils. Each oil is a complex mixture of thousands of chemicals, not all of which are hydrocarbons, and every oil has a unique chemical 'fingerprint'. Conventionally, petroleum is separated into four major fractions for analysis: saturates, aromatics, resins and asphaltenes. Whereas the structures of many saturated and aromatic petroleum compounds are known and have been studied individually or within an oil matrix, the chemically diverse, high molecular weight resins and asphaltene fractions have resisted characterization. Additional minor constituents in oil may include sulphur (e.g., as hydrogen sulphide gas), naphthenic acids, metals and minerals.

Spilling oil onto water progressively changes its chemical fingerprint through physical, chemical and biological processes collectively called 'weathering'. As oil spreads on the water surface, small molecules evaporate, others may be oxidized by sunlight, and the oil may form emulsions with water. In the water column oils may disperse as droplets and/or sink and/or form 'tar balls' after interacting with suspended particles; light components may dissolve in the water; others may be selectively biodegraded by microbes. Oil that reaches the shoreline or sediments may become sequestered and/or re-emerge over time, but oil interactions with ice are currently not well known. Measurable changes in the 'fingerprint' of spilled oil over time reflect its initial chemistry and the magnitude of weathering processes and therefore can be used to monitor remediation progress and determine endpoints. Importantly, just as each crude oil is chemically unique, each oil spill reflects the specific environmental conditions at the spill site acting on a particular oil over a given time period. The diverse petroleum types form a continuum of chemical compositions, physical properties and spill behaviours.

To provide background for later chapters on oil fate (Chapter 3), toxicity (Chapter 4), modeling (Chapter 5) and remediation of oil spills (Chapter 6), as well as spill response decision-making (Chapter 7), this chapter summarizes the common chemical components of crude oils, describes a suite of crudes representing the compositional range of oils commonly transported in Canada, and briefly outlines the general behaviour of oil spilled in marine and freshwater environments. Further research is needed to fully characterize the properties and spill behaviours of emerging oil types, including diluted bitumen blends and unconventional oils such as shale oil.

[1] *The terms 'petroleum' and 'crude oil' are considered here to be synonyms and are used interchangeably.*

2.1 Chemical Composition of Oils

> Crude oils are highly complex, diverse mixtures of chemicals. Each oil has a unique composition or 'chemical fingerprint' that usually consists of four major classes of chemicals: Saturates, Aromatics, Resins and Asphaltenes (SARA) and sometimes minor constituents like metals, sulphur, solids and water.

Crude oils are naturally-occurring complex mixtures of thousands of individual compounds, but primarily they comprise hydrocarbons (molecules consisting of only carbon and hydrogen) and lesser proportions of compounds containing heteroatoms (e.g., nitrogen, sulphur and/or oxygen) in addition to carbon and hydrogen. Commonly, small amounts of metals, minerals and sometimes inorganic sulphur are also present. The majority of petroleum components are derived from organic matter from ancient aquatic plants, animals and microbes, and their proportions in the oil reflect the source(s) and geological history of that oil during its formation.

2.1.1 Four Major Chemical Fractions of Crude Oil

Most crude oil constituents can be divided into four major chemical classes known by the acronym SARA: Saturates, Aromatics, Resins and Asphaltenes, as described below and illustrated in **Table 2.1**. Historically, these groups are defined as solubility fractions by liquid-solid chromatography, as explained in Appendix A (**Figure A1**). Appendix A also presents an overview of analytical methods commonly used to chemically characterize oils. Together these fractions contribute to the bulk properties of petroleum, such as viscosity, specific gravity and susceptibility to biodegradation, as discussed in detail below (Section 2.2).

It is important to note that **Table 2.1** presents only a few examples of the thousands of possible structures of petroleum components. Indeed, the presence and positions of one or more alkyl groups (e.g., $–CH_3$, $–C_2H_5$) on parent structures, whether saturated or aromatic, can produce myriad 'isomers' (chemicals having the same chemical formula but different structures) and 'homologous series' of similar chemicals that differ by the number of alkyl substituents. Isomers and members of homologous series may have very different adsorption properties, water solubility and susceptibility to biodegradation. A paraffin with four carbon atoms can exist in only two isomer forms, but one with 14 carbon atoms theoretically can exist as 60,523 isomers (Speight 2014). Multiple isomers cause technical problems for peak resolution by gas chromatography (GC) and contribute to the unresolved complex mixture (UCM) or 'hump' in gas chromatograms (Appendix A).

2.1.1.1 Saturates

> The saturate fraction is considered the least toxic of the four major petroleum fractions and the most readily biodegradable, with the exception of steroids and hopanoids that tend to resist biodegradation.

This chemical class is typically the major component of petroleum. It exclusively comprises hydrocarbon molecules having single carbon-carbon bonds, with all remaining bonds being saturated with hydrogen atoms (i.e., no double- or triple-bonded carbon). Three subclasses are defined within this fraction: *paraffins* and *isoparaffins* having straight or branched chain structures, respectively; *naphthenes* (*cycloparaffins*, also called *alicyclic hydrocarbons*) having one or more saturated ring structures; and fused-ring aliphatics, including *hopanoids* and *steroids*, having large, complex structures combining paraffinic and naphthenic structures (**Table 2.1**). Olefins (partially unsaturated hydrocarbons), such as alkenes and alkynes, are scarce or absent in petroleum (Speight 2014).

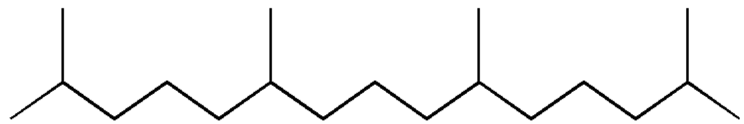
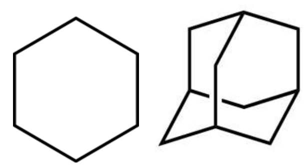
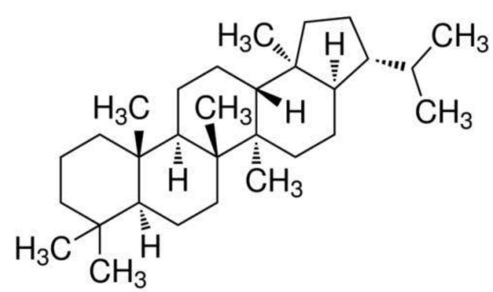
Petroleum paraffins range from gases and vapours of one to five carbon atoms (C_1-C_5) under normal pressure (e.g., methane gas, CH_4) to liquids of C_5-C_{16}, to crystalline waxes of $C_{>20}$. Normal (*n*-)alkanes have straight chains with no branching (i.e., no alkyl substitutions on the hydrocarbon backbone) and therefore have the general formula C_nH_{2n+2}. *iso*-Alkanes are branched structures with alkyl substitutions at single or multiple points on the backbone, creating numerous series of isomers having the same molecular weight but different structures.

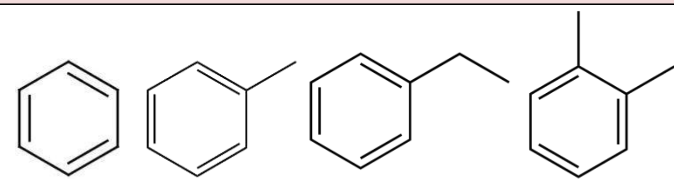
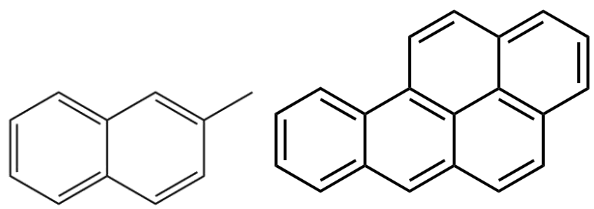
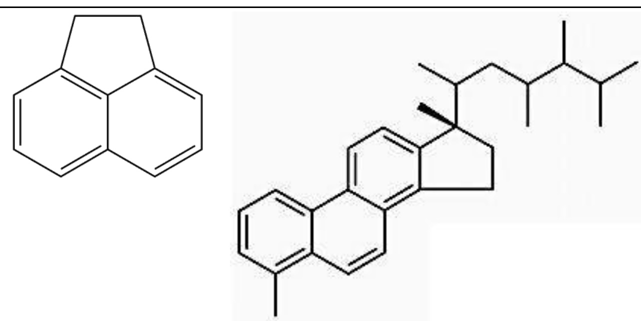
In general, *n*-alkanes $<C_5$ are highly volatile (and therefore not likely to remain in the water column for biodegradation, except at high pressures in deep water), and those between C_5 and ~C_{30} are biodegradable when present in crude oil. Therefore, *n*-alkanes of $\leq C_{30}$ are unlikely to persist in the environment and pose little toxicological risk to aquatic life, unless they are ingested in oil droplets, because they are essentially water-insoluble. *iso*-Alkanes tend to be more persistent in the environment because they are more slowly degraded than their *n*-alkane counterparts; in fact, pristane (**Table 2.1**) and phytane, which are common and often prominent *iso*-alkanes in petroleum (Appendix A, **Figure A2**), have been used as short-term petroleum biomarkers because they usually resist biodegradation until the *n*-alkanes have been depleted (Head et al. 2006). Therefore, petroleum biomarkers can be used as internal standards to monitor the biodegradation rates of susceptible oil components, or for forensic evidence to identify sources of contamination in the environment. For example, triaromatic steroids containing aromatic and aliphatic moieties (**Table 2.1**) were used to distinguish naturally-occurring background hydrocarbons from diluted bitumen (dilbit) contamination in the Kalamazoo River spill (US-EPA 2013a; Chapter 8). See Chapter 7 for a more complete discussion of petroleum biomarkers.

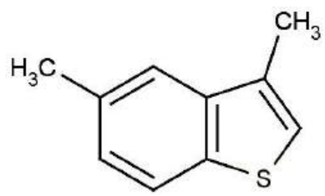
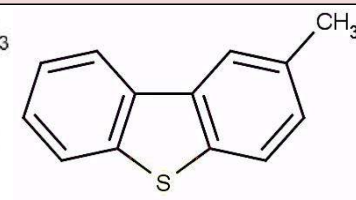
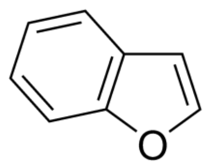
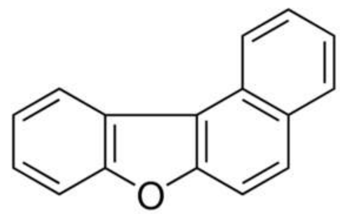
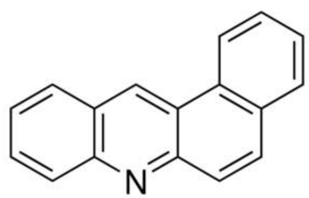
The term ‘biomarker’, as used in petroleum chemistry, designates a chemical compound originally derived from living organisms that is poorly biodegradable and therefore persists over geological time in the oil. This differs from the definition of ‘biomarker’ used in environmental toxicology (Chapter 4). Commonly used petroleum biomarkers include certain iso-alkanes and complex cyclic alkanes.

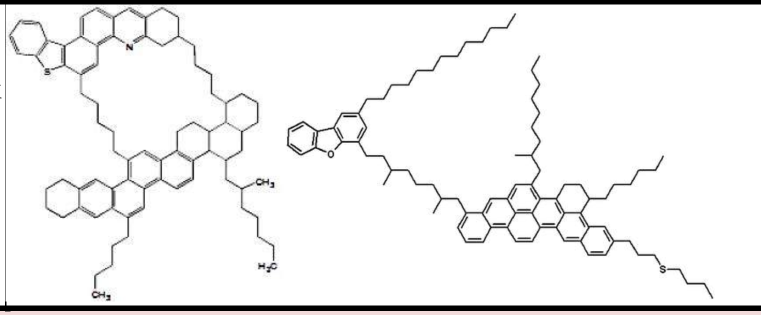
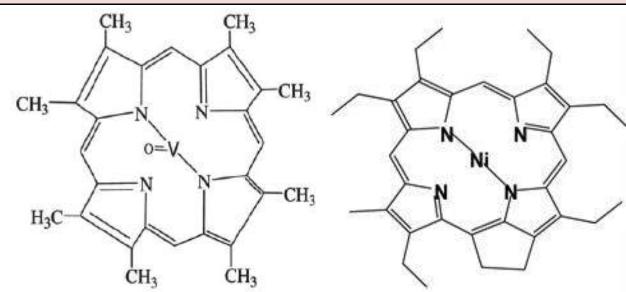
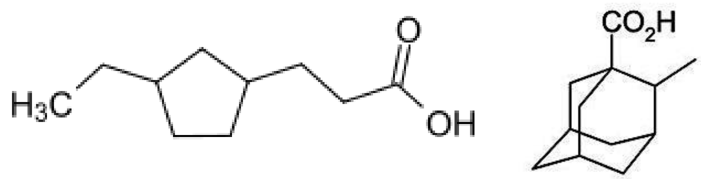
Naphthenes, or *cyclo*-alkanes, have the general formula C_nH_{2n} and can exist in multiple fused ring structures with single or multiple alkyl substitutions. Low molecular weight (LMW) *cyclo*-alkanes ($\leq C_6$) are volatile and can cause toxic effects (e.g., US-EPA 1994; Sikkema et al. 1995) because they can partition into biological membranes. As with *iso*-alkanes, *cyclo*-alkanes tend to be more resistant to biodegradation than *n*-alkanes of the same molecular weight (Head et al. 2006). Diamondoids (based on the adamantane structure; **Table 2.1**) are examples of multicyclic aliphatics, having cage-like structures with or without alkyl side-groups (Wei et al. 2007). They are found in significant concentrations in bitumen and are less susceptible to biodegradation than their polycyclic aromatic hydrocarbon (PAH) counterparts (Government of Canada 2013).

Table 2.1 Major chemical classes comprising petroleum, and structures of some example molecules

Name of chemical class or fraction	Example of class or fraction	Structure of example compound(s)	Properties and relevance of class or fraction
SATURATES			Usually the most abundant chemical class in petroleum; highly water-insoluble; typically are biodegradable and generally non-toxic
n-Alkanes	*n*- Hexadecane		*n*-Alkanes $<C_6$ are light liquids or gases and may be toxic; C_6-C_{18} are readily biodegradable; $>C_{20}$ are waxes and more difficult to biodegrade
iso-Alkanes	Pristane		*iso*-Alkanes are more resistant to biodegradation than *n*-alkanes; some, such as pristane and phytane, are used as short-term biomarkers for aerobic biodegradation
cyclo-Alkanes and Diamondoids	Cyclohexane; Adamantane		More resistant to biodegradation than *n*-alkanes; diamondoids may be used as robust biomarkers during biodegradation (de Araujo et al. 2012)
Hopanoids and Steroids	17α(H),21β(H)-Hopane (30αβ)		Many are non-biodegradable and therefore are used as long-term biomarkers for forensics and biodegradation assessment

Name of chemical class or fraction	Example of class or fraction	Structure of example compound(s)	Properties and relevance of class or fraction
AROMATICS		The examples shown below are strictly hydrocarbons; however, some aromatics having heteroatoms (i.e., S-, N- and O-heterocycles) fractionate with the aromatic hydrocarbons and are often considered together functionally. Examples of such aromatic heterocycles are shown in the resins fraction below.	A hydrocarbon class that is generally more toxic than saturates; many isomers and homologous series are possible when aliphatic groups are attached to the aromatic rings.
Monoaromatics	BTEX: Benzene, Toluene, Ethylbenzene and Xylene isomers (*ortho*-xylene shown)		The BTEX series is volatile, more water-soluble than other hydrocarbons, acutely toxic and/or carcinogenic, and relatively biodegradable under aerobic and anaerobic conditions
Polycyclic aromatic hydrocarbons (PAHs) and alkylated series (alkyl PAH)	2-Methylnaphthalene and Benzo[a]pyrene		Large number of isomers are possible due to multiple positions for alkyl side chains; some PAHs are toxic and/or carcinogenic; many persist in the environment because they resist biodegradation; benzo[a]pyrene is a US-EPA 'Priority Pollutant'
Naphtheno-aromatics; aromatic steroids	Acenaphthene and a triaromatic steroid		Combination of saturated and unsaturated cyclic hydrocarbons; acenaphthene is a US-EPA 'Priority Pollutant'; triaromatic steroids have been used for forensic attribution of environmental contamination

Name of chemical class or fraction	Example of class or fraction	Structure of example compound(s)	Properties and relevance of class or fraction
RESINS		The structures of individual resin compounds have not been determined, but they contain one or more S-, N- and/or O-heteroatoms; examples of aromatic S-, N- and O-moieties that may form part of resin structures are shown below. The individual chemicals below are commonly considered to be part of the Aromatics fraction (despite being heterocycles rather than hydrocarbons).	A solubility class related to asphaltenes (below), but of lower molecular weight, lower aromatic content and greater polarity; poorly detected and resolved by most GC-based methods
Examples of S-containing moieties that may be constituents of resin molecules	Moieties may include: Dimethylbenzothiophene and 2-Methyldibenzo-thiophene	 	Organic sulphur moieties such as these may contribute to total sulphur content of sour crude oils
Examples of O-containing moieties that may be constituents of resin molecules	Moieties may include:Benzofuran; Benzo[b]naphthofuran	 	Organic oxygen-containing groups in resins may be generated from PAHs by photooxidation or partial biodegradation
Examples of N-containing moieties that may be constituents of resin molecules	Moieties may include: Benz[a]acridine;Dibenzo[a,i]carbazole	 	N-containing groups contribute to polarity of the resins fraction
ASPHALTENES		The structures of individual asphaltene molecules have not been determined; they are related to resins (above) but have higher molecular weight, greater aromatic content and are less polar than resins.	A solubility class of complex high molecular weight (HMW), polar compounds that are water-insoluble; contribute to heavy oil viscosity; non-biodegradable

Name of chemical class or fraction	Example of class or fraction	Structure of example compound(s)	Properties and relevance of class or fraction
	Hypothetical asphaltene molecules, after Hoff and Dettman (2012) and Boek et al. (2010)		Numerous models of asphaltene structures have been proposed of different size, aromaticity and degree of condensation; different subclasses of asphaltenes with different chemical properties have been proposed recently
MINOR ORGANIC COMPONENTS			
Petroporphyrins (organometals)	C28 Etio vanadium porphyrin; Nickel deoxophyllo-erythroetioporphyrin (D PEP)		Vanadium and nickel are common metals coordinated in centre of the porphyrin structure; the core derives from (bacterio)chlorophyll molecules transformed over geological time by pressure and heat
Naphthenic acids	Ethylcyclopentane-3-propanoic acid; Diamondoid acid		Heterogeneous class of O-containing polar compounds associated with acute toxicity to aquatic life; may be products of partial biodegradation of hydrocarbons; many resist biodegradation

Fused complex alicyclic hydrocarbons include hopanoids and steroids that are derived from microbial, animal and plant sterols and terpenes. Some of these compounds are extremely resistant to biodegradation and therefore are ideal oil biomarkers that persist for thousands or even millions of years (Peters et al. 2005). Others, such as cholestane and possibly hopane, are less stable and may slowly biodegrade (Prince and Walters 2007).

Waxes (linear alkanes $>C_{20}$), which can represent a substantial proportion of certain crudes, may precipitate out of petroleum at low temperature and can also form coatings on surfaces, affecting the interfacial properties of the oil (Hollebone 2015). They are non-toxic but resist biodegradation due to low bioavailability in water.

2.1.1.2 Aromatics

Aromatic hydrocarbons are cyclic, planar, unsaturated compounds having structures based on a single benzene ring or multiple fused benzene rings. They can have one or more alkyl groups in various isomeric arrangements. The most common (alkyl)-monoaromatics in petroleum are the BTEX series (benzene, toluene, ethylbenzene and the three xylene isomers; **Table 2.1**). Benzene, ethylbenzene and toluene are on the US-EPA list of toxic 'Priority Pollutants' (*http://water.epa.gov/scitech/methods/cwa/pollutants.cfm*). They are also light enough to be volatile, presenting flammability and breathing hazards.

> Monoaromatics are the most water-soluble of the hydrocarbons and thus the most mobile in the water phase by diffusion. They may cause acute toxicity because of their ability to partition into biological membranes. PAHs having two or more fused aromatic rings are less volatile and commonly more persistent than monoaromatics.

PAHs have two or more fused aromatic rings and may additionally have alkyl side-groups (alkyl PAH). Many of the smaller PAHs are of intermediate biodegradability that is inversely proportional to the number of fused rings in the structure. Several 'parent' PAHs (i.e., unsubstituted PAHs such as benzo[a]pyrene; **Table 2.1**) are on the US-EPA list of 'priority pollutants' because of their toxicity, carcinogenicity (typically via inhalation) and/or resistance to biodegradation (van Hamme et al. 2003), even though these parent PAHs typically represent <15% of the total PAH (TPAH) in the oil. The bulk of PAHs have one or more alkyl substituents in various positions (e.g., 2-methylnaphthalene; **Table 2.1**), generating many homologous series of alkyl PAH with different physical and chemical properties and sometimes very different biological effects and biodegradability (Wang et al. 1998). The chronic toxicity of oil is attributed primarily to alkyl PAHs having 3–5 rings (discussed in detail in Chapter 4).

Naphthenoaromatic structures are combinations of saturated and unsaturated rings, with or without alkyl groups. Their concentrations, along with the naphthenes, tend to be greater in heavier oils (Speight 2014) and contribute to the overall resistance of these oils to biodegradation. An example is acenaphthene (**Table 2.1**), which is also a US-EPA 'priority pollutant'.

Some heterocycles (e.g., those shown in **Table 2.1** as moieties potentially found in resin structures), including dibenzothiophenes, furans, carbazoles and their alkyl-substituted homologues, fractionate with the aromatics even though they are not hydrocarbons. Some of these aromatic heterocycles are biodegradable, whereas some isomers resist enzymatic attack (Kropp et al. 1996) or are only partially oxidized, yielding dead-end products that are more water-soluble than the parent compound and have different toxicity.

2.1.1.3 Resins

Resins are not hydrocarbons since their chemical structures include elements other than carbon and hydrogen, i.e., the heteroatoms S, N and/or O.

Unlike saturates and aromatics that can be defined by their chemical structures, petroleum resins (and asphaltenes, Section 2.1.1.4) are defined on the basis of their solubility in hydrocarbon solvents rather than on discrete structures (Appendix A, **Figure A1**), with the resins fraction being soluble in *n*-pentane or *n*-heptane but insoluble in liquid propane (Speight 2004). The structures of individual petroleum resins have not been determined, although they all have one or more heteroatoms that may be incorporated into ring structures that are saturated, partially saturated or aromatic, and/or long-chain paraffin residues, with or without heteroatoms. Resins are chemically related to the asphaltenes (Section 2.1.1.4), but are smaller (molecular weights estimated at 500 – 1,000 daltons [Da]; Bertoncini 2013), have lower aromaticity and are more polar[2] than asphaltenes. In the petroleum industry, resins are considered the smallest of the polar compounds in oil (versus hydrocarbons that are non-polar). Light paraffinic crude oils may comprise >97% hydrocarbons and <3% resins, whereas heavy oils and bitumen may be only ~50% hydrocarbons with the remainder being resins, asphaltenes, naphthenic acids and metals (described below). In general, the resins constitute a greater proportion of petroleum mass than the other non-hydrocarbon components, although this is not apparent by GC methods because the resins either tend to be poorly resolved, contributing to the UCM 'hump' in chromatograms (Appendix A), or not to be resolved at all by GC.

The polarity of resins is contributed by the presence of heteroatoms in diverse moieties within the resin structure, such as those shown in **Table 2.1**, i.e., S-containing aromatic thiophenes, benzothiophenes, dibenzothiophenes, naphthobenzothiophenes and aliphatic alkyl sulphides; N-containing pyrroles, indoles and carbazoles; and/or O-containing hydroxyl, ester, carboxylic acid, carbonyl, furan and sulfoxide/sulfone functional groups. These heteroatoms make resins more polar than hydrocarbons (Speight 2004) and in some cases more toxic because of their water solubility (Melbye et al. 2009). Because of the dominant effect of these moieties on the resins fraction, the resins are also sometimes called the 'Polar' or 'NSO' fraction of petroleum.

Resins typically resist biodegradation, although some may be partially oxidized by microbes to generate products of greater polarity and water solubility and thus potentially greater mobility, toxicity and environmental persistence. In fact, some resins may represent the dead-end products of incomplete biodegradation of organic matter over geological time, which are resistant to further enzymatic attack, or that may have been generated from hydrocarbons in spilled oil by poorly-understood photooxidative processes (Section 2.4.1.3).

2.1.1.4 Asphaltenes

Asphaltenes are the most complex, most diverse and highest molecular weight components of petroleum. They are also the least susceptible to biodegradation. Asphaltenes comprise a small proportion of light crude oils and greater proportions of heavier oils and bitumens, conferring increased viscosity and density, among other properties.

Asphaltenes are not hydrocarbons because they contain S-, N- and O-heteroatoms, like the resins, but they have greater average molecular weight (>400 Da, mean weight ~1,200 Da [Gray 2015]). This chemical class (Speight 2004) represents myriad individual chemicals and is defined on the basis of insolubility in *n*-alkanes, such as pentane and heptane, but solubility in toluene (Appendix A, **Figure A1**). Thus, petroleum can be separated into

[2] *Polarity refers to the distribution of electric charge across a molecule. Simplistically, polar compounds dissolve better in water (a polar solvent) than do non-polar compounds.*

two major fractions simply by diluting it in 40 volumes of *n*-pentane (Speight 2004) or similar solvent, whereupon the asphaltenes precipitate and the nC_5-soluble fraction (known as the maltenes or de-asphalted oil) remains dissolved. The proportion of asphaltenes in a crude oil affects its properties by causing it to adhere to and affect the wetting characteristics of surfaces it attaches to, including pores and channels in sediments, earning this class the nickname 'the cholesterol of crude oil' (Boek et al. 2010).

Despite considerable research (e.g., Strausz et al. 1992; Peng et al. 1997; Sheremata et al. 2004; Dettman et al. 2005; Hoff and Dettman 2012), the structure of individual molecules within the asphaltene class has remained controversial due to their HMW, complexity, heterogeneity and propensity to intimately associate with other petroleum components like resins (Speight 2004). Asphaltene molecules are proposed to exist as nanoaggregates (Boek et al. 2010) and/or as colloidal micelles in the bulk petroleum, with resins forming the outer layer and preventing asphaltene aggregation (Petrova et al. 2011). Such properties and interactions make chemical characterization technically difficult. Asphaltenes are neither resolved nor detected by conventional GC but instead are subjected to alternative analyses, such as gel permeation chromatography, nuclear magnetic resonance and high-temperature simulated distillation (Appendix A). Speight (2004) considered that the predominant chemical groups in asphaltenes are aromatic (sometimes >50% of the total carbon) with saturated hydrocarbon linkages. Hoff and Dettman (2012) have isolated and defined different subclasses of asphaltenes having varying degrees of condensation and differing alkyl substitutions (**Table 2.1**) and therefore different properties. Yang et al. (2015) have further inferred and differentiated structural features of asphaltenes that stabilize oil:water emulsions through interfacial activity (Yang et al. 2014). Thus, the structures and properties of asphaltenes are gradually emerging with advances in analytical techniques but consensus has yet to be achieved.

Recommendation: **Continued fundamental research is needed into the composition of the high molecular weight, polar components of oil, and standardized analytical methods for characterizing these fractions should be developed and published. Characterization of the resins and asphaltenes classes is presently incomplete because of current analytical technical limitations preventing comprehensive, detailed monitoring and prediction of the behaviour and fate of many spilled oils, particularly heavy oils and bitumen blends that are rich in these fractions.**

Because of their size and complexity, asphaltene molecules are extremely resistant to biodegradation (despite a small number of questionable literature reports purporting to demonstrate asphaltene degradation). Their stability in the environment is shown by their preservation for thousands of years in ancient artifacts and their modern use in asphalt roads and roof shingles.

2.1.2 Minor Components of Crude Oils

> In addition to SARA fractions, petroleum may contain small and variable concentrations of non-hydrocarbon components derived from biological or geological sources, such as metals, organometals, sulphur, naphthenic acids, mineral particles and /or water.

Some of the minor constituents of crude oils include organometallic compounds, such as petroporphyrins (Caumette et al. 2009) containing vanadium (V), nickel (Ni), iron (Fe) or copper (Cu) derived from plant and microbial sources and dissolved in the bulk oil, as well as inorganic salts of these metals and others in colloidal suspension (Speight 2014). Metalloporphyrin structures (**Table 2.1**) are often associated with the asphaltenes; therefore, metals are more abundant in heavier petroleum fractions and in heavy bituminous crudes at concentrations up to hundreds of parts per million (Fingas 2015b).

Whether metal atoms that are strongly associated with their organic ligands in petroleum actually become water-soluble and bioavailable after oil spillage into water is a matter of debate (Joung and Shiller 2013). Thus, reports of environmental impacts of heavy metals from oil contamination vary. For example, concentrations of Ni and V in Saudi Arabian coastal sediments contaminated by massive volumes of Kuwait oil during the 1991 Gulf War were only slightly elevated above background values, and may have resulted from oil combustion as well as spillage (Fowler et al. 1993). In contrast, tonnes of Cu, Ni and V were estimated to have been released to the Atlantic Ocean during fuel oil leakage from the sinking of the *Prestige* oil tanker (Santos-Echeandía et al. 2008). Seawater concentrations of Cu and Ni (but not V) were elevated in the upper water column (0-50 m depth), associated with upward movement of escaping fuel, and in deep waters that had longer contact time with the oil (Santos-Echeandía et al. 2008). Similarly, Wise Jr. et al. (2014) detected increased concentrations of chromium (Cr) and Ni in floating oil and tar balls associated with the Deepwater Horizon (DWH) blowout in the Gulf of Mexico and elevated concentrations in sperm whale tissue samples collected in the Gulf versus control samples. In contrast, Joung and Schiller (2013) found that samples of surface waters near the DWH blowout site did not show unusual concentrations of Ni or several other metals, but deep water samples collected near the well had higher concentrations of cobalt (Co). Elevated barium (Ba) concentrations detected in deep water were likely associated with the drilling mud used to contain the blowout rather than the oil plume itself. Thus, the magnitude and effects of metal contamination from individual spills require additional study, whereas the accumulation of metals in chronically hydrocarbon-contaminated water and sediments (e.g., those impacted by refineries or shore-to-ship oil transfer) is well-known (e.g., González-Macías et al. 2006).

Inorganic S present in elemental form (S^0) or as gaseous H_2S may be a minor component by mass (often <1%), but H_2S is toxic to humans even at parts per million levels. H_2S is also a major concern regarding corrosion to infrastructure (e.g., pipelines and surface handling facilities) and explosion potential in confined spaces, including rail cars. Depending on the water content of the oil and its pH, H_2S may exist as a gas or may be dissolved in the water phase. H_2S may represent only a fraction of the total S in sour crudes, which can contain significant quantities of organic S compounds (**Table 2.1**) that contribute to total S.The organic S compounds have different chemical properties than H_2S, and are more problematic in refineries than in the environment. Oils with a significant proportion of total S (usually ≥1%) are called 'sour' crudes, as opposed to 'sweet' crudes with ≤0.5% S (Section 2.3.6). Sweet oils are generally more valuable than sour, as the presence of S imposes a price penalty at the refinery, and H_2S concentrations must be reduced before transportation for safety reasons.

Naphthenic acids (NAs; **Table 2.1**) comprise a large, diverse group of alkyl-substituted cyclic and noncyclic carboxylic acids, historically defined as having the chemical formula $C_nH_{2n}+_ZO_2$, where *z* reflects the number of rings in the structure (Clemente and Fedorak 2005; Johnson et al. 2011). Thus, they share similarities with the resins fraction, being composed of both hydrocarbon and heteroatom moieties and being polar. NAs have also been defined by the extraction methods used to recover them from samples and by their infrared (IR) absorbance spectra, but the range of possible structures has been controversial, currently precluding a definition accepted by both industry and academia (Grewer et al. 2010; Rowland et al. 2011). Whereas NAs were previously considered to be saturated compounds with a single acidic group, this class has expanded to include aromatic NAs (Jones et al. 2012) and NAs with multiple oxidized functional groups (i.e., carboxylic acids plus hydroxyl groups). Definition of NAs has become even more nebulous (Grewer et al. 2010) with the development of sophisticated analytical methods (such as ESI FT-ICR-MS and multi-dimensional GC-MS; Appendix A) that detect more isomers and analogues than previously recognized. NAs have been used industrially as components of wood preservatives and mixtures are commercially available. However, application of new analytical methods has shown that the component NAs in those mixtures differ significantly from naturally occurring suites of NAs in petroleum-impacted waters (Grewer et al. 2010), throwing into question some of the early research on NA biodegradation conducted using commercial mixtures.

NAs are ubiquitous, but have been associated particularly with biodegraded oil reservoir fluids and oil sands process waters in western Canada where they may represent the accumulation of dead-end products of incomplete microbially-mediated oxidation of *cyclo*-alkanes (naphthenes; **Table 2.1**) (Rowland et al. 2011) over geological time. This view is supported in part by NA persistence in the environment, as many resist further biodegradation (Whitby 2010). Current environmental interest in NAs arises from their reported acute toxicity to aquatic life (Allen 2008; Zhang et al. 2011), contribution to Total Acid Number (TAN; the petroleum acidity parameter), and accretion of precipitates (scale) that increase corrosion of pipelines, refinery units and other oil-handling infrastructure. Due to their acidic group(s), they are more polar than hydrocarbons, and this water solubility makes them more mobile in the environment than the oil itself. In fact, petroleum that has been 'water-washed' in the reservoir or the environment may become depleted in NAs as they dissolve into the water fraction. Conversely, spilled oil having high NA contents may be a source of toxicity in aquatic environments as the NAs dissolve in water. However, attribution of toxicity to specific NA compounds within a complex mixture of NAs is currently in flux due to the expanding definitions of NA structures, discussed above. Further discussion of NA toxicity in oil sands-associated environments is available (Gosselin et al. 2010).

Crude oils may also contain small amounts of minerals, such as clays, and emulsified water originating either from the geological formation (connate water) or from water injected into the reservoir during oil recovery (produced water). The great majority of entrained or emulsified water is removed from the oil to meet pipeline specifications (typically ≤0.5% water plus sediments).

It is clear that the chemical composition of crude oils is extremely complex and variable, and the structures of many oil components, including the UCM, are currently cryptic. The limitations of resolving and identifying individual molecules in the resins and asphaltenes fractions, particularly, are slowly being addressed with renewed scientific interest and development of new techniques. However, improved analytical methods for chemical characterization are still needed to gain a better understanding of the persistence and behaviour of these components in spilled oil. Additionally, the quality of data in different oil property archives varies according to methodology; development and adoption of standardized methodology with data quality indices would allow for comparisons among studies.

<u>Recommendation:</u> Additional analytical research is needed over the long-term to address gaps in fundamental knowledge of asphaltenes, resins and naphthenic acids, and to populate oil-property databases with verified data. Such knowledge provides insight into criteria that affect emulsification, photooxidation, biodegradation, toxicity, adhesion, etc., particularly for heavy oils and bitumens that have high proportions of such chemical classes.

2.2 Bulk Properties of Oil

Complex mixtures, such as petroleum, exhibit complex chemical and physical properties requiring suites of analytical methods to discern important differences between oils. Several properties are discussed below; they are interrelated because all are affected by oil composition. Appendix B (**Table B1**) comprises a summary of major oil properties, associated analytical methods and the relevance of those properties to oil spill cleanup (discussed fully in Chapter 7).

2.2.1 Density, Specific Gravity and API Gravity

Density is the mass of a given volume of oil, variously expressed in units of g/mL or g/cm^3 or kg/m^3. Two measures of density are commonly applied to petroleum: specific gravity and API (American Petroleum Institute) gravity. Specific gravity is the density of a substance compared to that of water (and as a ratio is dimensionless). Because most oils are lighter than water, they float on it. For example, fresh water has a density of 1.0 g/mL and sea water a density of 1.03 g/mL at 4 °C. Therefore, an oil of specific gravity <1.0 (e.g., gasoline at 0.8) will float on water at that temperature and one with specific gravity >1.0 will sink at that temperature. As the temperature increases, the density (and thus the specific gravity) of oil decreases (Nmegbu 2014). Thus, bitumen and certain heavy fuel oils may have densities greater than water at some temperatures and may submerge (Section 2.4.2.3).

API gravity (measured in degrees; ° API), devised by the American Petroleum Institute, is an inverse measure of density that is used to compare different petroleum types (**Table 2.2; Figure 2.1**; Appendix C, **Table C1**). Fresh water is assigned a gravity of 10° API at 15 °C; 'light' crude oils have API gravity of >31.1°; 'medium' crudes are 22.3-31.1° API; 'heavy' crudes <22.3° API (or, more stringently, 10-15°); and bitumens 5-10° API (Speight 2014). API gravity can also be considered a rough indicator of crude oil quality, since more valuable light oils have higher °API values.

Oils of API >10° will float on fresh water at 15 °C whereas bitumen, defined as <10° API (Speight 2014), will sink. However, the sinking or floating of oil on water is additionally affected by salinity (e.g., seawater density 1.03 g/ml), by temperature and by interactions with particles (Section 2.4.2.3). Weathering of spilled oil, particularly diluted bitumen, can have a profound effect on the oil's density because evaporation (Section 2.4.1.2) of the LMW components ('light ends') leaves residual oil of higher density that may no longer be buoyant. Thus, the decrease in specific gravity (increase in °API) of spilled oil at higher temperatures may gradually be overcome by faster evaporation rates, resulting in an oil that is more dense.

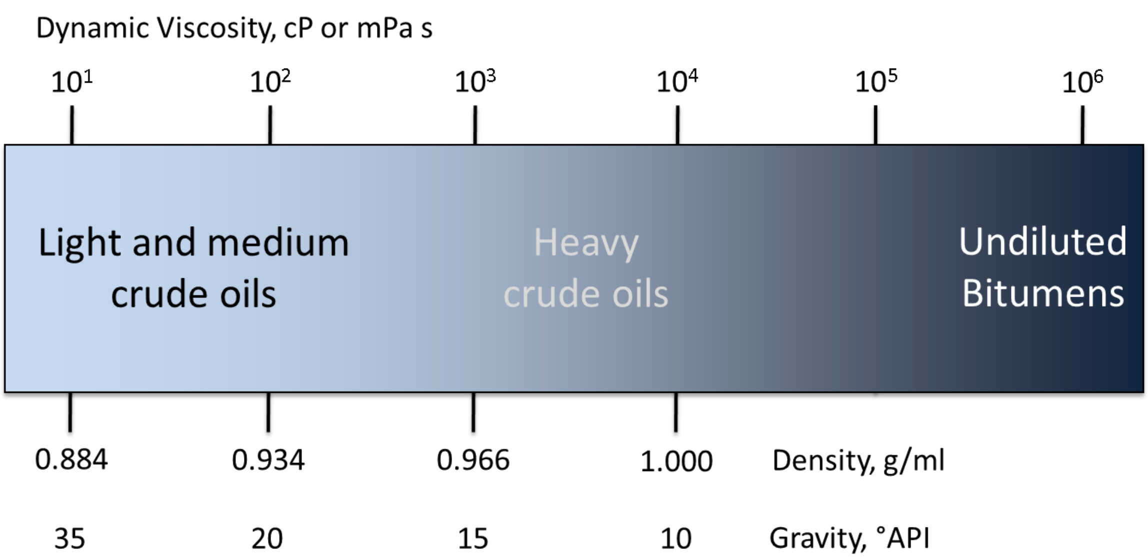


Figure 2.1 Relationship among viscosity, density and API gravity over a range of petroleum types. *Adapted from Speight (2014).*

2.2.2 Viscosity and Pour Point

Viscosity, defined as resistance of a liquid to deformation by shear or flow (WSP 2014), is also informally described as resistance to flow, or the 'thickness' of a fluid. The lower the viscosity, the more easily it flows. Two types of viscosity may be reported: 1) dynamic viscosity (resistance to shear, where adjacent layers move parallel to each other but at different speeds), expressed as centipoise (cP) or milliPascal second (mPa s); and 2) kinematic viscosity (the ratio of the dynamic viscosity to the

Oil viscosity, like density, is determined in large part by its chemical composition. Higher proportions of 'light' components, such as LMW alkanes and aromatics, contribute to lower viscosity; whereas, heavier components, such as asphaltenes and resins, increase petroleum viscosity.

density of the fluid) reported in centiStokes (cSt) or m^2/s. The significance of viscosity in oil spill response is discussed in Chapter 6.

Gasoline has a dynamic viscosity of 0.5 mPa s, light crude viscosity may be 5-50 mPa s, whereas 'conventional' crude oils have viscosity up to 10,000 mPa s (similar to that of molasses) and 'ultraheavy' oils and bitumen usually have viscosity >50,000–100,000 mPa s (Speight 2014), similar to peanut butter. The relationships between viscosity, density and API gravity are shown in **Figure 2.1**. Increased viscosity decreases oil spreading on water (Section 2.4.1.1), dispersion (formation of oil droplets in water; Section 2.4.2.2) and the efficacy of chemical dispersants during remediation (Chapter 6).

As shown in **Figure 2.2**, kinematic viscosity is not only a function of the average molecular weight of the oil, it also declines exponentially as temperature increases (Nmegbu 2014). Thus, temperature impacts the extent of oil spreading on surfaces and penetration of shoreline sediments. Temperature also defines the oil's pour point - the temperature below which an oil will not flow but rather starts to solidify or gel. Bitumen, for example, does not flow in the reservoir and must be heated or, alternatively, bitumen must be diluted with light oils for transport (Section 2.3.7). The interrelatedness of viscosity, pour point and temperature then becomes particularly important when considering the release of heavy oil or diluted bitumen from a heated pipeline or flow of an oil spilled onto ice or cold water.

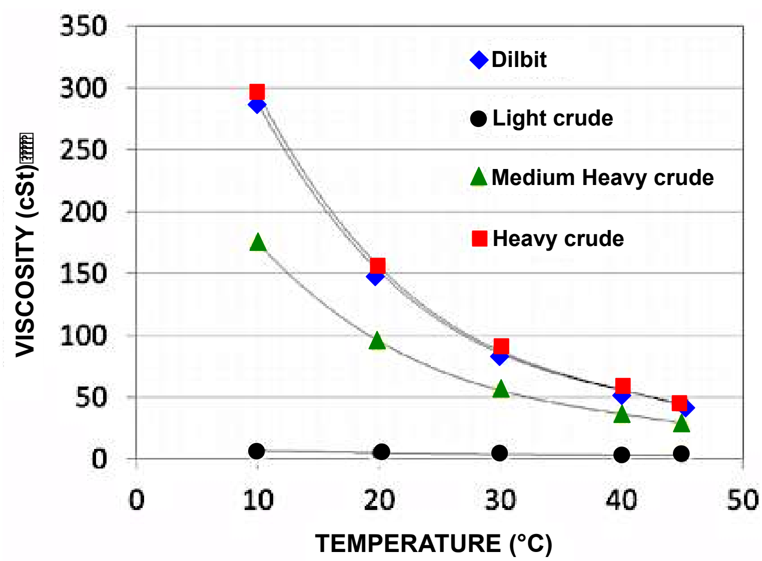


Figure 2.2 Relationship between temperature and kinematic viscosity *(reported in centiStokes [cSt]) for four oil types (Table 2.2). Adapted from Tsaprailis (2014)*

2.2.3 Volatility and Flash Point

> The 'light' components of petroleum that contribute to decreased viscosity and density (e.g., LMW saturates and aromatics) also tend to evaporate (volatilize) readily. Volatility is particularly important when considering diluted bitumen blends, which contain substantial proportions (≥30%) of light petroleum products that pose a flammability hazard, even though the majority of the oil mass (the bitumen) is considered non-flammable.

High concentrations of light, volatile hydrocarbons contribute to the flammability potential of an oil by lowering the flash point, the lowest temperature the fuel must experience to achieve ignition in the air. Notably, these light hydrocarbons, particularly the monoaromatics, also correlate with acute toxicity to life forms (as discussed in Chapter 4). Thus, vapours from an oil spill can pose a hazard to spill responders, as well as to wildlife exposed to the fumes.

After volatilization of some or most of the light components through weathering processes in open conditions (Section 2.4), the oils will have decreased flammability and acute aqueous toxicity. Temperature is obviously a primary factor affecting volatility and flash point, with higher temperature speeding volatility losses from spilled oil, but the thickness of the oil layer (which will also respond to temperature via viscosity changes) will also affect the rate of evaporation.

2.2.4 Water Solubility

In general, the saturates are highly water-insoluble compared with aromatics of a similar carbon number (e.g., the aqueous solubility of naphthalene, a C_{10} PAH, is approximately 600-fold greater than the C_{10} saturate *n*-decane). Monoaromatics are the most water-soluble of the hydrocarbons, whereas (alkyl-) PAHs are poorly soluble (e.g., at parts-per-billion concentrations) yet retain their toxic properties. For example, the aqueous solubility of benzene (**Table 2.1**), the most soluble BTEX compound, is 1.8 g/L water at 15 °C; solubility of *n*-hexane is 0.0013 g/L at 20 °C; naphthalene is 0.031 g/L at 25 °C; and *n*-hexadecane (C_{16}) and cyclohexane (C_6) (**Table 2.1**) are considered water-insoluble. Small aromatic heterocycles and resins, being polar, may be more soluble than their hydrocarbon counterparts. For example, whereas the hydrocarbon benzofuran (**Table 2.1**) is considered water-insoluble, its S-containing analog benzothiophene is soluble at 0.13 g/L at 25 °C and indole, its N-containing analog, is soluble at 3.6 g/L at 25 °C. However, large resin compounds and asphaltenes, despite their polarity, are water insoluble and the resins in particular tend to partition to the interface between oil and water.

> Most petroleum hydrocarbons are virtually insoluble in water. Only the LMW aromatics (e.g., BTEX), very small saturates and small polar compounds (some resins) have appreciable solubility in water, typically in the range of parts-per-million (ppm). Water solubility makes these molecules potentially more toxic because they are more 'bioavailable' to aquatic life if they subsequently partition into biological membranes.

High molecular weight components of bitumen, such as asphaltenes and most resins, are thought not to be toxic because they have extremely low solubility in water and do not readily cross biological membranes. However, diluents added to bitumens contain LMW compounds that can dissolve in water and contribute to acute aqueous toxicity before they are lost by weathering. In addition, heterocycles (e.g., dibenzothiophenes; **Table 2.1**) and 3-to-5-ringed alkyl PAHs detected in dilbit are derived from bitumen. Their concentrations in dilbit are similar to those of conventional crude oils and are thought to be the components causing chronic toxicity to fish embryos (Madison et al. 2015); see Chapter 4.

A measure of water solubility that is particularly pertinent to biological effects of petroleum is the octanol-water partition coefficient, which describes the concentration of a chemical in the solvent octanol ($C_8H_{15}OH$, a mimic for biological lipid membranes) versus its concentration dissolved in water, in a two-phase system at equilibrium for a given temperature. This ratio is usually expressed as the logarithm of the ratio (i.e., as log K_{ow}). The greater the K_{ow} value, the less polar and less water-soluble the chemical. Thus, K_{ow} helps predict the propensity of a petroleum constituent to dissolve into water and subsequently partition into a biological lipid membrane, an important factor in toxicity (Sikkema et al. 1995). K_{ow} and toxicity are discussed in detail in Chapter 4.

2.2.5 Surface Tension and Interfacial Tension

At liquid-air interfaces, surface tension is the measure of attraction (cohesion) between the surface molecules of a liquid rather than to molecules in air (adhesion). Information on the surface tension of different crude oils at various temperatures is available in Environment Canada's Oil Properties Database (http://www.etc-cte.ec.gc.ca/databases/oilproperties/). In the case of two immiscible liquids such as oil and water, the force between their surfaces is referred to as interfacial tension. The higher the interfacial tension, the less the oil will spread on water; whereas, if the interfacial tension is low, the oil will spread evenly without help from wind and water currents. Because higher temperature reduces interfacial tension, oil is more likely to spread in warmer waters than in cold waters. However, interfacial tension has less effect on oil spreading than viscosity.

2.2.6 Adhesion

Oil adhesion is the property of petroleum sticking to a surface, whether it is the rock formation comprising the oil reservoir, the production equipment or environmental surfaces after a spill. It is not included in the standard suite of oil properties reported by petroleum producers and is rarely discussed in the oil spill literature, but might be a predictor of oil spill cleanup needs if further measured and calibrated against a variety of oil types and their behaviour in the environment. A semi-quantitative gravimetric method has been proposed (Jokuty et al. 1995) in which a stainless steel needle is dipped in oil that is then allowed to drain, and the mass of oil adhering to the needle after 30 minutes of draining is weighed to produce a measurement with units of mass per surface area (g/m^2). However, the method has been neither adopted as a standard nor vetted. The relationship between evaporative weathering and adhesion is discussed in Section 2.4.1.2.

2.3 Examples of Oil Types

This section introduces a selection of oil types that are relevant to petroleum transport in Canada (**Table 2.2**) and/or to this Report. Within each oil type, one or more specific crude oils or blends is presented to highlight the differences between oils in terms of their chemical and physical properties, known or predicted behaviour and fate in the environment, timelines of weathering processes, and expected residues and spill response strategies (discussed in detail in later chapters).

With few exceptions this Report does not consider refined products, such as jet fuel, gasoline or diesel, nor liquefied natural gas or biofuels. The exceptions include products used to dilute bitumen for transportation and selected refined heavy fuel oils, for comparative purposes. The information presented in **Table 2.2**, and Appendix C (**Table C1**) has been collated from many different sources and is representative but not comprehensive. Two major online sources of information for oils transported in Canada are the Environment Canada Oil Properties Database (*http://www.etc-cte.ec.gc.ca/databases/oilproperties/*) and the Crude Quality Inc. industry website (*crudemonitor.ca*). However, both are incomplete in scope and compositional information. The Environment Canada website hosts a valuable catalogue of various chemical and physical data for 450 oils produced and transported globally but, regrettably, it lacks entries for many of the emerging unconventional oil types transported in Canada (e.g., dilbit, synbit, shale oil). The *crudemonitor.ca* website provides monthly analyses of oils currently transported inter-provincially in Canada, including unconventional oils, but publishes chemical composition data only for the light ends ($\leq C_8$) and general parameters, such as TAN, metals and sulphur content (and High Temperature Simulated Distillation curves [HTSD; Appendix A]) for heavy oils and blends. These data are relevant for achieving pipeline transportation specifications but not necessarily for oil spill response. Full spectrum analyses of heavier components that are predominant in heavy oils and bitumens and highly relevant to environmental cleanup are not available on this website.

<u>Recommendation</u>: Online public databases with compositions and properties of oils transported in Canada should be expanded to provide support for oil spill preparedness, response decisions and for the safety of first responders to a spill. To enable collection of relevant chemical data, expanded and standardized analytical methods must be developed, particularly for characterizing bitumen blends, such as dilbit and synbit.

Table 2.2 Properties of some oil types commonly transported in Canada and/or relevant to this Report.[a]

Oil type and examples	Region of origin	Relevance
Natural condensates and refined products used as diluents for transport		
Sable Island condensate	Nova Scotia	40° API; Naturally occurring sweet ultra-light crude oil, often produced in conjunction with natural gas; predominantly volatile hydrocarbons
Fort Saskatchewan condensate blend	Alberta	68° API; Refined products, predominantly LMW aliphatics (C_5-C_6), with minor BTEX; used as diluent for oil sands processing and for bitumen transport
Cold Lake Diluent	Alberta	69° API; Natural gas condensate used as a bitumen diluent
Naphtha	Alberta	57° API; Refined product, predominantly $\leq C_{12}$ saturates and monoaromatics used as diluent for oil sands processing and for bitumen transport
Southern Lights Condensate Diluent	US	80° API; US condensate shipped to Alberta; predominantly C_5-C_{12} saturates
Suncor Synthetic Crude Oil (SCO)	Alberta	33° API; Refined product derived from partially upgraded bitumen and used as diluent in synbit
Light crude oils		
Alberta Sweet Mixed Blend (ASMB) Reference #4	Alberta	36° API; Blended aggregate of light, sweet conventional crude oils shipped from Alberta; used as a benchmark and laboratory reference oil by Environment Canada
Macondo (MC252)	Gulf of Mexico, USA	35° API; Oil released during DWH blowout; rich in LMW saturates that are gases or light liquids at atmospheric pressure
Norman Wells	Northwest Territories	38° API; Light crude from Canadian Arctic; wells drilled from artificial islands in Mackenzie River
Statfjord	Norway	38° API; North Sea offshore light oil
Arabian Light	Saudi Arabia	~32° API; Sample from St. John, NL, refinery
West Texas Intermediate (WTI)	Texas, USA	36-41° API; Benchmark oil for North American oil market pricing
Medium crude oils		
Alaska North Slope (ANS)	Alaska, USA	29° API; Conventional oil from Arctic; spilled from *Exxon Valdez* oil tanker into Prince William Sound, AK, in March 1989
Atkinson Point	Beaufort Sea, Canada	24° API; Oil from an onshore discovery well on Tuktoyaktuk Peninsula, NWT; no current production
Prudhoe Bay-A (PBCO)	Alaska, USA	29° API; Alaska North Slope crude; Used as reference oil by US-EPA in 1995

Oil type and examples	Region of origin	Relevance
Gullfaks and Troll	Norway	29° API; typical North Sea oils; used for oil spill research in Arctic regions e.g., Svalbard
Shale oils (Tight oils)		
Bakken	North Dakota and Montana (USA), Saskatchewan and Manitoba	42° API; unconventional light crude produced by fracking; may contain H_2S (23,000 ppm in an exceptional case); flammable agent in the 2013 LacMégantic QC, derailment and explosion
Waxy crude oils		
Hibernia and TerraNova	Newfoundland	34° API; Offshore Atlantic oils transported to mainland by tanker ship
Sour crude oils		
Midale	Saskatchewan, Manitoba	31° API; 2.4% S; Benchmark for Canadian medium sour crude oils
BC Light	British Columbia	41° API; sour light crude spilled into Pine River, BC, in 2000
Western Canadian Blend (WCB)	Alberta	22° API; 3.1%S; A blend of heavy sour crude oils, deliberately undiluted with butane that is co-produced with the crudes (to reduce explosion hazard) but instead diluted with condensate or light crude for transport
Heavy oils and diluted bitumen (See **Table 2.3** for definitions of various bitumen blends)		
Bunker C fuel oil(No. 6 Fuel oil) including HFO 7102	International	11° API; Common refined fuel oil class, often diluted with lighter petroleum for transportation; heavy component of oil spill in Lake Wabamun AB, 2005
Cold Lake Blend (CLB) dilbit	Alberta	23° API; Oil sands bitumen diluted with lighter petroleum; highest volume dilbit type transported in Canada; tested in wave tank trials for sinking and emulsification; one of the dilbits in the Kalamazoo, MI, oil spill in 2010
Albian heavy synthetic crude (AHS)	Alberta	20° API; Partially upgraded heavy crude oil, transported as dilsynbit;, used as refinery feedstock
Access Western Blend (AWB)	Alberta	23° API; sour heavy oil (3.9% S) produced by SAGD; tested in wave tank trials (Government of Canada 2013) for sinking and emulsification; composition of pipelined oil changes with season
Wabasca Heavy	Alberta	16° API; Heavy oil spilled near Mayflower, AR, in 2013
Western Canadian Select (WCS)	Alberta	19-22° API; Considered the benchmark for heavy, acidic (high TAN) crudes blended with bitumen streams to maintain TAN <1; diluted 10-50% with sweet synthetic crude oil and/or condensates; a

Oil type and examples	Region of origin	Relevance
		component of the Kalamazoo, MI, dilbit spill in 2010
Synbit Blend	Alberta	21° API; Blend of several synbits plus heavy oils; evaporation behaviour differs from dilbit because of lower concentration of light ends in diluent
Athabasca/Cold Lake undiluted bitumen	Alberta	8-10° API; Density > 1.0; must be diluted or heated for transport
Orimulsion™	Venezuela	8° API; A proprietary emulsion of Orinoco bitumen with 26% fresh water and surfactant, density > 1.0; must be maintained above 30 °C to prevent gelling; limited production at present

[a]Additional data including composition, specific gravity, sulphur content, adhesion and dispersability, where available, are given in Appendix C, Table C1. Note that the composition of several oils, particularly blended oils and dilbits, changes seasonally to maintain pipeline specifications for viscosity.

2.3.1 Condensates and Refined Products Used as Diluents for Bitumen

> Condensates are conventional naturally-occurring ultra-light crude oils, often co-produced with natural gas (methane). For example, Sable Island Condensate is produced from natural gas fields (e.g., Thebaud and Venture) off Nova Scotia and shipped to the mainland (Point Tupper, NS) by pipeline.

Condensates are rich in LMW saturates and, if spilled, would experience rapid evaporation, losing a high proportion of the spilled mass of oil. Because of the high saturate content, after evaporation and dissolution a weathered condensate would typically be highly biodegradable, given appropriate conditions, and little residual oil would be expected to persist in an open water spill.

Historically, natural condensate from western Canadian gas fields was used to dilute bitumen and heavy oils from the Athabasca and Cold Lake regions, but more recently the diluents are blends of light oils and/or refinery fractions, including naphtha and synthetic crude oil that is itself derived from bitumen (Segato [no date]; Crude Quality Inc. 2015). Although the diluents are predominantly composed of LMW materials far lighter than the bitumen, it should be noted that most diluents also contain appreciable proportions of the same HMW compounds found in bitumen that may not be detected by conventional GC (GC-FID or GC-MS), but are revealed using HTSD (Appendix A).

2.3.2 Light Crude Oils

Light crudes with API gravity >31.1° (Speight 2014) are conventional oils found throughout the world. Examples include Arabian Light, WTI (used as a pricing benchmark in the oil market), Statfjord from the North Sea and Norman Wells from northern Canada. Alberta Sweet Mixed Blend (ASMB), a major crude shipped from Alberta, has been used as a reference oil by Environment Canada for chemical composition, biodegradability and emulsification studies. Perhaps the most infamous light oil is Macondo (MC252) from the DWH oil well in the Gulf of Mexico that suffered a catastrophic blowout in 2010 (Section 2.4.2.1, Section 2.4.2.3 and Chapter 8), injecting not only liquid oil into deep seawater, but also light saturates that are gases at atmospheric pressure (methane, ethane, propane and butane).

2.3.3 Medium Crude Oils

Oils between 22-31° API are considered ‘medium’ crudes (Speight 2014). These conventional crudes include many of the ANS oils, Prudhoe Bay crude oil from the Arctic, and Norwegian North Sea oils produced from offshore wells. The latter oils have been used for research projects in the Arctic to determine the behaviour and fate of oil spills onto Arctic beaches. ANS oil was spilled in the highly publicized 1989 grounding of the *Exxon Valdez* in Prince William Sound, AK (Chapter 8), where up to 25% of spilled oil mass was lost by weathering and another ~30% was estimated by some researchers to have biodegraded within a few weeks of the spill (Atlas and Hazen 2011).

2.3.4 Shale Oils (Tight Oil or Light Tight Oil)

Shale oils[3] are unconventional liquid crudes that have only recently entered the North American oil markets in substantial volumes. As opposed to being newly ‘discovered’, many shale oil reservoirs were already known but were inaccessible pending recent technological advances afforded by horizontal drilling and hydrofracturing (‘fracking’) to release liquid oil that otherwise cannot flow because of ‘tight’ pores in the formation. One large known reserve is the Bakken formation straddling North Dakota, Montana and parts of southern Saskatchewan and Manitoba. Although Bakken oil is generally considered ‘sweet’ (i.e., low organic S and low H_2S), occasional samples have had high H_2S concentrations (American Fuel & Petrochemical Manufacturers 2014). Bakken shale oil was the flammable product in the Lac Mégantic, QC, rail disaster in 2013 and H_2S was implicated as a possible contributor to the explosion.

2.3.5 Waxy Crude Oils

These crudes contain the typical suite of petroleum fractions but also significant proportions of waxes (HMW linear paraffins, typically $>C_{20}$) and large naphthenes (*cyclo*-alkanes; **Table 2.1**). When present at high concentrations in petroleum, waxes may crystallize (‘freeze’) and form micro- or macroscopic deposits in the reservoir or infrastructure, depending on temperature and pressure. Because HMW saturates are less biodegradable than those of $\leq C_{18}$, spills of waxy oils may persist in the environment longer than non-waxy oils, although the wax residues have low chemical toxicity to aquatic life.Oils produced from the Hibernia and Terra Nova fields off the coast of Newfoundland are considered waxy crude oils.

2.3.6 Sour Crude Oils

A crude is considered ‘sour’ if it has more than 0.5 wt% total S content (>1% in some markets), as opposed to ‘sweet crude’ that has <0.5 wt% S. Most S in petroleum is included within aromatic or saturated structures in resins or asphaltenes (e.g., in heterocycles; **Table 2.1**) or is S^0, in which case it is not considered hazardous but is removed in the refinery at considerable expense. However, where oils contain highly toxic and potentially explosive H_2S gas, the H_2S concentration is reduced to safe concentrations before transport. The amount of H_2S varies considerably with the crude oil source (Hess 2012). Thus, both conventional and unconventional oils can be ‘sour’, regardless of the concentration of H_2S, with the unconventional oils more likely to contain organic S compounds that may resist biodegradation. Examples include the conventional medium sour crude Midale, and the WCB and AWB dibits; the latter was a component of the dilbit spill in Kalamazoo, MI (Chapter 8).

[3] *Shale oil (‘tight oil’) should not be confused with oil shale. The latter is a sedimentary rock that harbours kerogen, a solid immature organic material that can be thermally processed at surface facilities into a shale oil that differs from the natural shale oil.*

2.3.7 Heavy Oils, Bitumen and Diluted Bitumen Products

Heavy oils are defined as being <22° API or, more stringently, 10-15° API, with bitumens being semi-solids having density >1.0 g/cm^3 or 5-10° API (Speight 2014). Some heavy oils are refinery products and represent the 'heavy ends' that remain after distillation of lighter fractions like gasoline and kerosene from lighter oils. Bunker C fuel oil (also called No. 6 fuel oil or residual fuel oil; **Table 2.2**) is one such refined product that can be blended with lighter fractions to make an oil for combustion or used undiluted to make asphalt.

> Heavy oils and bitumen are at the end of a continuum of increasingly heavy, viscous oils with increasing proportions of HMW resins and asphaltenes and decreasing proportions of light molecules.

The distinction between heavy oil and bitumen is blurred by their similar chemical and physical properties and obscured by the working definitions and colloquial terms used by industry. Thus, different entities may assign the same oils to different categories. As noted by Winter and Haddad (2014), Exxon and *CrudeMonitor.ca* both identified the Wabasca Heavy Crude that spilled in Mayflower, AR, in 2013 (Chapter 1) as a 'diluted heavy crude', but the Canadian Government, Battelle (acting for API) and Penspen (acting for Canadian Energy Pipelines Association, CEPA) initially labeled it a 'diluted bitumen' (later corrected). The WCS blend that spilled in Kalamazoo MI in 2013 (Chapter 8) was called 'heavy oil' by Enbridge, but 'dilbit' by environmental agencies, such as Environment Canada (Government of Canada 2013). According to Yang et al. (2011), bitumen products have unique chemical markers that distinguish them from conventional crude oils. These fingerprints include the distribution of PAH, which is generally skewed towards the smaller multi-ringed structures (e.g., naphthalenes; **Table 2.1**) in conventional crudes versus larger PAHs (e.g., chrysenes) in bitumens, and have different distribution profiles within the alkyl PAH isomer series. However, in practice the two types of oil may be conflated in definition.

Regardless of nomenclature, it is generally accepted that both heavy oil and bitumen represent former conventional crude oils that have been extensively biodegradedand thermally altered *in situ* over geological time during uplifting or migration of the petroleum (Strausz et al. 2010; Fustic et al. 2012). Biodegradation depleted the lighter saturate fraction of the crude oil first, leaving poorly-degradable, complex, heavy molecules as residues. In addition, the products of incomplete microbial oxidation over geological time likely contributed to an increased resins fraction, yielding an extremely viscous, heavy petroleum (bitumen and extra-heavy oil) that cannot flow to production wells under normal reservoir conditions. This concept of liquid oil biodegradation to semi-solid bitumen over geological time is supported by the chemical compositions of heavy oils and bitumen, which have small proportions of light compounds known to be biodegradable (such as *n*-alkanes, *iso*-alkanes, BTEX and LMW PAH) and correspondingly higher proportions of poorly or non-biodegradable components (resins, asphaltenes and, of course, biomarkers like hopanoids, steroids and diamondoids; **Table 2.1**). Canada and Venezuela have the world's largest deposits of these highly viscous extra-heavy oils. However, Venezuela's Orinoco Belt, which is sometimes described as oil sands, has lower viscosity than the Canadian oil sands bitumen and can be transported as a 70:30 oil:freshwater emulsion (Orimulsion®; McGowan 1990) rather than being heated or diluted with light hydrocarbons. Whether natural or refined, extra-heavy oils contain much less biodegradable material than lighter crude oils.

There is a variety of diluted bitumen blends (**Table 2.3**). The most common diluents for bitumen transport include condensate (ultra-light oils partitioned from natural gas wells) or naphtha (a refined product), often at a ratio of 30% diluent to 70% bitumen for transport by pipeline (Crosby et al. 2013; Dew et al. 2015), whereas railbit for transport by rail tanker car is diluted half as much (i.e., ~15% diluent and 85% bitumen; Fingas 2014-2015). Synbit is a blend of bitumen and synthetic crude oil, a product of partial upgrading of bitumen that is heavier than condensate, at a ratio of approximately 50:50 (Crosby et al.

2013). Synbit has different properties than dilbit because of the heavier nature of the diluent. Dilsynbit is bitumen diluted with synthetic crude oil plus diluent.

Whereas some heavy oils may be suitable for shipping without alteration, bitumen does not flow unless it is heated and/or diluted. Therefore, bitumen is diluted with various light petroleum products to make it less viscous for different types of transport (rail, ship, pipeline).

In addition to seasonal changes in dilbit blends, the composition and proportions of diluents may differ in blends transported by inter- versus intra-provincial pipelines. This is because producers must conform to regulations when shipping oil outside the province, but may use specific blends to move bitumen between their own facilities. Notably, although the *CrudeMonitor.ca* database provides information on oils that are transported inter-provincially, it does not cover intra-provincial pipelines or those internal to an operator's facilities, which may have different specifications. For example, a paraffinic $n\mathrm{C}_5$-$n\mathrm{C}_6$ solvent used for bitumen extraction from oil sands ores by Shell Albian Sands in northern Alberta is also used as a diluent to pipeline the bitumen to the upgrading facility near Edmonton, but the solvent is too expensive to use as diluent for shipping to the US; instead it is recovered and returned by pipeline to the extraction facility (NRC 2013). Another example is the bitumen:water emulsion that spilled from an intra-facility pipeline at Nexen's Long Lake operation in July 2015 (Chapter 8). It is also important, as noted previously, to be aware of the limited petroleum characterization published by Crude Quality Inc. (*crudemonitor.ca*), specifically alkanes $\leq C_6$ and BTEX contents. These light hydrocarbons are important for safety and viscosity reasons during transport, but represent only a small proportion of heavy oils and bitumen blends in which the predominant heavy components are more relevant to oil behaviour and post-spill cleanup. Thus, there is a need for more internet-accessible oil composition data for emerging and unconventional oils to assist with planning, preparedness and response to spills.

Table 2.3 Definitions of diluted bitumen products*. Data from Fingas (2014-2015; 2015d), Dew et al. (2015) and Crude Quality Inc. (2015)*

Product	Description
Bitumen, Neatbit	Undiluted extremely heavy oil extracted from oil sands. Must be heated to be shipped
Diluent	Any light petroleum used to dilute bitumen for transportation by pipeline or rail; traditionally a condensate or ultra-light crude oil but now often a refinery cut such as naphtha [a]
Synthetic crude oil (SCO)	A liquid product made by partial upgrading or refining of bitumen; used as a diluent in synbit
Dilbit	Bitumen diluted with ~30% diluent, such as condensate or naphtha, for pipeline transportation
Railbit	Bitumen diluted with ~15% diluent (i.e., half as much diluent as dilbit), typically for transport by rail tank car
Synbit	Bitumen diluted ~50% with SCO
Dilsynbit	Bitumen diluted with SCO plus another diluent, usually a condensate (currently Albian Heavy Synthetic is the only dilsynbit transported)
Lightened Dilbit or C_4/C_5 enhanced Dilbit	Bitumen blended with a diluent supplemented with LMW alkanes such as C_4 (butane) and C_5 (pentane) [b]

[a,] *For some examples of condensate sources, see ISCO report #457, p. 8 (Fingas 2014-2015)*

[b,] *Condensate is often in short supply in western Canada, in which case C_4 and C_5 may be used to replace a portion of the diluent while maintaining pipeline viscosity specifications. Potential problems with this supplement are that asphaltenes may precipitate during transport (Appendix A), and volatility and flammability increase (Section 2.2.3)*

Blends, such as dilbit and diluted Bunker C, may exhibit 'bimodal' properties that are non-linear with conventional crudes and therefore their behaviour can be difficult to predict based on chemistry alone. In fact, diluted bitumen may have the most variable composition of any transported petroleum product (Fingas 2015d) because of the composition and proportions of various diluents (natural condensates and ultra-light oils, butane-enhanced condensate, naphtha, synthetic crude, etc.) that are used to achieve pipeline transportation specifications of <300 mPa s and specific gravity <0.94 (Tsaprailis 2014; Fingas 2014-2015). Seasonal differences in diluent proportions and compositions (formulated to achieve regulated viscosity at ambient temperature) make chemical definition of diluted bitumens even more convoluted. This compositional variability gives the blends new properties that may not fully correlate with volume proportions and further confounds prediction of their behaviour in the environment.

2.4 Weathering of Oil Spilled in Aquatic Environments

> Interactions of complex non-biological and biological processes lead to different fates of oil spilled in the environment. All of these are influenced by oil chemistry, environmental conditions and time, making prediction complicated and unique for each oil spill.

Weathering is a general term encompassing the changes in petroleum properties brought about by physical, chemical and biological processes when oil is exposed to environmental conditions such as in aquatic systems (Figure 2.3). These combined processes, along with the original oil chemistry and the time elapsed since the spill, affect the behaviour, fate, chemical composition and mass of residual oil after a spill event.

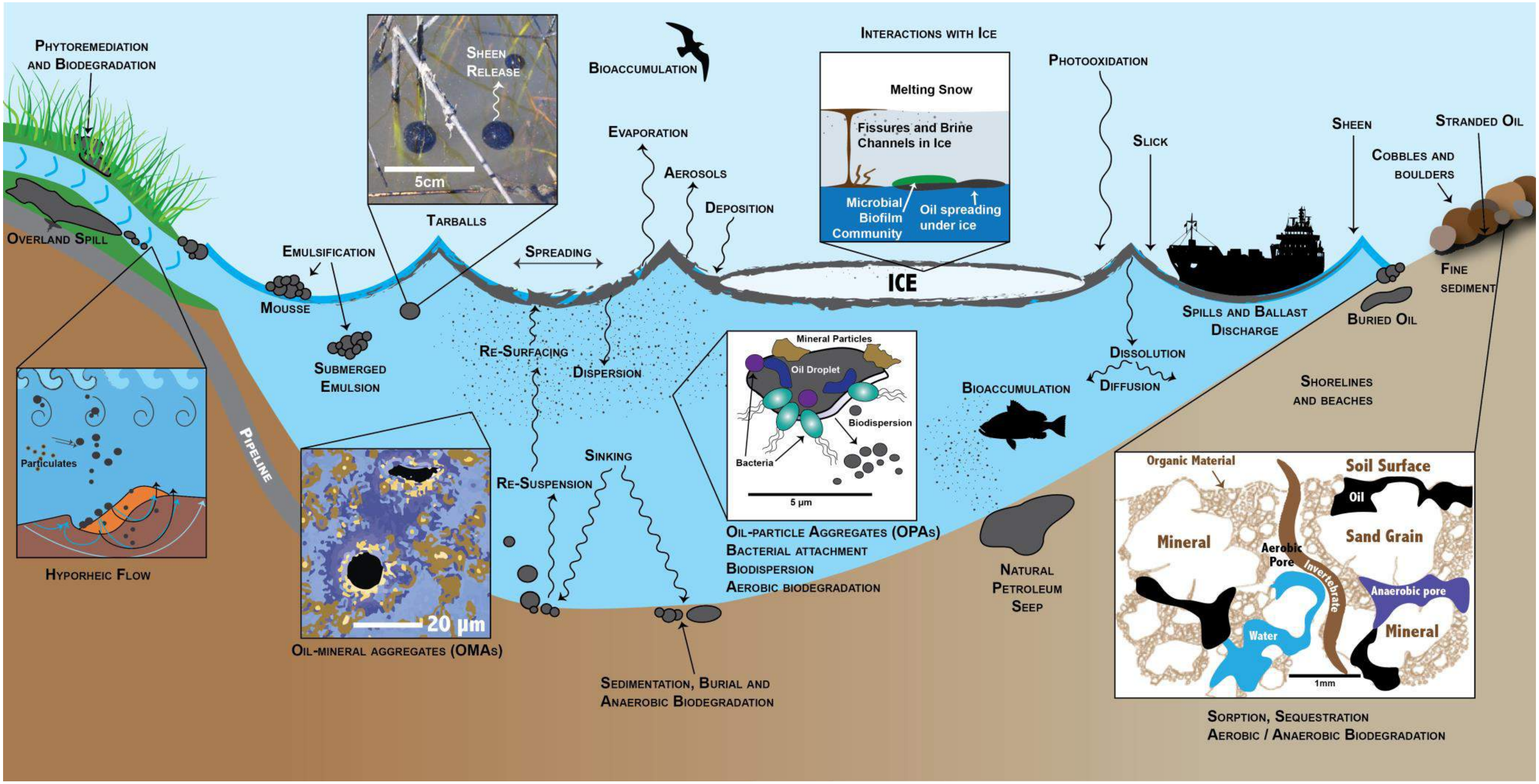


Figure 2.3 Overview of processes affecting the fate and behaviour of oil spilled in freshwater and marine environments. *The insets show processes at different scales. Adapted from Daling et al. (1990), Tonina and Buffington (2007, 2009), McGenity et al. (2012), AOSRT (2014), NRC (2014), WSP (2014) and Dew et al. (2015). Additional details on oil interactions with ice can be found in Figure 2.10.*

Weathering processes occur at different rates and with different onset times, resulting in progressive changes in oil composition and behaviour after the spill (**Figure 2.4**). Some weathering processes, such as evaporation, begin immediately and are most significant in the short-term (within hours or days); others such as biodegradation occur after a delay or more slowly (over months or years). Therefore, gross weathering rates are not constant following a spill and are generally highest immediately after the spill. Moreover, weathering processes are not constant in all areas of a spill site. Oil at the surface of a waterbody will experience certain processes more severely than oil below the water surface, beneath ice, on the shoreline or at the edges of the spill compared to the thicker slick centre (as discussed below). As a corollary, certain environmental factors are key to the rate of weathering, such as temperature, wave action (energy), sunlight, suspended sediment in the water and microbial activity (as discussed in Chapters 3 and 6).

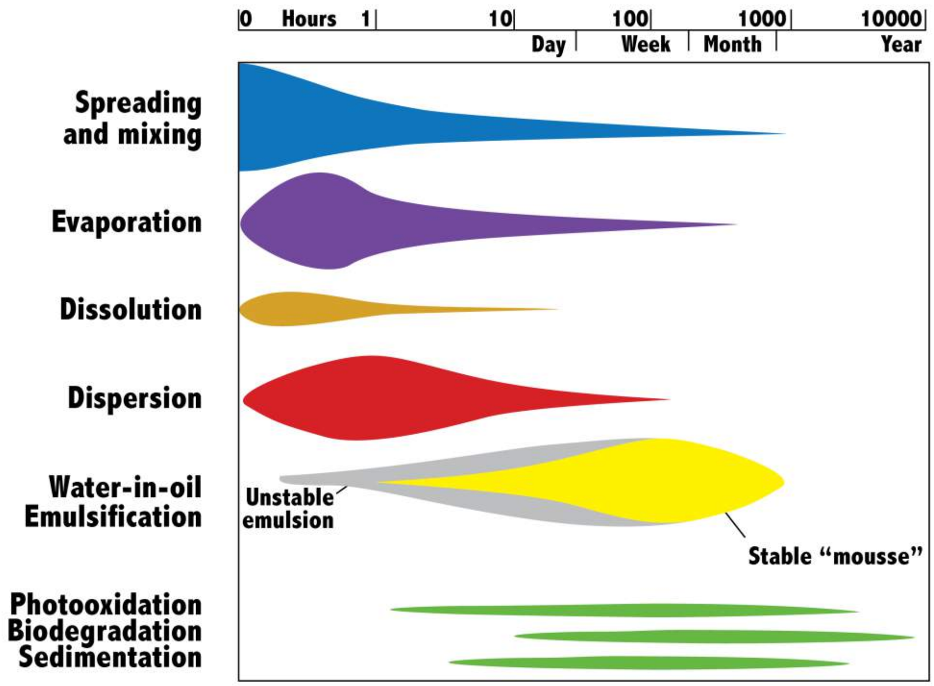


Figure 2.4. Time of onset and relative importance of weathering processes over time after an oil spill onto water. *The onset and magnitude of effect will vary with temperature and for different oils (note the time scale, which emphasizes the early onset of most processes). Figure adapted from AOSRT (2014).*

It is also important to note that weathering is influenced greatly by the type of oil spilled. For example, light crude oils with high proportions of LMW hydrocarbons spread on water more readily and therefore are more susceptible to evaporation at the surface, whereas heavier oils have lower proportions of volatile hydrocarbons and are more likely to sorb to suspended sediments and subsequently sink (Section 2.4.2.3).

General short-term physical and chemical weathering effects on oil (**Table 2.4**) are organized below according to processes occurring at the water surface (fresh or marine water), in the water column, andalong the shoreline (riverbank or beach) or in underlying sediments. Notably, discussion of some processes is skewed by the availability of data for certain well-studied oil spills (e.g., DWH blowout and *Exxon Valdez* Oil Spill [EVOS]). Specific processes that depend on environment type and local factors at the impacted sites, including biodegradation and remedial intervention, are discussed in Chapters 3 and 6.

Table 2.4. Effect of natural weathering processes on oil properties *(NRC 2014).*

Oil property	Natural weathering process	Effect on oil property
Viscosity	Loss of LMW components by evaporation and/or dissolution and/or biodegradation	Increased viscosity
	Formation of water-in-oil emulsions, including 'mousse'	Increased viscosity
Specific gravity	Loss of LMW components by evaporation and/or dissolution and/or biodegradation	Increased specific gravity
Volume of oil at surface	Loss of LMW components by evaporation and/or dissolution and/or biodegradation	Decreased volume
	Loss of small droplets by dispersion	Decreased volume
	Emulsification and/or biodispersion	Increased volume
Potential toxicity	Loss of LMW components by evaporation and/or dissolution and/or biodegradation	Decreased acute toxicity
	Formation of photooxidation products at surface, or of partially oxidized metabolites from incomplete biodegradation	Increased toxicity

2.4.1 Weathering Processes at the Water Surface

2.4.1.1 Spreading

When oil is spilled onto water and is allowed to spread unhindered, it moves away from the source where the oil layer is thicker (a 'slick'), forming a thin 'sheen' at the edges (**Figure 2.3**), e.g., the familiar 'gasoline rainbow' of 5-10 μm thickness to nearly invisible sheens of <1 μm. As it thins, the slick may form patches or 'ribbons' (AOSRT 2014). Thus, spreading increases the spill area and decreases the average thickness of the oil layer. In the case of a sheen, the area of oil contamination can appear to be very large, but the actual mass of oil involved can be far smaller than in a slick. Spreading is influenced by the oil viscosity, water and air temperature, and wind, wave and/or current action; in turn, spreading affects evaporative losses (discussed below).

However, spreading is typically non-uniform, thicker 'windrows' (streaks of floating oil) separated by oil-free water or sheen are commonly observed as the spill progresses (Simecek-Beatty and Lehr 2007). These are understood to arise from mixing forces (Langmuir circulation) in the surface water (discussed in Chapter 5). The action of such vortices (Langmuir cells) producing patchy oil slicks will affect the efficiency of mechanical recovery of floating oil (Chapter 8).

2.4.1.2 Evaporation, Aerosolization and Atmospheric Re-deposition

> Among the significant weathering processes occurring at the water surface, evaporation is usually the most immediate and rapid and has the greatest effect on the mass of spilled light and medium crude oils.

Evaporation can account for 75% of mass lost from condensates and ultra-light oils and 20-30% of losses from light oils, but ≤10% from heavy oils (NRC 2003), reflecting the different concentrations of volatile hydrocarbons in these different oil types. Saturates $<C_{15}$, monoaromatics (BTEX) and some small PAH are particularly subject to evaporative loss (AOSRT 2014) and 50% of hydrocarbons $\leq C_{16}$ were lost within 1 hour of an experimental oil spill by a combination of evaporation and dispersion/dissolution (Gros et al. 2014). The thickness of the oil layer also affects the rate of evaporation, with sheens evaporating more quickly than thick slicks and typically following an exponential curve (Fingas 2015e). Thus, evaporation can significantly reduce the total spill volume of a light oil. It also dynamically changes the composition of the surface oil which, subsequently, changes behaviour of the residual oil. For example, because volatile hydrocarbons, such as BTEX, tend to be the most acutely toxic, evaporation can reduce the acute toxicity of the spilled oil, but volatilization creates a potential explosion hazard above the spill and potential breathing hazards for oil spill responders. Simultaneously, with the loss of 'light ends', the residual oil becomes enriched in the HMW compounds and therefore becomes more viscous and dense, as well as becoming enriched in alkyl PAH that increase the chronic toxicity of the residual oil (Chapter 4). When the oil is unable to spread due to confinement or low wind/wave action, such as on a pond, a 'skin' of resins and asphaltenes can form on the surface, decreasing further evaporation of lighter components.

There is currently debate about the influence of surface winds over an oil spill. Fingas (2015c) pointed out that the air boundary layer above an oil spill theoretically can regulate the rate of evaporation, but that evaporative losses from light oils (e.g., ASMB, diesel, gasoline) in laboratory trials appeared to be limited more by slick thickness (affecting diffusion of volatile molecules to the oil surface) than by simulated wind speed. A previous report (Fingas 2004) indicated that temperature and time were greater factors in oil evaporation than surface wind velocity or oil layer thickness for a wide range of crude oils in which the bulk of hydrocarbons are $>C_{10}$. In contrast, Gros et al. (2014) determined that wind speed strongly influenced evaporation (as well as dispersion and dissolution) very early in an experimental spill of a Norwegian crude in the North Sea.

Recommendation: More information is needed for early evaporation and dissolution processes in actual oil spills to resolve present debate.

Whereas evaporation from a light or medium crude can be substantial (>30-50%), heavy oils experience far less evaporative loss. AWB and CLB dilbits lost only 15-18 % mass under quiescent conditions in an outdoor flume tank (King et al. 2014), and under laboratory conditions the latter lost a maximum of 17.4% mass at 22 °C (Waterman and García 2015). Synbit blends should experience even less evaporative loss than dilbits because the diluent (synthetic crude) has higher average molecular weight than the condensates or naphtha used in dilbit (Dew et al. 2015; Fingas 2015e). Diluted bitumen blends show bimodal behaviour, with light diluent components evaporating at a rate that decreases with time as the spilled oil becomes more viscous, slowing losses of volatile hydrocarbons. For example, elevated benzene levels measured in the air after dilbit spilled into the Kalamazoo River, MI (Crosby et al. 2013) (Chapter 3) represented evaporative losses from the diluent fraction. Dilbit that is initially buoyant (specific gravity <1.0) becomes denser (≥1.0) during evaporation, increasing the potential for sinking through the water column and subsequently contaminating sediments (Winter and Haddad 2014). Therefore, the early period of a diluted bitumen spill may be very important for efficient recovery and cleanup (Winter and Haddad 2014).

Evaporative losses from dilbits are substantially less than from light crude oils, but have a greater effect on physical properties. As dilbit weathers, it exhibits bimodal behaviour as diluent volatilizes and bitumen dominates the chemistry of the weathered oil. Current questions include whether blending bitumen with a diluent yields a homogeneous fluid equivalent to a conventional heavy oil and, conversely, whether loss of diluent restores dilbit to the original bitumen composition and properties.

Yarranton et al. (2015) recently showed in laboratory tests that evaporation of diluent from Cold Lake Winter Blend dilbit was comparable regardless of whether it occurred from the surface of a glass slide or fresh water; i.e., contact with quiescent water had no additional effect on evaporative losses and, furthermore, air flow had little effect on evaporation rate. They determined that ambient temperature (5 °–25 °C) and dilbit film thickness (1.6–5.4 mm) were key parameters and that evaporation rate was limited by diffusion of the light diluent components through the dilbit film, which, in turn, correlates with changing density and viscosity of the product during weathering. In contrast, the evaporation rate of the light reference oil ASMB was limited by convective mass transfer of volatile components. This highlights the concern that existing evaporative models of dilbit spills may not adequately predict evaporative behaviour of dilbit, and that further testing using a range of diluted bitumen products is required for validation or refinement of evaporation models. Additionally, these laboratory observations highlight the potential for sinking of diluted bitumen products that reach densities >1 g/cm^3 by evaporative weathering, and may inform prediction of adhesion of the weathered product to surfaces or suspended sediments.

There is debate whether 100% of the diluent component of bitumen blends can be lost by natural evaporation (Fingas 2015e) or whether the residual bitumen/heavy oil will retain some of the diluent components as intimately blended constituents, conferring novel properties on the partially weathered oil (Winter and Haddad 2014). This is particularly important for predicting if weathered dilbit, synbit, etc., will float or sink in water (Section 2.4.2.3). It seems plausible that some higher molecular weight components of the diluent would be retained in the weathered oil, but at concentrations too low to significantly change the physical behaviour of the residual oil compared with the original bitumen or heavy oil stock. Although research has been initiated recently into the evaporative behaviour of various bitumen blends under actively mixed conditions (King et al. 2015a), these data are not yet published and further scrutiny is warranted. The observation of evaporative mass losses of <20% after rigorous weathering at environmentally-relevant temperatures for dilbits nominally comprising ≥30% diluent suggests that a substantial proportion of diluent remains intimately associated with bitumen.

The effect of evaporation on adhesion by dilbit is significant during the initial weathering phase when diluent is being lost at the fastest rate. For example ,AWB dilbit showed a rapid increase in adhesion during the first 24 hours of natural weathering on seawater in open-air flume tanks (**Figure 2.5**). The effect on intermediate fuel oil (IFO 180) adhesion was less and after 24 hours there was little change in adhesion (or composition) of either oil.

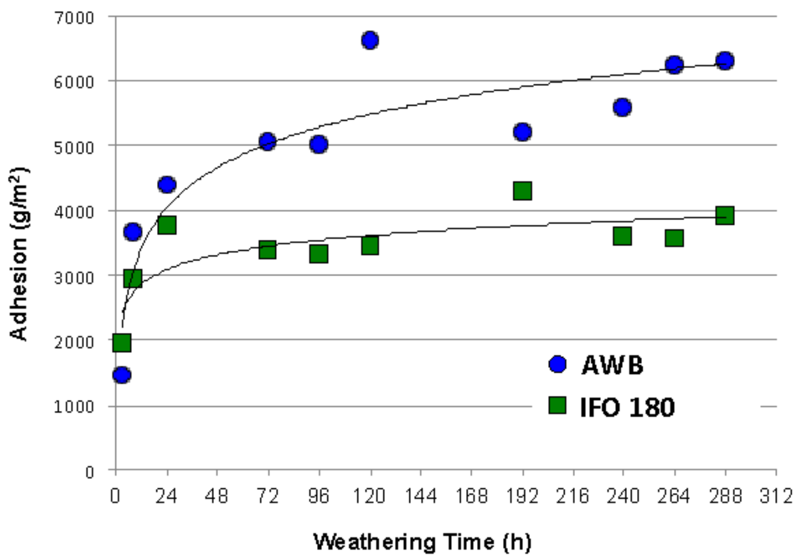


Figure 2.5 Effect of progressive natural weathering on adhesion. *Unpublished data for Access Western Blend (AWB) dilbit and an intermediate fuel oil (IFO 180) provided by Fisheries and Oceans Canada. Natural weathering was achieved in an open-air seawater flume tank, and adhesion of the recovered oil was determined using the semi-quantitative method of Jokuty et al. (1995).*

Hollebone (2015) measured adhesion for several oils that experienced progressive evaporation in the laboratory. A range of semi-quantitative adhesion values for selected oils is given in Appendix C, **Table C1** and a comparison of adhesion by selected light, medium and waxy crudes, CLB winter blend dilbit and Bunker C fuel oil during controlled weathering is shown in **Figure 2.6**. Adhesion affected by evaporative loss follows a continuum, with near-linear responses by light crude oils having high proportions of saturates (Hollebone 2015) versus exponential responses by heavy oils with high resins and asphaltene contents, consistent with observations by Jokuty et al. (1995). As expected, the sole dilbit sample showed bimodal behaviour, with little initial change in adhesion followed by an exponential increase similar to that of the heavy oils.

<u>**Recommendation:**</u> **Further study on a range of oils under varied environmental conditions is needed to resolve the current uncertainty around evaporative losses experienced in surface spills, including the effect *of* oil layer thickness and surface winds, the role of photooxidation and formation of weathered 'skin'. Field work especially, but also lab work, are essential to determine the extent and kinetics of diluent evaporation from various bitumen blends, and the resultant behaviour of such blends due to weathering processes.**

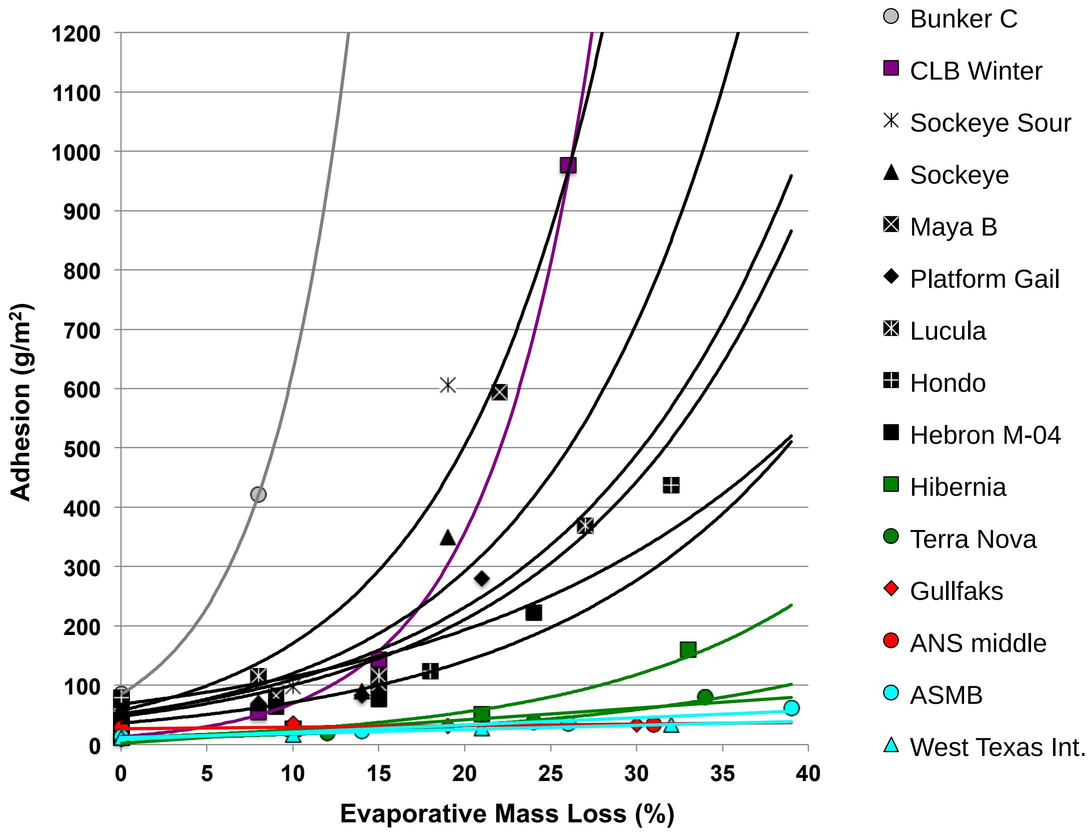


Figure 2.6 Correlation between adhesion and evaporation of selected oils. *Data compiled from Hollebone (2015) and unpublished data from Environment Canada (dilbit values); trend lines were drawn in Excel v.14.4.6. Evaporative loss was achieved using rotary evaporation in a laboratory and adhesion was measured using the semi-quantitative gravimetric method of Jokuty et al. (1995). Blue symbols, light crude oils; red, medium crude oils; green, waxy crude oils; black, heavy crude oils; purple, dilbit (Cold Lake Blend-Winter); grey, Bunker C.*

Aerosolization is a recently proposed dispersal route for atmospheric transport of crude oil spilled onto water. Laboratory studies have shown that bubble bursting (e.g., due to ebullition of gases from a shallow subsea blowout) and/or wave action (e.g., simulated white caps) can create hydrocarbon aerosols by mechanisms similar to those that generate ocean spray (Ehrenhauser et al. 2014). Likewise, hydrocarbon aerosols are formed by the impact of raindrops on an oil slick (Murphy et al. 2015). In both cases, the presence of dispersant, such as Corexit 9500 used in the DWH spill (Section 2.4.2.1), enhanced the effect. Notably, this dispersion route could also significantly increase evaporation from air-borne droplets.

Atmospheric re-deposition of the aerosolized oil (SL Ross 2012) onto water or land could distribute the hydrocarbons beyond the extent of the main spill. Anecdotally, during the 1984 Uniacke G-72 surface blowout off Sable Island, NS, which ejected a plume of condensate into the atmosphere, responders reported ‘hydrocarbon rain’ near the spill site (K. Lee, pers. comm. 2015); a similar phenomenon occurred during the 1982 onshore blowout of a sour condensate well near Lodgepole, AB (J. Foght, pers. comm. 2015). However, literature on the magnitude and impacts of atmospheric hydrocarbons on water and land is sparse (NRC 2003), warranting further study.

2.4.1.3 Photooxidation

In a poorly understood free-radical-generating process, aromatic hydrocarbons (particularly PAHs and including aromatic N-, S- and O-heterocycles) react with oxygen in the presence of sunlight, yielding oxygenated products that are more water-soluble and usually more resistant to biodegradation than the parent compounds. Whereas removal of PAH from the oil is beneficial, as some PAHs contribute to its potential carcinogenicity and embryotoxicity, the increased mobility and persistence of the photooxidized products in the water column are likely detrimental. The full suite of photooxidation products is currently unknown, although they are known to have impacts on aquatic life (Chapter 4). Notably, the susceptibility of PAH to photooxidation is the opposite of biodegradation potential: the smaller the PAH the more biodegradable and less susceptible to photooxidation; conversely, the more aromatic rings, the less biodegradable but more susceptible to photooxidation.

It is likely that photooxidation is most important relatively early in the weathering process. Recent laboratory studies with fresh and weathered oils from the *Heibei Spirit* spill (a mixture of light and heavy crudes; Yim et al. 2012) used ultra-high resolution GC to show that photooxidation preferentially increased the proportion of oxygenated compounds in fresh oil versus weathered oil (Islam et al. 2005). The N-containing resins (**Table 2.1**), particularly compounds with secondary and tertiary amine groups, such as phenylamines, were most vulnerable to photooxidation. S-containing resins, such as aromatic dibenzothiophenes, were also photooxidized, with unknown environmental consequences for toxicity and persistence of the weathered oil.

Photooxidation is obviously affected by sun angle and season, particularly at higher latitudes in the Arctic. However, even at lower latitudes the process appears to be slow, accounting for <0.1% of total losses per day (WSP 2014). Although photooxidation may not directly achieve significant mass losses, it can have indirect effects on subsequent weathering processes. For example, oxidized products may contribute to emulsification (Fingas 2015e) and crust or ‘skin’ formation on the surface of an oil slick (Bobra and Tennyson 1989) that decreases evaporative losses, as discussed above. Unexpectedly, ultraviolet irradiation of light Macondo oil from the DWH oil spill affected formation of microbial flocs in seawater compared with fresh Macondo oil (Passow 2014). This ‘photo-chemical aging’ appears to have promoted subsequent sinking and sequestration of some of the oil in the Gulf of Mexico seabed (discussed in detail in Section 2.4.2.3).

It appears that there may be only a small window of time for oil spill response to reduce the effects of photooxidation on other weathering processes, but further research into the products and magnitude of photooxidation is required, especially for emerging, unconventional oils and blends.

2.4.1.4 Emulsification

Formation of emulsions (**Figure 2.7**) is important for several reasons. By incorporating up to 60-80% water, stable emulsions increase the effective volume of the spilled oil up to two to five fold and increase the oil’s viscosity by up to 1,000-fold (Fingas and Fieldhouse 2015). This decreases evaporation of volatile components and reduces oil spreading. Oil entrained in mousse emulsions resists dispersion with chemicals and biodegradation due to its viscosity, low bulk surface area and hindered nutrient replenishment (AOSRT 2014). Emulsions tend to move from floating on the water surface to being submerged in the water column, where physical recovery may be hampered. All of these behaviours affect cleanup and remediation response options (Chapter 6).

The type of emulsion formed, whether water-in-oil (w/o) or oil-in-water (o/w), depends on the environmental conditions (temperature, mixing) and on the mass and chemical composition of the oil. Some crude oils form w/o emulsions rapidly but soon revert to two discrete oil and water phases; others, such as heavy fuel oils, form w/o emulsions poorly or only slowly. Some w/o emulsions can be stable for months or years (Fingas and Fieldhouse 2015), likely stabilized by sub-fractions of asphaltenes (Yang et al. 2014, 2015), waxes acting synergistically with asphaltenes (Kokal 2002), resins (WSP 2014), or even by bacterial cells (Dorobantu et al. 2004) that prevent coalescence of the oil by aligning at the oil:water interface (**Figure 2.7**). Eventually the emulsions may separate into oil and water again by natural processes, including additional weathering, oxidation and/or freeze-thaw action (Fingas 2014).

When sufficient mechanical energy (e.g., wind and/or wave activity) is applied to mix oil and water, unstable or stable emulsions may be generated; the latter may take the form of oil droplets dispersed in the bulk water phase or, conversely, water droplets in a bulk oil phase commonly known as 'chocolate mousse'.

In light of the proposed roles of asphaltenes and resins in stabilizing emulsions, it is both interesting and unexpected that bitumen and severely weathered diluted bitumen that have a high content of both classes do not appear to form stable emulsions (Fingas and Fieldhouse 2015), although lightly weathered bitumen blends can incorporate water droplets given sufficient mixing energy. During outdoor wave-tank tests where two weathered dilbit products (AWB and CLB, **Table 2.2**) were applied to seawater at an average temperature of 8 °C with and without artificial sediment (fine clay minerals), breaking waves caused the oil to form unstable w/o emulsions and large submerged droplets that readily coalesced into a surface slick (Government of Canada 2013). This observation was confirmed by another study of fresh and weathered Cold Lake dilbit and ASMB light oil (**Table 2.2**) agitated at 15 °C in an indoor wave tank with river water containing natural floodplain sediment (Zhou et al. 2015). The ASMB immediately dispersed into the water column whereas the dilbit formed an unstable emulsion that subsequently separated and remained floating for eight days or became stranded on the apparatus 'beach'; no formation of mousse was observed with the dilbit. Poor emulsion formation by heavy oils and weathered dilbits may occur because high viscosity limits dispersion and therefore the amount of water incorporated, and such water is only transiently entrained not actually emulsified. It is notable that this unanticipated behaviour was revealed only by experimentation rather than from first principles, highlighting the importance of research on unconventional oils. Further studies on the fundamental mechanisms of dilbit interactions with water are underway to help address this knowledge gap (e.g., Dettman and Irvine 2015), including the effects of emulsification on adhesion properties (Section 2.2.6).

<u>Recommendation:</u> Laboratory and field trials are needed to determine the conditions under which fresh and weathered diluted bitumen blends will form stable or unstable emulsions in fresh water and seawater. A variety of bitumen blends would be essential to investigate under various agitation conditions and salinities to inform modeling and response to spills.

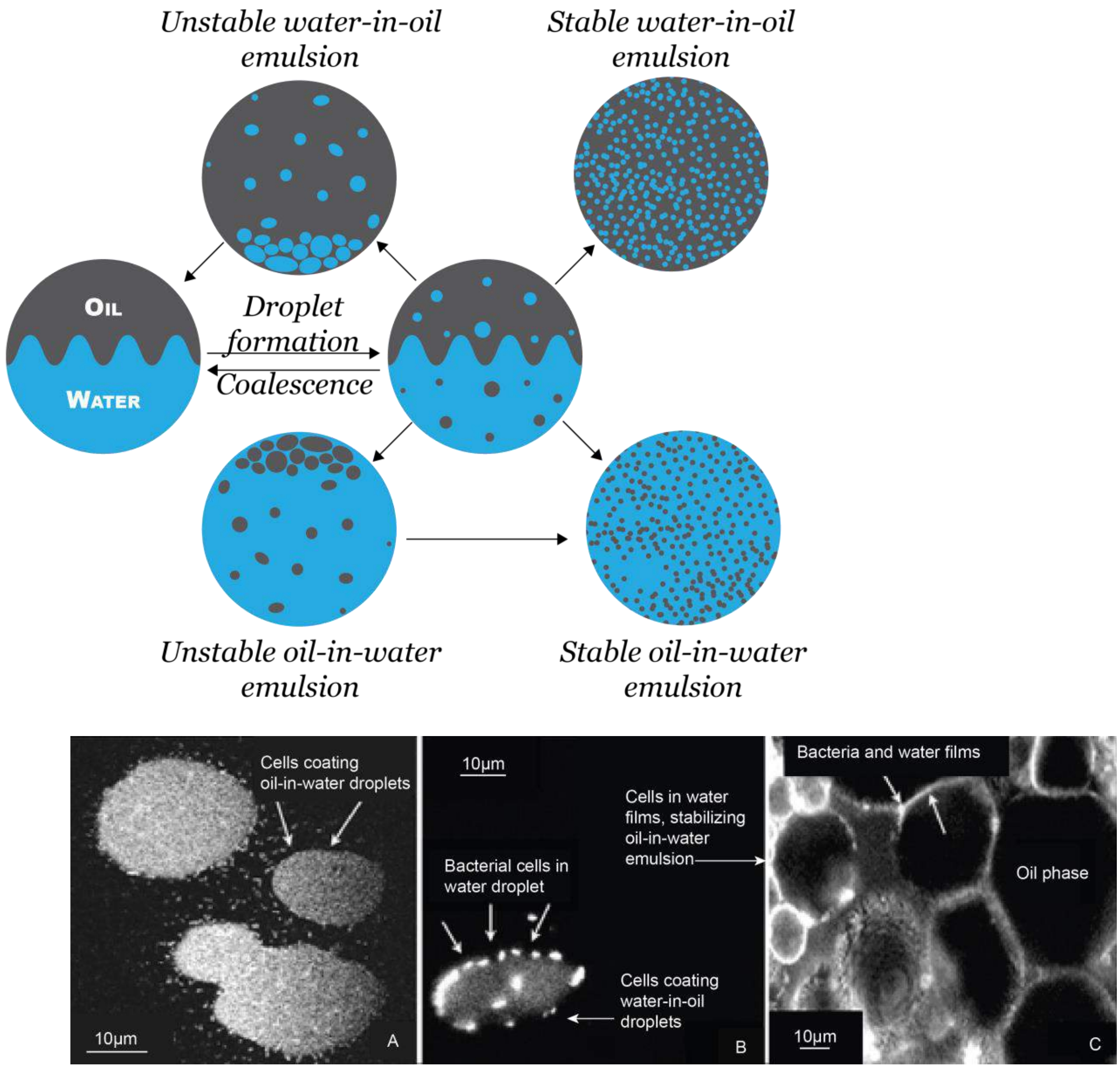


Figure 2.7 Emulsification of oil and water. *Upper panel: Generation of stable and unstable water-in-oil (w/o) and oil-in-water (o/w) emulsions in seawater. Lower panel: Stabilization of o/w and w/o emulsions in artificial fresh water by cells of hydrocarbon-degrading bacteria. Lower panel adapted from Dorobantu, L.S., Yeung, A.K.C., Foght, J.M. and M.R. Gray. 2004. Stabilization of oil-water emulsions by hydrophobic bacteria. Applied and Environmental Microbiology 70(10): 6333-6336.Copyright © American Society for Microbiology.*

2.4.2 Weathering Processes in the Water Column

2.4.2.1 Dissolution

Evaporation and dissolution are interrelated and competing processes. In the former process, petroleum constituents are moved to the atmosphere from the surface of the slick, and in the latter, they are diluted in the water column from the underside of the slick. Both processes reduce the potential acute toxicity of the residual oil while potentially increasing the chronic toxicity by enriching the remaining oil in alkyl PAH (Chapter 4). However, evaporation typically accounts for far greater mass losses of spilled oil than dissolution.

> Dissolution is important because many of the most water-soluble components of petroleum (e.g., BTEX) are also the most volatile and most acutely toxic.

Hydrocarbons typically have very low solubility in water (Section 2.2.4), which decreases with molecular size. Monoaromatics and the lightest saturates are the most water-soluble, whereas larger saturates and PAH have lower solubility, and asphaltenes (and most resins) are considered water-insoluble. For this reason, heavy oils and bitumen do not readily dissolve in aqueous solution (the water soluble fraction is <10 ppm) and dissolution does not significantly reduce the total mass of heavy oils spilled onto water. However, LMW components of the diluents in dilbit and synbit will have some aqueous solubility, in which case dissolution of even a small fraction of a very large dilbit spill may represent a large mass of dissolved chemical. Dispersion of the oil as small droplets with large ratios of surface area to volume would hasten and increase such dissolution.

The relative importance of dissolution increases in deep subsurface spills, such as the DWH blowout, where the long travel time for oil droplets to rise or travel laterally through the water column increases the opportunity for small molecules to dissolve rather than evaporate upon reaching the water surface (FISG 2010). Furthermore, subsurface application of the chemical dispersant Corexit 9500 to the DWH blowout (Chapter 6) decreased oil droplet size, increased the total oil:water surface area to facilitate partitioning into the water phase, generated a subsurface plume of droplets <100 µm diameter that moved horizontally with deep currents in the Gulf of Mexico, and prolonged oil contact with the water (Thibodeaux et al. 2011). This 'continuous molecular extraction' of oil droplets by the water column, which did not reach equilibrium, preferentially depleted the oil of the most soluble monoaromatics, some resins and even PAHs, alkyl PAHs and light alkanes $<C_8$, and enriched the alkanes $\geq C_9$ and heavier compounds in the oil droplets. This phenomenon may have decreased the acute toxicity of dispersed Macondo oil and thereby increased its biodegradability (Section 2.4.2.5 and Chapter 6).

<u>Recommendation</u>: There is a need for the development of new dynamic (non-steady state) models describing dissolution of hydrocarbons in deep seawater and turbulent rivers, especially for diluted bitumens where the fate of such hydrocarbons is not yet understood. Similarly, toxicity testing of different water-soluble fractions (with and without dispersant addition) is needed for unconventional oils and blends that exhibit bimodal behaviour.

2.4.2.2 Natural dispersion

Natural dispersion of oil in the water column (as opposed to addition of chemical dispersants as a cleanup intervention; Chapter 6) occurs when the mechanical action of waves or turbulence detaches oil droplets from the slick and forces them into the water column. Likewise, turbulent flow likely leads to oil dispersion in rivers having steep gradients, high-velocity flows and/or boulder/cobble substrates, and during offshore subsurface well blowouts like the DWH (Zhao et al. 2014). Depending upon droplet size, depth and energy of the system, droplets may remain dispersed (i.e., suspended in the water column) or may resurface with or without coalescing with other droplets (**Figure 2.8**). Droplets <20 µm (0.02 mm) may remain stably dispersed in water without resurfacing for a long time (Fingas 2014b), as observed with the DWH oil (Valentine et al. 2014).

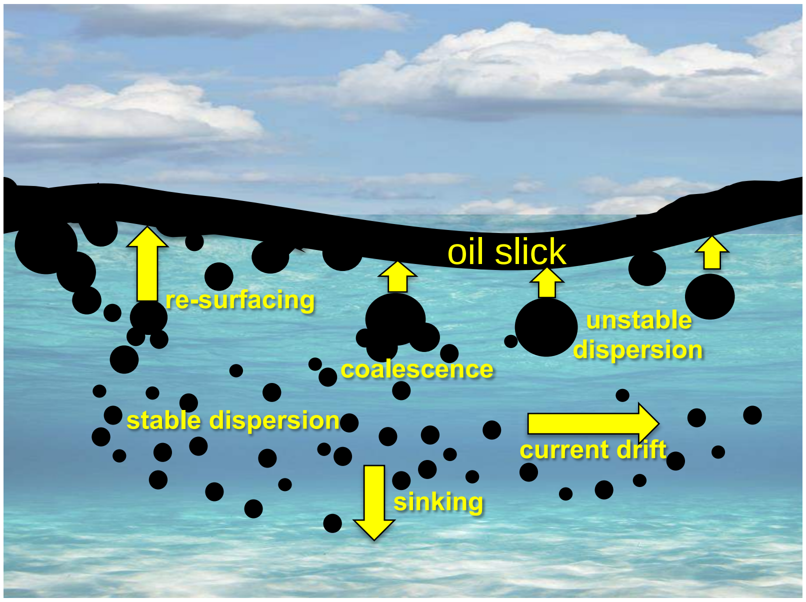


Figure 2.8 Natural dispersion of oil into the water column.

Dispersion affects oil behaviour in several ways. First, stable dispersion removes oil from the surface, reducing evaporation and photooxidation. Second, the greater surface area afforded by small oil droplets makes the oil more available for dissolution (Section 2.4.2.1) and biodegradation (Brakstad et al. 2015; Prince 2015; Section 2.4.2.5). In fact, the rate of oil biodegradation has been suggested to correlate with oil droplet size distribution (Venosa and Holder 2007). Moreover, many oil-degrading microbes are attracted and attach to the oil–water interface (Kang et al. 2008a,b; Abbasnezhad et al. 2011a,b) where they may: (a) produce biosurfactants to further increase droplet formation; and/or (b) stabilize oil droplets by preventing coalescence, as described for emulsions (Dorobantu et al. 2004; **Figure 2.7**). Oil droplet size is a factor in toxicity to aquatic organisms, as zooplankton may ingest tiny droplets and thus pass the hydrocarbon up the food chain, and smaller droplets (with a higher ratio of surface area to volume) facilitate dissolution of hydrocarbons associated with toxicity (**Figure 2.3** and Chapter 4).

Although dispersion of conventional crude oils is relatively well understood (see Daling et al. [2003]), considerably less is known about dispersion of bitumen blends in fresh water, estuarine (brackish) water or seawater (Dew et al. 2015). Recently, dispersion of CLB dilbit in filtered seawater was conducted in a wave tank under spring-time and summer temperatures (~8.5 °C and 17 °C, respectively), with or without addition of fine mineral particles (King et al. 2015b) and with or without chemical dispersant. With breaking waves, the dilbit showed poor natural dispersion (only 6% dispersion effectiveness) in the presence and absence of suspended fine mineral particulates. Addition of chemical dispersant alone efficiently produced droplets (45-59% dispersion effectiveness), but the droplet size distribution differed from that of chemically-dispersed conventional crude oils. Additional studies of dilbit dispersion are underway in Government of Canada laboratories, but data are not yet available for review.

<u>Recommendation:</u> More data are required for natural and chemically-enhanced dispersion of unconventional oils and diluted bitumen blends, especially in fresh water.

2.4.2.3 Submergence, sinking, sedimentation and re-suspension of oil

Multiple processes can alter oil density to influence submergence, sinking and sedimentation, including: increased density due to evaporation and/or dissolution of light components (Section 2.4.1.2 and Section 2.4.2.1); emulsification (Section 2.4.1.4); and interactions with particles. The latter process can be further delineated by considering inorganic particles (e.g., minerals and detritus suspended offshore, or onshore sediments if the oil spills over land before entering the water body) or organic particles (e.g., flocs of microbial biofilms, biological detritus and/or phytoplankton mucus).

> Oil may submerge through dispersion or emulsification and eventually sink through the water column to become entrained in the underlying sediments (marine or freshwater) in a process called 'sedimentation'. If disturbed, sunken oil may become re-suspended to enter the water column again, resurface and/or be re-distributed in the subsurface.

The density of many crude oils, including diluted bitumen products, is less than that of both fresh water (~1 g/cm^3) and sea water (~1.03 g/cm^3) and therefore these oils will float when spilled. However, bitumen by definition has a density >1 g/cm^3 and, if diluent evaporates from dilbit during a spill, the residual bitumen will become more dense and may become submerged or sink. Even so, oil droplets of density ~1.0 can be neutrally buoyant and remain suspended in the water column, especially if present in turbulent water such as in a rapidly flowing river or high wave energy system. In rivers or at beaches, suspended oil droplets could be entrained into porous gravel by hyporheic flows (**Figure 2.3)**, creating a potential for contamination of sediments and pore water with free-phase oil or dissolved hydrocarbons (reviewed in more detail in Chapters 3 and 5). In addition to evaporation, other environmental processes, such as photooxidation (Section 2.4.1.3), can affect oil buoyancy (NRC 1999; Government of Canada 2013). As water temperature generally decreases with water depth, the oil density will increase, possibly causing it to remain submerged or sink, and temperature cycling between day and night may cause oil to alternatively submerge and float. Emulsification can also cause floating oil to become submerged (but typically not to sink).

> OMAs form when oil interacts with and adheres to inorganic particles. A more general term, OPAs, includes OMAs plus oil associated with organic particles.

Interaction of oil with non-oil particulates changes the properties of the aggregates, causing normally buoyant oil to sink, for example, or liquid oil to become semi-solid. 'Oil-Mineral Aggregates' (OMAs) can form when oil interacts with inorganic materials, such as clay minerals suspended in the water column (Lee 2002), or with soils or shoreline sediments during overland flow into a waterbody. The term oil-particle aggregates' (OPAs) collectively encompasses OMAs as well as oil associated with organic material, such as detritus and living microbial cells (Fitzpatrick et al. 2015; Waterman and Garcia 2015), and combinations of these particles (**Figure 2.9**). OPAs may have neutral buoyancy and float at or below the water surface, or may sink and become entrained in sediments. The latter fate would potentially place the oil in anaerobic conditions where biodegradation is slower (Chapter 3), although shallowly buried oil may be re-suspended by wave action or by ebullition of gases from the sediments. If the OPAs remain suspended, the additional reactive surface area afforded by the minerals or organic matter may enhance bacterial attachment (**Figure 2.3**) and aerobic biodegradation (Chapter 6).

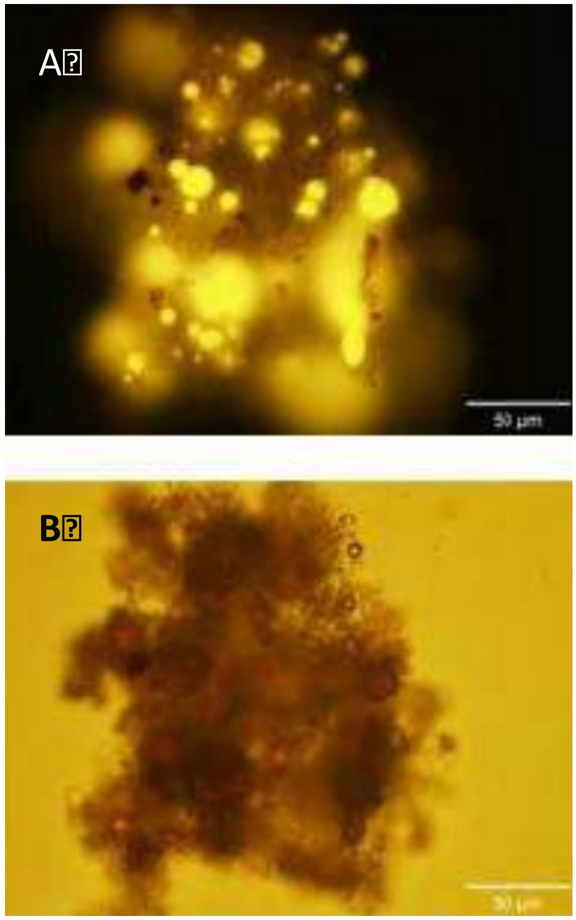


Figure 2.9 Oil-particle aggregate (OPA) formed by interaction of weathered dilbit with natural Kalamazoo River sediments. *A, appearance of an OPA under ultraviolet light; yellow areas are oil. B, the same OPA observed under visible light, showing oil plus sediment particles. Scale bars in bottom right are 50 µm. Images from Lee et al. (2012).*

OPAs can be generated by overland spills where oil initially contacts sediments on shorelines or riverbanks before entering the water column and sinking. Alternatively, oil that strands on beaches, interacts with shoreline sediments, then re-enters the water column with accumulated mineral particles may sink. Another natural mechanism for generating OPAs in the water is association of floating or submerged oil droplets with suspended particles in the water column, especially near the shore or in estuaries where the suspended sediment load is high. In fact, incorporating as little as 2–3% mineral content into the oil phase is sufficient to cause some oils to sink (NRC 1999). The degree of interaction between oil and minerals depends on oil viscosity and the mineral type, but may begin with formation of an oil monolayer around the mineral followed by further accumulation of oil on the hydrocarbon surface (Omotoso et al. 2002).

The importance of submergence, OMA or OPA formation and sedimentation in the recovery and overall fate of spilled oil was highlighted in the DWH subsurface blowout in which chemical dispersants were injected into the escaping plume of light Macondo oil (**Table 2.2**). The large initial subsurface plume of suspended dispersed oil droplets (<100 µm diameter) at depths of 900-1,200 m was undetectable a few months after the discharge and was initially presumed by some researchers to have been rapidly biodegraded by indigenous bacteria (e.g., Hazen et al. 2010) that had been enriched by natural oil seeps in the Gulf (**Figure 2.3**). However, two independent analytical methods (hopane biomarkers and natural abundance radioisotopes) applied to sediment cores collected from the vicinity of the blowout have recently revealed elevated concentrations of hydrocarbons patchily distributed in a thin sediment layer overlaid by cleaner sediments from post-spill deposition (Valentine et al. 2014; Chanton et al. 2015; Joye 2015). This sequestered oil within a 3,200 km^2 footprint on the Gulf seabed may account for 2-14% of the total volume of discharged Macondo oil (Valentine et al. 2014; Chanton et al. 2015; Joye 2015).

Two complementary mechanisms are proposed to have promoted this sedimentation pattern (Thibodeaux et al. 2011). One is the formation of OMAs as the circulating subsurface oil plume interacted with suspended mineral particles near the continental shelf, the concentrations of which may have further increased when flow from the Mississippi River was diverted to flush Macondo oil out of shorelines (Passow 2014). Sinking of these OMAs to the seafloor (**Figure 2.3**) is proposed to have led to a 'bathtub ring' of oily sediments around the Gulf's continental shelf (Valentine et al. 2014).

A second mechanism of oil submergence, sinking and sedimentation, presumed to be biologically-driven, was also observed by analysis of Gulf sediments and in laboratory simulations. In fact, this phenomenon may account for a large proportion of oil 'missing' from initial oil budgets for the DWH spill (e.g., FISG 2010; Joye 2015) and may be more important than OMA sedimentation in this particular spill. Creation of an oily 'footprint' or 'fallout plume', predominantly of microbial origin (Passow et al. 2012; Passow 2014; Valentine et al. 2014) may have formed as follows: even in uncontaminated ocean waters, marine phytoplankton and zooplankton near the sea surface naturally secrete sticky polymers that aggregate particulate and dissolved organic material into >0.5 mm flocs called 'marine snow' (Azam and Malfatti 2007; Kleindienst et al. 2015). These flocs slowly settle to the seafloor over months or years to form new sediments enriched in recalcitrant organic matter. During and briefly after the DWH event, unusually elevated concentrations and sizes of such flocs (mm to cm diameter) were observed (Brooks et al. 2015). These are proposed to represent blooms of hydrocarbon-degrading bacterial communities attached to weathered Macondo oil droplets at or near the sea surface (**Figure 2.3**). Additional organic material in the flocs may be mucus produced by oil-stressed phytoplankton. These large, dense, oil-rich organic flocs rapidly sank over days or weeks while incorporating additional submerged oil in the subsurface plume (and possibly mineral particles), creating a transient 'dirty blizzard' of oil-laden marine snow (Passow 2014; Valentine et al. 2014; Brooks et al. 2015). It is possible that some degree of aerobic oil biodegradation occurred during sinking of the OPAs, but the fallout area created an 'oily footprint' on the Gulf seafloor. Thus, both surface and subsurface oil are thought to have been transported to the seabed in microbe-rich aggregates.

Weathering of Macondo oil at the surface, including photooxidation, affected floc formation (versus fresh Macondo oil that did not promote floc formation) and may have enhanced the rate of sinking of the oily marine snow (Chanton et al. 2014; Passow 2014). The role of Corexit 9500 dispersant in floc formation appears to be concentration-dependent (Passow 2014). Furthermore dispersion of Macondo-like oil with Corexit 9500 may lead to enrichment of specific *Colwellia* subtypes capable of growing on the dispersant itself and indirectly influencing floc formation (Kleindienst et al. 2015). These authors have recently claimed, based on laboratory experiments, that Corexit 9500 may suppress oil biodegradation by indigenous hydrocarbon-degrading microbes in deep Gulf waters, although divergent opinions have been expressed regarding the effects of chemical dispersants on oil biodegradation (e.g., Prince 2015).

These types of hydrocarbon-rich sediment layers were gradually overlaid by clean sediments and post-spill marine snow through natural deposition processes, sequestering the oiled sediment layer (Romero et al. 2015). The long-term fate of this buried light Macondo oil is not yet known. However, it is possible that the sequestered oil will be biodegraded (even under anaerobic conditions in the sediment layer) because it is a light oil rich in alkanes, and because dissolution during initial rise of droplets to the surface (Section 2.4.2.1) and subsequent surface weathering (evaporation, photolysis) may have reduced the oil's toxicity. Also, attachment of active hydrocarbon-degrading microbes during floc formation may have 'inoculated' OPAs to promote biodegradation during and after sedimentation; however, this possibility remains to be investigated.

> Even the relatively simple, well-characterized Macondo light crude exhibited unexpected sinking behaviour when dispersed. The submergence and sedimentation of chemically complex heavy oils and diluted bitumen blends is even more unpredictable, especially since dispersion of both fresh and weathered dilbits is not yet understood. Furthermore, there are very few published reports on formation of OPAs from heavy oil or bitumen products, especially in fresh water. This hampers understanding and modeling of dilbit submergence, incorporation into sediments, re-emergence and transport in rivers. The role of microbial flocs in sedimenting heavy residues into shallow receptors (e.g., river sediments and lakebeds) is unknown, as this mechanism was not recognized until very recently from DWH studies.

Formation of OPAs likely contributed to sedimentation of a diluted Bunker C-class heavy fuel oil spilled into Lake Wabamun, AB, by a train derailment in 2005 (Chapters 4 and 8). During the overland flow of this heavy oil into the lake the lighter diluent components evaporated, allowing the weathered oil to interact with shoreline material and subsequently with suspended organic particles in the water column. In addition to forming tar balls (Section 2.4.2.4), some oil sank, impacted the lake sediments, and continued to resurface over subsequent years (Hollebone et al. 2011). Floating, sinking, submerged, sedimented and refloating oil, including the production of sheens, were all observed in the year following the spill (Hollebone et al. 2011).

Currently there is considerable debate regarding the fate of weathered and unweathered diluted heavy oils and bitumen blends: will they float on the surface, submerge, sink or sediment with OPAs? An early literature review (NRC 1999) found that only 20% of heavy oil spills resulted in a significant portion of the products sinking or being submerged in the water. However, a more recent review (Winter and Haddad 2014) concluded that dilbit has a greater potential for sinking than conventional oils. First, evaporation of the diluent could increase the oil density, causing the residual oil to submerge or sink. Second, in theory, the majority of weathered dilbit would be available for interaction with suspended sediments as OMAs because so little of the bitumen itself will evaporate or biodegrade, further increasing the possibility of sedimentation and sequestration. It is not yet fully known how adhesive properties (which change with evaporative losses; Figures 2.5 and 2.6) affect OPA formation by diluted bitumen products in the field.

Field experience with the highly-publicized overland spill of dilbit into the Kalamazoo River, MI, in 2010 (Chapters 6 and 8) indicated that the dilbit, with an initial density of 0.96-0.98 g/cm^3 and near neutral buoyancy, initially floated. Interaction with soil particles before entering the river and subsequently with elevated suspended sediment loads in the water due to high rainfall events preceding the spill enabled a considerable proportion of the dilbit to become submerged in the river water and eventually sink (Crosby et al. 2013). This phenomenon contaminated the river sediments at natural collection points. The oil-sediment aggregates were stable for at least two years (Lee et al. 2012), and at three years post-spill were estimated to represent 20-30% of the initial oil volume (US-EPA 2013b).

This case supports the statement by Crosby et al. (2013) in a report from the US National Oceanographic and Atmospheric Administration (NOAA) that: ‘Little research is currently available regarding the behavior of oil sands products spilled into water, and how they weather in the environment. Most tests have been conducted in the laboratory, so predicting the actual behavior of oil sands products for a range of spills is difficult.’

<u>Recommendation:</u> Additional study is needed to examine OPA formation by dilbits and heavy oil samples that have experienced various stages of weathering (including

photooxidation, which may be important for heavy products that are enriched in PAH), using various types and loads of suspended sediments at various temperatures and salinities.

Some research is beginning to emerge to address this gap. Waterman and Garcia (2015) performed laboratory studies with CLB dilbit (**Table 2.2**) and Kalamazoo River sediments to examine the kinetics of OMA formation. The dilbit was artificially weathered (without UV exposure) over six days to achieve different mass losses (0%, 9.9% or 17.4% loss; density range 0.932–0.993 g/ml), then added to the surface of tap water containing uncontaminated Kalamazoo River sediments of different mesh sizes. With conventional gyrotory mixing at 21-22 °C the dilbit formed stable small-diameter (<200 µm) spherical droplets coated with particles (similar to those shown in **Figure 2.9** and in Stoffyn-Egli and Lee [2002]). However, larger (>1 mm) irregularly-shaped 'solid' OPAs formed with unconventional mixing intended to simulate sinking, re-suspension and droplet coalescence, possibly from folding of the sediments into the oil rather than simple attachment to the surface of droplets per the mechanism proposed by Stoffyn-Egli and Lee (2002). Some OMAs of each type were positively buoyant (floated in tap water), whereas others sank, depending on the relative proportions of oil and incorporated sediment. Thus, the behaviour of diluted bitumen is not predictable without experimental data to inform predictions.

Other recent laboratory studies in seawater found that weathered dilbit achieved densities >1 g/cm^3 and furthermore adhered to fine sediments (kaolin clay) added to the water, forming OMAs that sank in saltwater, as well as forming floating tar balls (Government of Canada 2013; reviewed by Dew et al. 2015). Additional details about floating and sinking behaviours of AWB and CLB dilbits in saltwater can be found in a Government of Canada (2013) report. The authors noted that bitumen is predicted to sink in fresh water after extensive weathering, but the behaviour of dilbit during weathering in the marine environment is currently poorly delineated. The relevance of using laboratory conditions to simulate oil behaviour in the environment has been questioned, as some studies have failed to use UV irradiation (to cause photooxidation) and/or to consider microbial interactions or temperature effects on density and sinking (e.g., weathered bitumen may float at 15 °C but sink at 5 °C; Section 2.2.1). As reviewed by Short (2013), other studies used unrealistically thick dilbit slicks or inappropriately slow wind speeds. To begin to address the need for open-air studies, experiments were performed on two fresh (unweathered) dilbit samples (AWB and CLB; **Table 2.2**) in outdoor wave tanks containing filtered seawater at ~19 °C (King et al. 2014). In only six days the AWB dilbit weathered sufficiently for droplets to detach from the slick and sink in the upper 10 cm of brackish water. This sinking was not enhanced by OMA formation because the seawater had been filtered to remove particles >5 µm. The density of CLB dilbit increased more slowly over 13 days, likely because of its naturally higher concentration of alkyl PAHs, which are more resistant to weathering (King et al. 2014).

Despite increased interest and research activity, such as laboratory and field tests that are currently underway in government laboratories (the results of which are not yet available for review), the conditions under which dilbit will float, submerge or sediment constitute a knowledge gap that warrants further investigation, particularly for freshwater systems. For example, the magnitude of microbially-driven sedimentation is currently cryptic, with or without photooxidation, OPA formation and different combinations of other weathering processes. If this sedimentation process is as significant for dilbit spilled in shallow water and freshwater systems as it appears to have been in the light Macondo oil subsurface spill, it is a major process that should be incorporated into oil spill models. The bimodal evaporation kinetics of dilbit and the longer time needed for onset and action of microbial processes to affect sinking versus physical processes (**Figure 2.4**) suggest that experiments on unconventional oils should be conducted for much longer time periods than trials with conventional crude oils.

When oil sinks and becomes sequestered in sediments, it is less likely to be quickly or extensively biodegraded (Section 2.4.2.5) because the sediment pore spaces are usually anaerobic below the interface and nutrient replenishment is hindered. The fate of sequestered OPAs is largely unknown and requires study over long time periods (years) to account for the slow rates of anaerobic biodegradation. In the case of sequestered weathered dilbit and heavy oil, it is possible that the oil becomes virtually chemically inert to benthic organisms, although it may still have physical impact.

Recommendation: The long-term biodegradation of sedimented and sequestered oil in anaerobic marine and freshwater sediments requires long-term study (i.e., over years to decades) to provide reliable information for modeling and oil spill budgets.

2.4.2.4 Formation of tar balls, tar patties and tar mats

Tar balls are typically discrete, roughly spherical conglomerations of oil <10 cm in diameter, tar patties >10 cm in diameter, and tar mats ≥ 1 m in diameter (Fingas 2015b) that may be partially or completely submerged (Warnock et al. 2015). Pelagic tar floats or is shallowly submerged (and can travel considerable distances with waves and currents, where it can become stranded on the shore), whereas benthic tar residues are immobilized by sinking to the sea floor. The impact of marine tar residues on aquatic life is less than that of fresh oil in the water column, although tar balls may serve as a reservoir of PAHs that partition into surrounding water (Martin et al. 2014), and tar residues that strand on beaches may release sheens of nearly-fresh oil if physically disrupted.

> Weathered oil that has acquired a surface 'crust' through weathering, emulsification, photooxidation and/or sediment interaction may form spherical tar balls, flattened tar mats or patties (collectively, marine tar residues) that may float, submerge or sink, depending on the oil type and severity of weathering.

Marine tar residues can be produced from 'chocolate mousse' emulsions (Section 2.4.1.4) and, due to entrained water, may harbour microorganisms within the structure, as well as at the surface. However, the small surface area:volume ratios of tar residues, as well as the presence of a crust, hampers biodegradation of the oil (Warnock et al. 2015). The crust may be enriched in asphaltenes and resins as these are the most polar compounds in oil and are prone to alignment at the oil:water interface; therefore, heavy oils are more likely to form tar balls and mats. If suspended, the balls and mats may intermittently release a sheen of fresh oil from breaches in the crust (Hollebone et al. 2011). Small tar mats may persist for decades, as noted after the 1979 Ixtoc I blowout in the Gulf of Mexico and the *Prestige* oil tanker sinking off Spain in 2002 (reviewed by Warnock et al. 2015). In 2013 an enormous tar mat estimated at 18 tonnes was discovered in the Gulf of Mexico as a consequence of the DWH subsurface spill in 2010. It consisted of 15% oil and 85% sand, shells and water (Buskey 2013).

2.4.2.5 Biodegradation

> Biodegradation is a natural process in which living organisms and/or their enzymes break down organic material to produce simpler chemical compounds such as organic acids, alcohols and/or gases. Bioremediation is the application of biodegradation processes to help clean up a polluted site. Petroleum biodegradation in aquatic environments is primarily achieved by bacteria.

Oil spill biodegradation processes and limitations are discussed in detail in Chapter 3 and bioremediation in Chapter 6. Briefly, oil susceptibility to biodegradation primarily depends on: chemical composition (ratio of biodegradable alkanes and aromatics to recalcitrant resins and asphaltenes); physical state (surface area available at the oil:water interface for microbial attachment or dissolution of light hydrocarbons and hence also dependence on spreading, dispersion and emulsification state of the oil); temperature (biochemical activity being slower at low temperatures); nutrient availability (particularly soluble nitrogen and sometimes phosphate, as discussed in Chapter 6); and available electron acceptors for redox reactions (aerobic or various anaerobic conditions). Regarding the latter, oil degradation is generally faster and more efficient under aerobic conditions, such as in a well-aerated water column or in the uppermost layer of sediment, but may also occur slowly in buried sediments under anaerobic conditions (Section 2.4.3.1). The range of susceptible hydrocarbons under anaerobic conditions appears to be smaller than with aerobic degradation (e.g., reviews by Foght 2008; Mbadinga et al. 2011) and the enzymes, pathways, end products and residual oil composition also differ.

Oil biodegradation also requires competent microbes. Hydrocarbon-degrading bacteria are ubiquitous, and although they may be present in a pristine environment in only small numbers, they can flourish after an oil spill because they have an advantage over microbes that cannot utilize hydrocarbons. Environments that are routinely exposed to oil spills or natural hydrocarbon seeps, such as in the Gulf of Mexico, usually have indigenous microbial communities that are enriched in hydrocarbon-degraders and thus can respond more quickly to an incursion of oil. However, the widespread synthesis of alkanes by marine cyanobacteria may help maintain a baseline level of competent hydrocarbon-degrading bacteria even in pristine waters (Lea-Smith et al. 2015).

Notably, because biodegradation and physical weathering processes, such as evaporation and dissolution, target many of the same compounds (light hydrocarbons) but at different rates, it is often important to discriminate between biological and non-biological changes to oil chemistry. This can be done by the judicious selection of reference samples and the use of biomarkers (e.g., Blenkinsopp et al. 1996; Wang et al. 1998). As with chemical weathering, biological weathering is greatly influenced by oil composition, and each oil has different susceptibilities to aerobic and anaerobic biodegradation under specific environmental conditions. For this reason, surveys of oil biodegradability are useful for predicting oil fates. An example is the Environment Canada report by Blenkinsopp et al. (1996) in which a suite of oils transported in Alaska was tested in a laboratory for relative susceptibility to biodegradation by a standardized microbial consortium under cold freshwater conditions, with extended incubation times.

Recommendation: To complement catalogues of chemical and physical properties of oils, a biodegradability survey should be conducted on conventional and unconventional oils commonly transported in Canada. The survey should consider aerobic biodegradation potential under fresh- and saltwater conditions at cold and moderate temperatures, and anaerobic biodegradation in water-saturated sediments. If conducted under optimum laboratory conditions with fresh and weathered oils, the results would delineate the maximum biodegradation expected under actual environmental conditions.

The paucity of research on biodegradation of heavy oils and diluted bitumen must be addressed. It is certain that the majority of the bitumen in the blends is highly recalcitrant to biodegradation (Section 2.1.1.3 and 2.1.1.4). Even if some of the constituent bitumen chemicals were altered, would that change be detectable using current analytical methods (Appendix A) that are inadequate for characterizing asphaltenes and resins? Theoretically, the diluent components of bitumen blends should be relatively biodegradable (and resolvable by chromatography), but few blends have been subjected to controlled biodegradation experiments either aerobically or anaerobically to ascertain what proportion of the diluent is degradable in fresh or weathered dilbit. This uncertainty arises from the question raised in Section 2.3.1.2: does all diluent evaporate from diluted bitumen under natural conditions, leaving only recalcitrant bitumen? If so, there will be very little light hydrocarbon mass to be biodegraded in weathered dilbit. If not, is any of the residual diluent 'bioavailable' to microbes? It is possible that diluent chemicals are intimately associated with the resins and asphaltenes and therefore not available for microbial attack. Additionally, the diluent may be protected from microbial attack because the high viscosity of the weathered bitumen affords only a small surface area for microbial access.

Recommendation: Biodegradation of different bitumen blends and diluted heavy oils should be tested under a range of laboratory incubation combinations and analyzed using complementary suites of techniques to determine whether and how much biodegradation of constituents can be achieved. Comparison to multiple control conditions will be essential for rigorous interpretation of the results.

2.4.3 Oil Interactions with Shorelines and Sediments

Oil can impact shorelines and sediments via different routes. Overland spills will first impact the soil or beach so that the oil may be partially weathered by the time it reaches the water, as well as having incorporated mineral and organic matter (as discussed in Section 2.4.2.3). Oil that is spilled onto water and is subsequently stranded on the shoreline or riparian zone (the interface between a river or stream and the land) or buried in sediments will have different fates, including interaction with vegetation and possible re-mobilization.

2.4.3.1 Sorption, penetration and sequestration

Oil is adhesive, particularly when weathered (Fingas 2015b; **Figure 2.6**) and may attach to suspended particles (Section 2.4.2.3) and surfaces. If OPAs sink and are buried by additional sediment, the oil may be protected from remobilization, and biodegradation rates will be limited in instances where the water in sediment pore spaces is not adequately replenished with oxygen or nutrients. That is, oil buried in sediments, such as found in mudflats or deep ocean, may persist virtually unchanged.

Oil that remains floating or submerged in the water column can reach the shore and adhere to sand, cobbles, bedrock and shells, as well as man-made structures like piers and jetties; the same behaviour might be expected in the riparian zone. Once onshore in the intertidal zone, a light oil may penetrate by gravity into beach sediments due to its low viscosity, where it may sorb to the minerals and/or be retained (sequestered) in small pools, with reduced exposure to further weathering. This was observed after EVOS at many cobble beaches in Alaska. Relatively fresh oil can still be found in patches below the surface cobble and gravel more than 25 years after the spill (Atlas and Hazen 2011). This persistence is due in part to poor access of oxygen and nutrients to the buried oil, limiting remobilization and biodegradation of the oil (discussed in Chapter 3), as well as limited photooxidation, emulsification and other weathering processes (Boufadel et al. 2010).

Viscous heavy oils or highly weathered oils are less likely to penetrate deep into intertidal sediments, but may be forced to depth by wave action on high-energy beaches. Weathered oil that is thrown above the tidal zone will continue to experience physical and chemical weathering and may form an ‘asphalt pavement’, as observed on Chedabucto Bay beaches, persisting decades after the 1970 *Arrow* spill in Nova Scotia (Advanced Technology and Continental Shelf Associates 1990), and after the Baffin Island Oil Spill field experiment in the Canadian Arctic (Owens et al. 1987).

Although it is generally assumed that spills of light oils, such as condensate, in the open ocean would cause little or no harm due to rapid losses by evaporation, coastal studies in Nova Scotia have shown that condensate entrained within intertidal sandy beach environments can persist for extended periods (Strain 1986; Lee and Levy 1989). The implication is that evaporation of the diluent portion of dilbit that is sequestered in beach sediment may be retarded if unweathered dilbit is buried.

> Recent field observations and laboratory tests suggest that ‘armoured beaches’ (those that have boulders and/or cobbles underlain by fine sediments) may retain viscous heavy oils and heavily weathered oils, with the oil penetrating only to the surface of the packed sediment but not further.

On low-energy beaches, cobble and boulder ‘armour’ (**Figure 2.3**) prevents the sediments from being mixed by wave action and therefore protects the sequestered oil beneath (Harper et al. 2015). This oil, retained in the upper fine sediments, would be alternately replenished with oxygen and nutrients by tidal action and might undergo limited evaporation and dissolution, but the low surface area:volume ratio could slow biodegradation rates.

The presence of aquatic ‘biofilms’ (layers of living or recently living plants, animals and microbes) on rocks and structures could potentially reduce the adherence and sequestration of oil, particularly if the living material is highly hydrated (e.g., wet algae). The prevalence of algae on exposed bedrock shorelines is a component of ongoing baseline surveys in Canada that may yield observations about biofilm protection of substrata from oiling (Laforest et al. 2015).

There is much interest in the fate and behaviour of oil that enters aquatic areas having extensive vegetation (e.g., wetlands, estuaries, riparian zones) and impacts the underlying sediments. In this case, rates of submerged oil biodegradation may be retarded by anaerobic conditions in saturated sediments or by diauxic growth conditions (i.e., utilization of elevated levels of readily-degraded organic detrital matter by microbes, in preference to recalcitrant or toxic hydrocarbons). Alternatively, oil biodegradation may be stimulated by microbial associations with plant roots and the rhizosphere (soil surrounding roots and root hairs) in the process of ‘phytoremediation’ (**Figure 2.3**; Chapter 6). The latter interactions could also potentially contribute to biodegradation of components of the stranded residual oil in the sediments. Toxicity of dilbit spills to aquatic vegetation represents a current knowledge gap that has only recently begun to be studied (Dew et al. 2015).

2.4.4 Perspective

Based on review of the literature and on interviews conducted by the Expert Panel, it is clear that there is currently insufficient information about the chemical composition and environmental behaviour of emerging petroleum types, including diluted bitumen products, synthetic crude oils and perhaps shale oils. The question was raised by the Panel and others whether unconventional oils, such as diluted bitumens, are sufficiently different from conventional oils to be relegated to distinct classes for regulatory or spill response purposes. Based on current analytical capabilities, heavy oils and bitumen appear to fall along a recognizable chemical continuum spanning condensates to bitumen. However, in the case of diluted bitumen blends it is their physical behaviour in the environment, such as bimodal weathering, that currently appears to distinguish them from conventional petroleum and to confound extrapolation of their properties from the two components: diluent and bitumen. This lack of knowledge stems from insufficient information from laboratory tests, wave tanks or field trials to use in comparing bitumen blends with conventional oil behaviour, particularly in fresh water, in cold conditions and over prolonged time in the environment. For example, the basic question of how much diluent will evaporate from a particular diluted bitumen under environmental conditions has only begun to be addressed in laboratory and field trials. Emulsification of diluted bitumens is beginning to be tested under a variety of conditions, but much of the work to date has focused on seawater emulsification, with little work on fresh water. Similarly, new dynamic models are needed for predicting dissolution and dispersion of diluted bitumen, and there is a paucity of controlled trials showing the effects of particulates on dilbit sinking and sedimentation behaviour, whether accumulated from soils in overland spills or from interaction with suspended solids and microbes in the water column. Some of these parameters are currently being tested in wave tank studies with natural seawater, but the data are not yet available for the Panel to review. The US National Academy of Sciences (NAS) has commissioned a report on dilbit to be released shortly after this Report; the information in the NAS document may begin to address some of these gaps.

Recommendation: Each oil spill is unique due to the convergence of individual oil compositions with specific suites of environmental parameters. Therefore, the environmental behaviour of unconventional oils, blended heavy oils, bitumens and diluted bitumens needs to be investigated under a wide range of relevant environmental and climatic conditions, including long-term, large-volume outdoor trials. Online availability of such data would help inform first responders, remediation personnel and modelers. To conduct such research requires sustained funding and rapid access to funds set aside for investigating 'spills of opportunity'.

2.4.5 Oil Interactions with Ice

Petroleum resource development in the Arctic raises the potential of oil spills in cold, pristine, ice-impacted waters (Lee et al. 2011a). After having been given conditional regulatory approval in May 2015 and spending $7 billion to begin oil exploration in the Chukchi Sea off Alaska (Davenport 2015), Royal Dutch Shell PLC halted exploration in October 2015 citing reasons of insufficient quantities of oil, low crude prices, 'high costs associated with the project, and the challenging and unpredictable federal regulatory environment in offshore Alaska' (Katakey and Zhu 2015). In response the US Department of Interior cancelled the 2016 and 2017 auctions of natural gas and offshore oil leases (Kaufman 2015). Even with this recent turn of events, the likelihood of increased shipping traffic through navigable areas of the Northwest Passage brings greater risk for spillage of fuel oils, at the least. Furthermore, the concept of exporting Alberta bitumen from Churchill, MB, via tanker ships (Welch 2014) highlights the need for oil spill planning, preparedness and response in Arctic waters. Therefore, a brief summary of oil interactions with ice is presented here as a special case affecting oil behaviour, in addition to site-specific information presented in Chapter 3. Complete discussion of oil behaviour in/on ice and description of the different types of ice on water are beyond the scope of this Report; the reader is directed to comprehensive reviews (Lee et al. 2011a; AOSRT 2014; NRC 2014) and a list of ice definitions (Fingas 2015a). In addition, the longstanding, well-recognized Arctic and Marine Oilspill Program (now the AMOP Technical Seminar on Environmental Contamination and Response; http://ec.gc.ca/amop/) organized and sponsored by Environment Canada has published a large body of peer-reviewed physical, chemical and biological research, although much of it is not easily accessible. The reader is also directed to papers arising from the 1980-1983 Baffin Island Oil Spill (BIOS) project, several of which are published in a special issue of the journal *Arctic* (for an overview see Sergy and Blackall 1987). The BIOS project focused on oil spill countermeasures for Arctic near-shore and shoreline oil spills, particularly the use of chemical dispersants.

> Considering that large-scale oil spills, such EVOS in Alaska and DWH in the Gulf of Mexico, held surprises even for professionals in oil spill modeling, clean-up and response, the potential for a 'Coldwater Horizon' scenario in the Arctic Ocean is a daunting prospect.

Certain weathering processes discussed in Sections 2.4.1–2.4.3 (e.g., spreading, evaporation, dispersion, emulsification, biodegradation) are slower or may be eliminated seasonally at high latitudes under ice (e.g., photooxidation, formation of tar balls), whereas others may be enhanced (e.g., sinking). Some of these effects of ice are due to the increased viscosity and density of oil at low temperatures, to the lack of sunlight to form oxidized crusts on tar balls, or to the lack of open water. Generally, oil evaporation on water varies with the degree of ice coverage, wave height and air temperature (Brandvik and Faksness 2009). As ice forms, oil can remain on the ice surface (**Figure 2.10**), pool beneath it (Payne et al. 1990) or migrate upward through brine channels (Petrich et al. 2013) and fissures in the ice to the floe surface. In spring, if oil under the ice is warmed by sunlight, the lower albedo of the oil versus overlying snow and ice may allow the oil to surface through the ice and float on melt pools. Heavy or emulsified oil may be too viscous to migrate upwards and may remain pooled at the water–ice interface until disturbed by ice movement or melting. The smaller oil surface area and low temperatures decrease dissolution and dispersion into the underlying water and reduce evaporation into the atmosphere, thus retaining toxic LMW hydrocarbons. Conversely, evaporation may be the major process affecting oil stranded on the ice surface or absorbed into snow (Lee et al. 2011a). Oil trapped in pack ice will tend to move with the ice as it is driven by wind and currents, but spreading of oil on top of ice and snow is retarded, creating thicker, localized slicks. Spreading of oil under ice is much slower than on the water surface and the extent is largely dictated by the roughness of the under-ice surface; the ice:water topography may slow oil spreading (reviewed by Lee et al. 2011a). Emulsification may be reduced as ice dampens wind and wave action and as the oil is confined in thicker slicks within smaller open water areas (Brandvik and Faksness 2009). However, heavy fuel oils may remain suspended in ice–water slush (AOSRT 2014), rapidly becoming encapsulated in layers of ice during freeze-up (Dickins 2011) and isolating the oil from the underlying water, further reducing weathering. Interaction of oil with suspended minerals and organic particulates to form OPAs (Section 2.4.2.3) may still occur provided sufficient mixing, as observed in a field trial in the St. Lawrence River (Lee et al. 2011b).

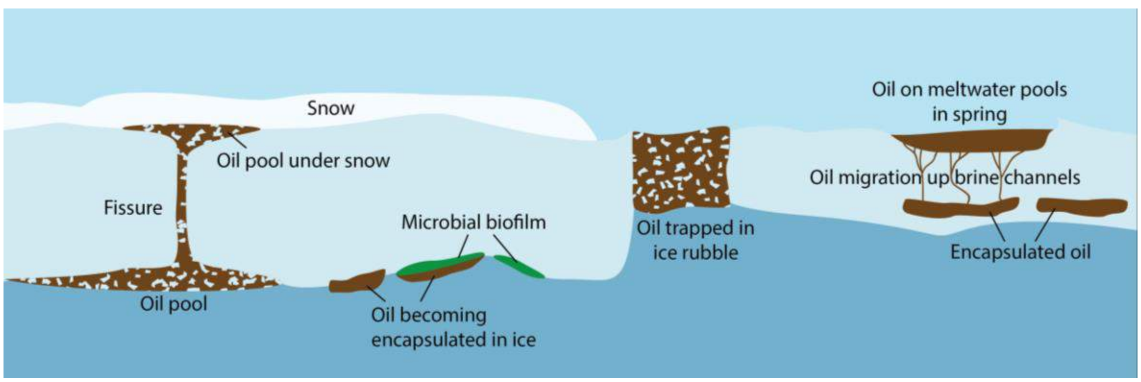


Figure 2.10 Summary of interactions of oil with ice and snow. *Additional detail can be found in AMAP (1998) Figure 10-5 and accompanying text.*

Cold marine waters are higher in dissolved oxygen and often also in dissolved nutrients, which should promote biodegradation, but the rates are likely slower in the Arctic than in more temperate water because enzyme processes and mass transport (discussed in Chapter 3) are slower at low temperatures. Nonetheless, biodegradation of two North Sea oils by microbes from Arctic Ocean water and sea ice has been demonstrated in the laboratory (Deppe et al. 2005), and versatile hydrocarbon-degrading bacteria have been recovered from seawater exposed to an experimental oil spill in the North Sea (Chronopoulou et al. 2015). Interestingly, diverse cold-adapted microbial communities, including species known to degrade hydrocarbons, can be found in biofilms up to several centimetres thick at the bottom of sea ice in contact with the water column along with pooled oil, where they may be able to biodegrade oil components (Greer et al. 2015). Recently, biodegradation of chemically- and physically-dispersed ANS oil was demonstrated at near-freezing temperature (-1 °C) by microbes in seawater from the Chukchi Sea, in the absence of additional nutrients (McFarlin et al. 2014). Arctic lakes, however, may present additional biodegradation constraints due to limited concentrations of nutrients and major ions.

The need for expanded testing of oil–ice interactions and oil behaviour in Arctic conditions merits special attention. Specifically, significantly more research is needed to understand the behaviour and fate of oil spilled into cold, deep seawater, including the rates and extents of physical, chemical and biological processes. Most published observations of oil–ice interactions have been made with first-year ice, but long-term studies of oil distribution and effects on multi-year ice are lacking. This is a time-sensitive knowledge gap, as increased shipping and the possibility of offshore drilling in Arctic waters could impact Canadian Arctic shorelines and seabeds. Likewise, future development of Canadian onshore Arctic resources and pipeline transport will demand investigation of oil effects on cold freshwater rivers and lakes and their porous shorelines.

Recommendation: Additional information is needed to describe and model the fates of petroleum in and under sea ice and freshwater ice. Most of the limited research to date has been conducted on first-year sea ice, but studies with multi-year ice are needed.

The facilities to conduct such oil–sea ice interactions may soon be available at the newly announced Churchill Marine Observatory (Hudson Bay) to be constructed in Canada's only Arctic deepwater port (http://news.gc.ca/web/article-en.do?nid=996359). A purpose-built 'Oil in Sea Ice Mesocosm' (OSIM; (http://news.umanitoba.ca/new-research-facility-to-open-in-churchill/) coupled with an Environmental Observing system will enable investigation, detection and mitigation of oil spills in Arctic sea ice.

2.5 Summary of Identified Research Needs and Recommendations

2.5.1 Research Needs

2.5.1.1 Short Term (High Priority)

Conduct research on the behaviour of unconventional crude oils, particularly diluted bitumen blends, spilled into marine and fresh water

The behaviour of unconventional oils and bitumen blends currently cannot be predicted with confidence. This knowledge gap affects risk assessments, spill response planning and cleanup decisions. Accelerated research is needed in the form of laboratory experiments and field trials to define the behaviour of diluted bitumen and unconventional crude oils (e.g., shale oils) under various seasonal and site conditions relevant to Canada.

Information needed about the effects of various weathering processes on such oils includes:

- Evaporation, particularly the bimodal behaviour of various bitumen blends;
- Emulsion formation, particularly of weathered diluted bitumen in fresh water;
- Susceptibility of dilbit spills to chemical dispersion;
- Sinking behaviour, including interactions with suspended particulates; and
- Susceptibility of fresh and weathered heavy oils and diluted bitumen products to biodegradation.

Combinations of environmental conditions, such as water temperature, salinity, mixing, aeration and sediment load, must be considered under laboratory and mesocosm (e.g., wave tank) test facilities over time scales of hours to days. Some trials are underway, but many relevant combinations of products and conditions exist and should be explored until general rules of oil behaviour can be discerned.

Information generated from such studies must be made readily accessible to first responders, regulators, remediation personnel, modelers and oil spill scientists.

2.5.1.2 Medium Term

Perform baseline physical, chemical and biological environmental surveys, including natural microbial communities and natural environmental variability.

To discern the impact of an oil spill we must have an understanding of the natural level of variability of sites under pre-spill conditions. Each oil spill is unique, not only to the specific oil product, but also to environmental and climate factors. It is thus essential to collect baseline physical, chemical and biological information for Canadian environments that are potential receptors of conventional or unconventional oil spills, particularly for sensitive ecosystems.

Of the factors reducing residual oil concentrations in the environment following a spill, biodegradation is the ultimate process for oil removal from the aquatic environment over the long-term. Therefore, the baseline surveys should include the composition of natural microbial communities in Canadian aquatic environments, particularly for sensitive ecosystems that may be impacted by spilled oil. Knowing the presence (or paucity) of natural hydrocarbon-degrading microbes in an ecosystem would help selection of cleanup strategies and predict the duration and success of cleanup efforts.

Information generated by the surveys must be made readily accessible to first responders, regulators, remediation personnel, modelers and spill scientists to support monitoring needs, the selection of response strategies and predictions of impact and recovery.

Develop a 'Biodegradation Index' that correlates with chemical composition of oils.

Twenty years ago Environment Canada was commissioned by the Alaska Department of Environmental Conservation to determine the susceptibility of nine crude oils and oil products commonly transported in Alaska to biodegradation under cold, freshwater conditions (Blenkinsopp et al. 1996). This type of study should be conducted using representative oils transported in Canada.

The study should include aerobic biodegradation potential under fresh- and saltwater conditions at cold and moderate temperatures, and anaerobic biodegradation in the presence of sediments. If conducted under optimum laboratory conditions, the results would delineate the maximum biodegradation to expect under actual environmental conditions. Furthermore, data generated from the screen should be used to construct a 'Biodegradation Index' correlating oil composition with susceptibility to biodegradation as a reference tool for oil spill remediation.

Augment online catalogues of crude oil composition and properties

Existing online catalogues, such as Environment Canada's Oil Properties Database and *CrudeMonitor.ca*, are incomplete in scope and in compositional information. Expanding and augmenting such catalogues would be useful for oil spill response planning and preparedness, particularly for diluted bitumen blends, and for the safety of first responders and the public.

2.5.1.3 Long Term

Support for fundamental petroleum chemistry research.

Fundamental understanding of oil composition and properties is lacking in several areas. These knowledge gaps can be addressed primarily in laboratory studies. Needs include:

- Development of validated and standardized methods to enable detailed chemical characterization of poorly-characterized oil components, including alkyl PAH, asphaltenes, resins, naphthenic acids and unresolved complex mixtures. Although this information may not have direct practical importance for oil transportation *per se*, it would provide insight into the fate and behaviour of spilled oil, including emulsification, photooxidation, biodegradation, toxicity, etc. This is a particularly critical gap for heavy oils and bitumen blends that have large proportions of these chemical classes, where such information should be used to refine oil spill models;
- Development of validated and standardized analytical methods and a framework to enable comparison of conventional and unconventional crude oils. This would help

determine whether all transported oils simply reflect a continuum of chemical composition, or whether diluted bitumens represent a novel oil class. A forthcoming report by the US NAS may address part of the latter question, but the need for robust analytical methods remains; and

- Development of refined and standardized methods for measuring physical weathering processes, including evaporation, dissolution and oil:particle interactions. Such information should be used to improve predictive spill models and inform mass balance budgets post-spill.

Apply research results to address the longstanding remediation question 'How clean is clean?'

Data obtained from laboratory studies, large-scale open-air experiments, long-term field research and baseline data surveys should be compiled and interpreted with the intention of determining acceptable endpoints of spill remediation based on chemical and biological indices. Long-term monitoring of follow-on effects after experimental spills and spills of opportunity would inform regulatory guidelines for cleanup endpoints.

2.5.2 Operational Preparedness Needs

Arctic preparedness: There is urgent need for expanded documentation of oil–ice interactions and oil behaviour in Arctic conditions.

This is a time-sensitive knowledge gap, given predictions of commercial tanker traffic through the Northwest Passage and the potential for Arctic Ocean oil exploration and production. The facilities to conduct such oil-sea ice interactions may soon be available at the newly announced Churchill Marine Observatory in Hudson Bay. It is also important to note that most published observations of oil–ice interactions have been made with first-year ice, but long-term studies of oil distribution and effects on multi-year ice are lacking.

CHAPTER 3: EFFECT OF ENVIRONMENT ON THE FATE AND BEHAVIOUR OF OIL

Abstract

Following Chapter 2, which describes oil properties in terms of its chemistry and composition, this chapter is divided into three main topical areas, namely: 1) key environmental factors affecting spilled oil fate and behaviour, 2) oil impacts on different aquatic environments, and 3) importance of oil type in relation to the environment. Under each main section, up to nine subsections discuss in detail how the biological, chemical and physical characteristics of each environment bring about change to the oil and the ramifications these changes have on the ecology of the biosphere. Section 3.1 outlines how microorganisms degrade the different hydrocarbon classes in oil and how temperature, dissolved oxygen, nutrient supply, salinity and pH affect and change the behaviour of the contaminating oil. Section 3.2 describes how oil impacts a wide diversity of environmental systems, such as freshwater ponds, lakes and rivers; estuaries, including bordering wetlands; seawater, both surface and deep sea; and Arctic environs, including permafrost, ice and snow. Section 3.3 concerns the three main types of oil (light, medium and heavy) and how they differ in their behaviour in relation to the various environments.

Research recommendations based on the discussion of knowledge gaps were consolidated and prioritized at the end of the chapter. In summary, research is needed to further our understanding of how the Arctic environment affects oil spilled into that harsh but sensitive ecosystem and how the spilled oil affects the biology and ecology of that environment. Oil interactions with permafrost and spring melt are important unknowns in terms of access to sites for spill response, rapid spreading of oil during freshet, slow rates of weathering, and how hydrocarbons interact with ice and suspended particulate matter. Research is also needed to further our understanding of the effects of spilled oil on permafrost ecosystems and how best to develop appropriate response strategies that mitigate the damage without causing further harm. In addition, little has been done to advance our knowledge of how to deal with subsurface blowouts in ice-covered marine environments. Given that Arctic drilling will likely ramp up in the future, improved methods will be needed to detect and monitor the behaviour of spills on, in and under ice and within the water column in the event of such a subsurface deep sea blowout. While the National Energy Board has identified the need for additional precautionary measures (e.g., same season relief well capacity), further research is needed to aid in development of oil detection and response strategies in these important environments. Finally, although microorganisms represent the ultimate cleanup of oil-impacted environments, microbial activity is slower in temperatures near freezing. Yet such activity was found to be relatively fast in the 5 °C deep sea of the Gulf of Mexico during the Deepwater Horizon spill (Hazen et al. 2010). Confirmation of this finding would greatly advance our knowledge of the role microorganisms might play in Arctic spill cleanup in the future.

Introduction

Whereas Chapter 2 described the major physical and chemical properties that influence oil behaviour, Chapter 3 discusses what happens to oil spilled in various aquatic environments. Types of waterbodies that can be affected by oil spills include rivers, streams, mud flats, wetlands (including bogs, fens and marshes), salt marshes, offshore (surface, water column and deep ocean), reservoirs, permafrost, muskeg, ponds, lakes and groundwater.

With or without human intervention, spilled oil is affected by microbes naturally present in the environment that are in turn influenced by prevailing physical and chemical conditions at the spill site. Therefore, this chapter provides detailed discussion of key environmental factors that affect petroleum biodegradation, including indigenous microbial species, temperature, dissolved oxygen concentration, presence of nutrients, salinity (marine, estuarine and freshwater environments), pH and the type of environment impacted, such as shoreline type (e.g., lacustrine, riverine, marine and estuarine) and location (e.g., intertidal, supratidal, subtidal). Other factors include non-biological weathering processes, oil type, amount spilled and components in oil causing short-term and long-term impacts. As discussed in Chapter 2, each type of oil has distinct physical and chemical properties that will influence the way it will spread and break down, the hazard it may pose to aquatic and human life, and the likelihood that it will pose a threat to natural and man-made resources. All these factors are discussed below in the context of aquatic environments.

3.1 Key Environmental Factors Affecting Spilled Oil Fate and Behaviour

Petroleum and its precursor materials have been present in the Earth's biosphere for tens of millions of years, and certain microbes have adapted to utilizing such high-energy compounds for growth. Even in the present time, some algae synthesize alkanes (Lea-Smith et al. 2015), calanoid copepods synthesize pristane from ingested chlorophyll (Short and Harris 1997), many plants synthesize waxes (Baker 1982), and petroleum naturally seeps from the earth's crust (such as in the Gulf of Mexico seabed, the Santa Barbara, CA, seafloor, at the sea bottom off the coasts of Baffin Island, NU, and the Queen Charlotte Islands, BC, and in the Athabasca River, AB, as it cuts through oil sands deposits). Thus, oil-degrading microbes are ubiquitous, and diverse microbes having the ability to degrade hydrocarbons will always occur in aquatic ecosystems, although in pristine sites they comprise a small proportion of the total microbial community. Oil incursion provides a competitive advantage for oil-degrading microbes compared to those that cannot utilize hydrocarbons. Oil degraders will thrive while the hydrocarbons are present and their proportions in a contaminated site will be much greater than in a pristine site, while overall microbial biodiversity decreases during active degradation. As the degradable components are depleted, the oil degraders will decrease in numbers and diversity will again increase.

> Hydrocarbons have been ubiquitous on this planet for millennia. Over this time, diverse microbes have adapted to consuming hydrocarbons under myriad different environmental conditions, typically cooperating as microbial communities to degrade complex oils.

Natural attenuation is the result of petroleum biodegradation by oil-degrading microbes naturally present in the biosphere and is unassisted by humans. These natural rates of oil degradation may be enhanced by bioremediation, which is a human intervention practice that accelerates the rate of oil decomposition by microbes either through biostimulation (a process used to accelerate biodegradation by supplying the indigenous oil-degrading communities with nutrients or other growth needs, as discussed below, or bioaugmentation (addition of exogenous oil-degrading bacteria to augment the natural populations to degrade the contaminating hydrocarbons). Bioremediation is normally used as a polishing step after oil that can be removed by other means has first been removed, so that the microbes have only a small mass of oil to degrade. These processes are discussed in greater detail in Chapter 6. Regardless of intervention, microbial hydrocarbon degradation is still subject to physical and chemical conditions in the impacted environment.

3.1.1 Presence of microbial species in oil-impacted water, sediments, shorelines and wetlands

Much progress has been made in recent years in our knowledge of hydrocarbon-degrading microbial communities, especially in marine ecosystems. This research has identified a group of aerobic microorganisms called obligate hydrocarbonoclastic (hydrocarbon-degrading) bacteria (OHCB), which have been shown to play a key role in eliminating petroleum hydrocarbons contaminating marine waters (natural seeps as well as accidental spills). According to Yakimov et al. (2007), when hydrocarbon contamination occurs in marine ecosystems, successive blooms occur in indigenous bacterial genera belonging to the OHCB group (*Alcanivorax*, *Cycloclasticus*, *Marinobacter*, *Thallassolituus* and *Oleispira*, among others), which were present at undetectable levels prior to the spill. The most notable genera are *Alcanivorax,* which contains several key enzymes that confer the ability to metabolize alkanes for carbon and energy acquisition (Schneiker et al. 2006), and *Cycloclasticus,* which degrades polycyclic aromatic hydrocarbons (PAHs) (Table 2.1). Microbes, such as *Alcanivorax borkumensis,* are exquisitely adapted to biofilm formation (Figure 2.3), oil solubilization, degradation of *iso*-alkanes (Table 2.1) that are considered recalcitrant, and tolerance of oil-induced stress (Schneiker et al. 2006; Sabirova et al. 2008). In addition to OHCB, many generalist (non-obligate) hydrocarbon-degraders, such as *Pseudoalteromonas*, are also prevalent in marine water (e.g., in the North Sea; Chronopoulou et al. 2015). OHCB have not yet been reported in marine sediments, shorelines and wetlands, although these environments do harbour diverse generalist oil-degrading microbes. The difference in sediments and soils may be due to anaerobic conditions versus aerated/aerobic conditions in surface water (Section 3.1.3), resulting in the presence of different predominant microbes.

Some bacterial species are specialists in degrading saturated hydrocarbons and others in aromatics (Foght et al. 1990). Thus, a suite of different microbes (a 'community') is required to achieve maximum oil biodegradation. Some microbes possess complete biodegradation pathways and therefore can mineralize hydrocarbons, oxidizing them completely to carbon dioxide (CO_2) and water without requiring a partner microbe. Mineralization is the preferred outcome for oil spill cleanup. However, some microbial species have incomplete pathways and are only able to partially oxidize ('transform') the hydrocarbon, especially if it is complex (e.g., an alkyl PAH). In the latter case, the transformation product from the first attack may subsequently be mineralized by other species in a combined or concerted effort by a microbial community, or it may resist further degradation and accumulate. These partially oxidized products may be more or less toxic than the original substrate, depending on the chemical properties of the transformed product. Furthermore, some bacteria have the ability to exchange genetic material (DNA) so that species previously unable to degrade hydrocarbons may acquire that ability by obtaining some or all of the genes encoding the requisite enzymes. Thus, the products of microbial oil biodegradation can vary depending on the composition of the oil, the microbial community and gene transfer among species.

The enrichment of the aforementioned bacterial genera is affected by temperature, salinity, oxidation-reduction potential and other physical/chemical factors. *The rapid development of these classes of microorganisms can be accelerated by the use of biostimulation procedures, such as the addition of nutrients (for example, nitrogen and phosphorus) that frequently exist only in limiting quantities in nature (discussed in greater detail in Chapter 6).*

Many of the constituents of petroleum oils have been known to be biodegradable for decades. Biodegradation of oil is one of the most important processes involved in weathering and the eventual removal of petroleum from the environment, particularly for the non-volatile components of petroleum. Numerous scientific review articles have covered various aspects of this process and the environmental factors that influence the rate of biodegradation (Zobell 1946, 1973; Atlas 1981, 1984; NRC 1985; Leahy and Colwell 1990; Johnsen et al. 2005; Head et al. 2006; Yakimov et al. 2007; Singh et al. 2012; Gutierrez et al. 2013). Two comprehensive EPA reports on oil spill bioremediation covering all aspects of microbial interactions with spilled oil and providing guidelines on how to implement bioremediation in the field were published in 2001 and 2004 and are still relevant today (Zhu et al. 2001, 2004).

Microorganisms capable of degrading petroleum hydrocarbons and related compounds are ubiquitous in marine, freshwater and soil habitats (Head et al. 2006; Yakimov et al. 2007; Atlas and Hazen 2011), and degradation mediated by indigenous microbial communities is the ultimate fate of most of the hydrocarbons that contaminate the environment (Leahy and Colwell 1990; Foght 2008; Prince 2010; Atlas and Hazen 2011; Kostka et al. 2014). Hundreds of species of bacteria, yeasts and fungi have been shown to degrade hydrocarbons ranging from methane to compounds of over 40 carbon atoms and in temperatures spanning psychrophilic (-20 °C to +10 °C) to thermophilic (41°C – 122 °C) (Zobell 1973; Floodgate 1984; Jordan and Payne 1980; Cooney 1984; Margesin et al. 2013).

Despite their ubiquity in nature, hydrocarbon degrading microorganisms are distributed in relation to the historical exposure of the environment to hydrocarbons. Those environments with recent or chronic oil contamination, in particular the Gulf of Mexico with its myriad natural petroleum seeps, will have a higher percentage of hydrocarbon degraders than unpolluted areas. Notably, no single strain of bacteria has the metabolic capability to degrade all the components found in crude oil (Karrick 1977; Leahy and Colwell 1990; Vinas et al. 2002). In nature, biodegradation of a crude oil typically involves a succession of species within the consortia of microbes present. Microorganisms classified as non-hydrocarbon utilizers may also play an important role in the eventual removal of petroleum from the environment. Degradation of petroleum involves progressive or sequential reactions, in which certain organisms may carry out the initial attack on the petroleum constituent, producing intermediate compounds that are subsequently utilized by a different group of organisms, in the process that results in further degradation.

Petroleum is a complex mixture of many thousands of compounds consisting mostly of carbon and hydrogen. As mentioned in Chapter 2, these compounds have been divided into four major groups, abbreviated as SARA (saturates, aromatics, resins and asphaltenes). In general, the saturates fraction is the most biodegradable with the exception of the fused complex alicyclic ring compounds, such as the hopanes and steranes. The aromatic compounds, especially the PAHs, are of intermediate biodegradability (which is inversely proportional to the number of fused rings), whereas the polar fractions (i.e., resins and asphaltenes) have been long thought resistant to biological degradation (Pineda-Flores et al. 2004; Naveenkumar et al. 2010).

With respect to saturates, the predominant mechanism of *n*-alkane degradation involves terminal oxidation to the corresponding alcohol, aldehydes or fatty acid functional group. Branched alkanes are less readily degraded in comparison to *n*-alkanes. Methyl branching increases the resistance to microbial attack because fewer alkane degraders can overcome the blockage of beta-oxidation (NRC 1985). Highly branched alkanes, such as pristane and phytane, which were earlier thought to be resistant to biodegradation, have also been shown to be readily biodegradable, although at lower rates than normal alkanes. Cycloalkanes, however, are more resistant to biodegradation. Complex alicyclic compounds, such as hopanes and steranes (see Table 2.1), which belong to the class of pentacyclic triterpanes, are among the most persistent compounds of petroleum spills in the environment (Wenger et al. 2002; Peters et al. 2005). Because of their relative resistance to microbial attack, these compounds are used to normalize the concentrations of the more biodegradable petroleum compounds as a chemical forensic tool.

By normalizing biodegradable petroleum hydrocarbons to the relatively non-biodegradable hopane, the variability of loss among alkane and aromatic compounds can be significantly mitigated, thereby facilitating the calculation of rates of biodegradation of petroleum hydrocarbons in field studies.

Although the aromatics are generally more resistant to biodegradation than the alkanes, some low molecular weight (LMW) aromatics, such as naphthalene, may actually be oxidized before many saturates (Foght 2008). Monoaromatic hydrocarbons, such as benzene or toluene, are toxic to some microorganisms due to their solvent action on cell membranes, but in low concentrations they are easily biodegradable under aerobic conditions. PAHs with 2-4 rings are less acutely toxic and biodegradable at rates that decrease with the level of complexity. PAHs with five or more rings can only be degraded through cometabolism, in which microorganisms fortuitously transform non-growth substrates while metabolizing simpler hydrocarbons or other primary substrates in the oil. Alkylated aromatics are degraded less rapidly than their parent compounds; the more highly alkylated groups are degraded less rapidly than less alkylated ones. The metabolic pathways for the biodegradation of aromatic compounds have been the subject of extensive study (Atlas 1981; Cerniglia 1992; Prince 1993). The bacterial degradation of aromatics normally involves the formation of a diol (two adjacent hydroxyl groups attached to the aromatic ring), followed by ring cleavage and formation of a di-carboxylic acid. Fungi and other eukaryotes normally oxidize aromatics using monooxygenases, forming a trans-diol.

Compared to saturates and aromatics, little is known about biodegradation of resins and asphaltenes due to their complex structures, making them difficult to analyze. Resins and asphaltenes have previously been considered to be refractory to biodegradation. However, recent evidence suggests that asphaltene degradation may occur through cometabolism (Leahy and Colwell 1990) or by other means (Liao et al. 2009).

Biodegradation typically affects the physical properties of oil by causing a decrease in the LMW alkane and aromatic fractions and enrichment in the polar resins and asphaltene fractions (Liao et al. 2009). The increase in the fraction of asphaltenes in heavy oil is attributed to the selective loss of alkanes and some aromatic hydrocarbons. The asphaltene fraction is defined typically to contain those species that are insoluble in low carbon number *n*-alkanes, such as *n*-hexane or *n*-heptane, while resins are soluble in such solvents (Tissot and Welte 1984). In their study of biodegradation of asphaltenes, Liao et al. (2009) concluded that the products of biodegradation, such as carboxylic acids, phenols and alcohols, may not only contribute to the resin fraction of crude oils, but are also linked with functionalities of resins and asphaltenes. The amount of asphaltenes increases because some resin molecules are enlarged and their polarity increased such that they can be precipitated by hexane as newly generated asphaltenes.

One study (Uraizee et al. 1998) involved systematically altering the concentration of non-biodegradable material in crude oil and analyzing its impact on transport of the biodegradable components of crude oil to the microorganisms. They did this by first fractionating crude oil into its primary SARA classes, then reconstituting the oil with increasing concentrations of the asphaltene fraction, and finally subjecting the reconstituted oil to biodegradation in the laboratory as measured by respirometry. The authors developed a mathematical model to explain and account for the dependence of biodegradation of crude oil through a putative bioavailability parameter. Experimental results indicated that as the asphaltene concentration in oil increased, the maximum oxygen uptake in respirometers decreased. The mathematically fitted bioavailability parameter of degradable components of oil also decreased as the asphaltene concentration increased. This was offered as one explanation for the lower biodegradation rates of heavy oils vis-à-vis lighter oils.

Mass transfer is often overlooked as an important aspect of hydrocarbon biodegradation. If one assumes that the aqueous solubility of PAHs limits their microbial degradation, mass transfer becomes important in understanding and predicting the fate and rate of biodegradation in aqueous solution (Volkering et al. 1992, 1998; Harms and Bosma 1997; Bosma et al. 1997; Johnsen et al. 2005). Optimization of mass transfer can be achieved in several ways:

- The production of biosurfactants by the degrading microbial communities, which facilitate transmembrane diffusion of hydrocarbons into the cell by increasing the diffusion coefficient governing the flux, and
- Exogenous addition of surfactants, such as dispersants, which tend to increase the interfacial area, also resulting in a higher flux of substrate (PAH).

The rate at which microorganisms degrade a substrate at low concentration depends on their specific affinity toward the substrate (Harms and Bosma 1997), defined as the ratio of the maximal substrate uptake rate to the half saturation constant (Button 1985). High specific affinities lead to efficient low-concentration PAH removal from the environment at the cell surface, steeper concentration gradients and higher substrate transfer rates.

In addition to affecting diffusion as discussed above, surfactants also influence dissolution and subsequent uptake of PAHs into the cell by attaching to the oil-water interface where micelles facilitate PAH release from the interface (Volkering et al. 1998). Alkane degraders are known to produce biosurfactants to increase the bioavailability of the poorly soluble hydrocarbons (Beal and Betts 2000; Noordman and Janssen 2002). Such biosurfactants, especially those produced by *Pheudomonal*

> Hydrocarbon biodegradation can occur over a wide range of temperatures, but rates generally increase with increasing temperature to an optimum for each environment.

aeruginosa, are commonly comprised of rhamnolipids, which are characterized by a sugar head group and a fatty acid tail. However, biosurfactant production is not as common among the PAH degraders (Itoh and Suzuki 1972; Oberbremer and Muller-Hurtig 1989; Johnsen et al. 2005), which means that biosurfactants may not be as important for PAH metabolism as for alkanes. In fact, because surfactants are known to interact directly with cell membranes, surfactants such as those in dispersants may negatively affect uptake of PAHs into the cell and subsequent metabolism by disrupting the integrity of the membrane, and it is possible this may even be exacerbated at deep sea hydrostatic pressures (Campo et al. 2013).

Studies involving hydrocarbon-degrading communities, mostly conducted in laboratory cultures, have been very helpful in elucidating the role of oil biodegradation in nature. However, laboratory studies can also be misleading to our complete understanding of the behaviour and fate of oil when released into the environment. A fuller understanding of the dynamics of *in situ* biodegradation affecting our ability to predict the ultimate fate of hydrocarbons remains a challenge (Prosser et al. 2007).

3.1.2 Temperature

Temperature exerts major effects on the physical properties of oil, such as viscosity, surface tension and density, that may influence the oil's physical transport and environmental persistence, including biodegradability, within the environment (Chapter 2). Temperature also influences the activity and composition of the microbial community that responds to oil.

3.1.2.1 Physical-Chemical Properties of the Oil Influenced by Temperature

At low temperatures, the viscosity of the oil increases (Figure 2.2) and the volatility of toxic LMW hydrocarbons declines, delaying the onset of biodegradation (Atlas 1981). This property may be somewhat advantageous when a spill occurs in cold regions because it will allow response teams more time to deploy treating equipment. Some hydrocarbons are more soluble at lower temperatures (e.g., short-chain alkanes) and some LMW aromatics are more soluble at higher temperatures (Polak and Lu 1973), altering susceptibility to biodegradation. Specific gravity of oil is dynamic in that it will increase over time as the lighter components within the oil evaporate, dissolve or biodegrade, and it also responds to temperature. Heavier oils, such as refined oils, dilbit and Orimulsion™ (bitumen mixed with water), may sink and form tar balls at low temperatures or may interact with rocks or sediments on the bottom of the water body.

3.1.2.2 Effect of Temperature on Biodegradation

Figure 3.1 shows that highest degradation rates generally occur in the range of 30–40 °C in soil environments, 20–30 °C in some freshwater environments, and 15–20 °C in marine environments (Jordan and Payne 1980; Bartha and Bossert 1984; Cooney 1984). These general increases with temperature reflect the reaction rates of enzymes required for oil biodegradation, which generally double with a temperature increase of 10 °C, to an optimum for each enzyme type. The variation among media reflects the preferred growth temperatures of the different microbial communities that have adapted to their environment. In addition to direct biochemical effects, increased temperatures can reduce a liquid's surface tension, making oil more likely to spread on warmer water than very cold water, thus affecting the surface area of oil available for interaction with microbes.

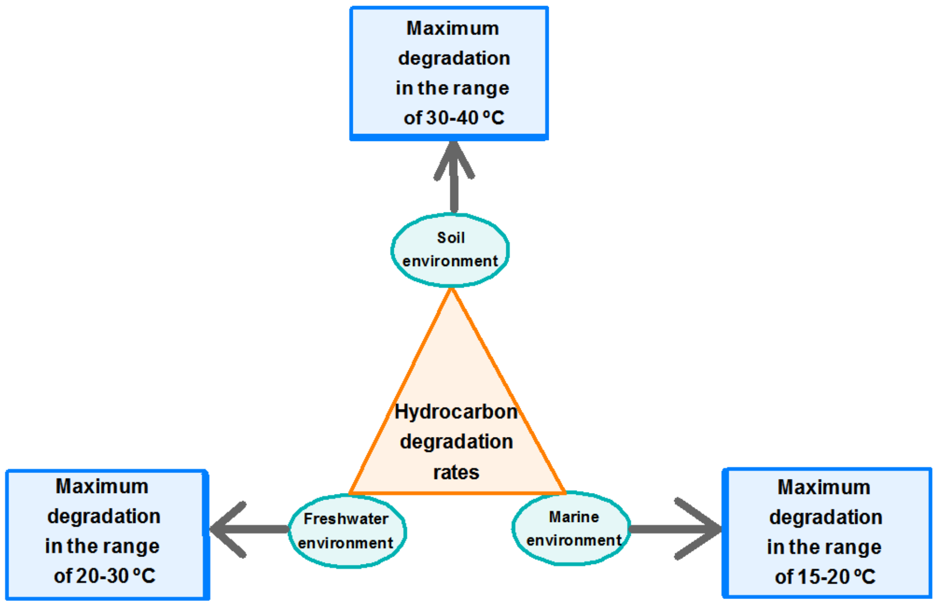


Figure 3.1 Optimum temperatures for hydrocarbon degradation rates in soil, fresh water and marine environments. *Adapted from Das and Chandran (2011).*

Although biodegradation typically occurs faster and more completely at higher temperatures, in environments where a cold-adapted microbial community has been established (e.g., one that prefers temperatures < 15 °C, such as in perennially cold environments), degradation can also occur at significant rates. Hydrocarbon biodegradation has been observed at temperatures as low as 0-2 °C in seawater and -1.1 °C in soil. Colwell et al. (1978) reported greater degradation of Metula crude oil at 3 °C than at 22 °C with a mixed culture in beach sand samples. Westlake et al. (1974) found that bacteria capable of degradation at 4 °C would metabolize oil at 30 °C, but those populations that developed at 30 °C had a limited activity at 4 °C. Lee et al. (2011) collected samples from the St. Lawrence River during a winter field trial study following the release of Heidrum crude oil (25 °API; Chapter 2) in ice-infested waters, and used the samples to monitor time-series changes in oil concentrations and composition in laboratory microcosms. Detailed chemical analysis (GC-MS with hopane as the normalizing biomarker; Appendix A) from these studies showed that more than 60% of the total petroleum hydrocarbons, 75–88% of total alkanes, and 55–65% of total PAHs were degraded after 56 days of incubation at 0.5 °C. McFarlin et al. (2014) recently reported on the biodegradation of Alaska North Slope crude oil in Arctic seawater collected from the Chukchi Sea, AK, incubated at −1 °C. Indigenous microorganisms degraded both fresh and weathered oils, in both the presence and absence of the chemical oil dispersant Corexit 9500, with oil losses ranging from 46−61% and up to 11% mineralization over 60 days.

Temperature affects microbial communities and oil properties in complex ways, so the rate and extent of biodegradation does not have a simple relationship with temperature.

A review by McGenity et al. (2012) presented strong evidence for oil biodegradation in cold marine environments. Instead of *Alcanivorax*, which is a halophilic[1] oil degrader found mostly near the ocean's surface and able to grow at temperatures from 4 to 35 °C, the alkane-degrading obligate psychrophile[2] *Oleispira* has been commonly associated with biodegradation of oil spills in cold marine environments and in fact can constitute as much as 90% of the microbial community near the oil spill. This genus has a

[1]Halophiles are species that require a substantial concentration of dissolved salt to survive.
[2]Psychrophiles are species that require constant low temperatures (usually < 10 °C) and die at higher temperatures.

wide global distribution and other genera are being isolated and characterized, such as *Oleibacter* sp. (Teramoto et al., 2011) and microorganisms belonging to the order *Oceanospirillales* (Golyshin et al. 2002; Hazen et al. 2010). Likewise, the bacterial genus *Thalassolituus* is a marine OHCB that has been observed as the dominant member of an oil-degrading microbial community in the Arctic seawater surface (Yakimov et al. 2007). Understanding presence, abundance, activity and needs of cold-adapted hydrocarbon degraders is becoming important with the announcements of offshore oil and gas exploration at high latitudes in regions such as the Chukchi and Beaufort Seas and with anticipated increases in shipping in the Northwest Passage (http://www.alaskapublic.org/2015/07/31/shells-exploratory-drilling-commences-in-the-chukchi-sea/). However, more recent research casts doubt on future utility of transportation in the Northwest Passage as findings by Haas and Howell (2015) show that even in today's warming climate, ice conditions must still be considered severe (i.e., thick ice more than 100 m wide and thicker than 4 m has been observed to occur frequently).

Recommendation: Confirmation of the finding that microbial activity was relatively fast in the 5 °C deep sea of the Gulf of Mexico during the Deepwater Horizon spill (Hazen et al. 2010) would greatly advance our knowledge of the role microorganisms might play in Arctic spill cleanup in the future.

3.1.3 Dissolved Oxygen

Various microbes are able to grow with or without oxygen for their metabolism, and some can alternate depending on the available oxygen in their environment. Oxygen has finite solubility in water (~7.5 mg/L at 30 °C, increasing to ~15 mg/L at 0 °C for water in equilibrium with air at sea level) and, if oxygen is depleted by microbial activity, it must be replenished to maintain aerobic metabolism. Replenishment is readily accomplished in most shallow water columns by wind and wave action, so conditions of oxygen limitation normally do not exist in the upper levels of the water column in marine and freshwater environments and in the surface layer of most beach environments. Therefore, dissolved oxygen is unlikely to limit biodegradation rates in these environments except under certain conditions, such as strong stratification, although the physical state of the oil and the amount of available substrates also affect oxygen availability.

Aerobic conditions are generally considered necessary for extensive degradation of oil hydrocarbons in the environment since major degradative pathways for both saturates and aromatics involve oxygenases (Atlas 1981; NRC 1985; Cerniglia 1992), and biodegradation of petroleum in the field has been shown to occur substantially faster under aerobic than anaerobic conditions. Although aerobic degradation of crude oil has been well-known for decades (e.g., Atlas 1981), mechanisms are still being elucidated for both alkane and PAH metabolism (Rojo 2009; Kanaly and Harayama 2010; Pérez-Pantoja et al. 2010; Fuchs et al. 2011).

> The major pathways for removal of hydrocarbons from the environment involve aerobic conditions.

There is little doubt about the importance of oxygen in determining the rates and pathways of hydrocarbon biotransformation in ecosystems that are dominated by anaerobic and/or anoxic conditions including: subsurface sediments (marine, riverine and lacustrine); most fine-grained marine shorelines; coastal and inland wetlands beneath the top several millimeters of soil; salt marshes; mud flats; groundwater; muskeg; bogs and fens; anoxic zones of water columns; and any others where oxygen is limiting. Bottom sediments are typically stratified, with dissolved oxygen and redox potential[3] decreasing sharply with depth, often to0 mL L^{-1} and -300 mV or less, respectively—

[3]*In environmental chemistry, redox potential is an electrochemical measurement or calculation to determine whether reducing or oxidizing conditions prevail. Aerobic sites usually have positive redox values and anaerobic sites have progressively more negative redox values.*

i.e., stringently anaerobic conditions. Anoxia is primarily a result of the high affinity of aerobic micro-organisms for oxygen, leading to its depletion in sediments where oxygen cannot diffuse quickly enough from bottom water into pore water to replenish concentrations and maintain aerobic conditions.

Under anaerobic conditions the ultimate degradation of organic matter is generally much slower (Head and Swannell 1999). Anaerobic degradation mechanisms involve different microbial species, degradation enzymes and pathways, metabolites and end products than aerobic biodegradation and apparently also impose a narrower substrate range (Schneiker et al. 2006; Sabirova et al. 2006; Foght 2008). Furthermore, whereas a single species can usually accomplish complete aerobic hydrocarbon mineralization using well-studied pathways, anaerobic hydrocarbon biodegradation has only recently been recognized, many of the key microbes and their pathways are still cryptic, some metabolites are unknown, and need for a community of microbes appears to be more prevalent. Anaerobic oil degradation was deemed in early studies to occur only at negligible rates, leading to the conclusion that the environmental importance of anaerobic hydrocarbon degradation could be discounted in terms of remediation response. More recently, the biodegradation of some aromatic hydrocarbons, such as BTEX compounds and a few PAHs (Foght 2008), *n*-alkanes (Mbadinga et al. 2011) and *iso*-alkanes (Abu Laban et al. 2014), has been clearly demonstrated to occur under a variety of anaerobic conditions. Studies have also demonstrated that in some marine sediments, PAHs and alkanes can be degraded under sulfate-reducing conditions at similar rates to those under aerobic conditions (Coates et al. 1997; Caldwell et al. 1998). *Regardless of the large gaps in understanding anaerobic hydrocarbon metabolism, the occurrence of anaerobic environments in marine ecosystems is sufficiently great that the anaerobic fate of crude oil must be considered and the overall importance of anaerobic biodegradation of crude oil in the environment requires further study.*

> Anaerobic hydrocarbon metabolism is emerging as an important mechanism for hydrocarbon biodegradation.

It is important to note that all biodegradation of crude oil, whether anaerobic or aerobic, freshwater or marine, aquatic or terrestrial, is selective in that some components are only partially degraded because of their size or complexity or not modified at all (Wang et al. 1998). Thus, *there will always be a residue of original petroleum components, like asphaltenes and resins, partly degraded intermediates and other end products of mineralization that may be generated (CO_2, CH_4, H_2S, etc.), the mass of which will depend on the interplay between environmental conditions, petroleum chemistry and microbial community composition.*

<u>Recommendation</u>: Further research is required on the mechanisms, pathways and rates of anaerobic biodegradation of hydrocarbons, particularly with respect to circumstances where oil has penetrated into sediment (riverine, lacustrine, estuarine or marine) where it could persist for decades.

3.1.4 Nutrient supply and stoichiometric ratios of C:N:P

The incursion of crude oil into an environment represents a large influx of carbon that is normally nutrient-poor. In particular, nitrogen (N) and phosphorus (P) are required for balanced growth of microbes that biodegrade the oil and other microbial community members that comprise the base of the food chain. In the 1930s, Alfred Redfield made thousands of measurements of the stoichiometric ratios of C:N:P in oceanic plankton (Redfield 1934). These ratios were strikingly similar to the dissolved concentrations of N and P found in the deep sea. This C:N:P relationship became known as the Redfield Ratio, which is 106:16:1, and has stood the test of time. Thus, in marine environments, nutrient limitation is generally correlated to the low background levels of N and P in seawater. The C:N:P stoichiometry of phytoplankton ultimately controls the nutrient ratios of the deep ocean (Arrigo 2005). These interactions produce a self-regulating, biogeochemical system that maintains quasi-stable oceanic nutrient inventories over both short and long timescales (Arrigo 2005). These stoichiometric ratios are important in understanding the role microbes play in the event of a catastrophic oil spill when carbon is in great excess to N and P. *Once the oil is beached, the only way to accelerate biodegradation is to add limiting nutrients in appropriate amounts to produce approximately the Redfield Ratio*.

Freshwater systems (lakes and wetlands) range from oligotrophic[4] to eutrophic[5]. Rivers may be nutrient-poor at the source but generally become nutrient-rich downstream after receiving industrial and domestic effluents and agricultural runoff (Cooney 1984). Freshwater wetlands are typically considered to be nutrient limited, due to heavy demand for nutrients by plants. They are also viewed as being nutrient traps, as a substantial amount of nutrients may be bound in biomass (Mitsch and Gosselink 1993). Both freshwater lakes and wetlands may also exhibit seasonal variations in nutrient levels, which will affect the performance of oil biodegradation. *Ward and Brock (1976) found that the rate of hydrocarbon biodegradation in an oil-contaminated lake was greatest during early spring when the nutrient content was also high. As N and P levels declined in the summer (probably due to uptake by algal growth), oil biodegradation also decreased.*

Thus, although oil is rich in energy, carbon and hydrogen needed for microbial growth, it is poor in essential nutrients, such as N and P. To balance the 'diet' of oil-degrading microbes, these nutrients can be added in water-soluble form (such as conventional fertilizers) often, but not always, in ratios of C:N:P approximating the 106:16:1 Redfield Ratio, such as the commonly used ratio of 100:10:1. Adding nutrients is particularly important for beached oil, which no longer has access to dissolved N and P in the water column: the only way to restore the C:N:P balance and accelerate biodegradation is to add the elements that are limiting, i.e., N and P. This process, called 'biostimulation', is discussed in greater detail in Chapter 6.

The largest use of biostimulation to aid in cleaning up a major oil spill was in Prince William Sound, AK, during the 1989 *Exxon Valdez* incident (Atlas and Hazen 2011). Nutrients in various formulations were used to accelerate the biodegradation of oil that contaminated the sand and gravel beaches. Field evidence showed that biodegradation was indeed accelerated but, after a few years, both the treated and untreated sites were equivalent in terms of residual oil remaining (Pritchard et al. 1992). *It is generally true for almost all countermeasure technologies that, eventually, nature catches up with accelerated recovery and intervention does not necessarily result in greater total oil degradation, just faster rates.* However, biostimulation is not recommended for use in accelerating oil biodegradation on open water because nutrients cannot be retained effectively at high enough concentrations in the water column due to dilution. The same is true for bioaugmentation; dilution reduces the bioaugmenting culture rapidly. Use of bioremediation for oil spill cleanup likely should be based on a Net Environmental Benefit Analysis (NEBA) described in Chapter 4.

3.1.5 Salinity

Although microbial degradation of oil has been observed over the salinity range observed in the natural environment, changes in salinity may affect oil biodegradation by changing the composition of the microbial population. For example, dramatic variations in salinity may occur in estuarine environments where marine organisms mingle with freshwater species. Salinity is relevant not only to marine ecosystems but also to fresh waters, shorelines and overland spills where brine may be a co-contaminant with the oil.

Hydrocarbon biodegradation has been reported to be inhibited in non-saline environments and groundwater when salinity increases (Margesin and Schinner 2001; Minai-Tehrani et al. 2009; Ulrich et al. 2009). In contrast, most marine species have an optimum salinity range of 25 to 35and grow poorly or

[4] *Oligotrophic environments have very low concentrations of carbon and nutrients suitable for sustaining life.*
[5] *Eutrophic environments are the opposite of oligotrophic, having excess nutrients that can lead to unbalanced growth, such as algal blooms, that have subsequent deleterious effects.*

not at all at salinity lower than 15 to 20 (Zobell 1973). In a study of hypersaline salt evaporation ponds, Ward and Brock (1978) showed that rates of hydrocarbon metabolism decreased with increasing salinity in the range of 33 to 284. Whitehouse (1984) reported an inverse relationship between salinity and solubility of PAHs. Thus, in general, a less saline environment may mean more soluble PAHs and better biodegradation rates.

Microbial mats in an Arabian Gulf environment having chronic exposure to oil spills and highly variable daily salinity and temperature fluctuations were studied by Abed et al. (2006). They reported almost complete degradation of the PAH phenanthrene and the heterocycle dibenzothiophene at a salinity of 35, and the best biodegradation of the *iso*-alkane pristane and *n*-octadecane between 35 and 80 salinity. However, inhibition of hydrocarbon biodegradation by high salinity has been reported even in environments where salt-tolerant or slightly halophilic microorganisms are dominant, such as mangroves and intertidal microbial mats. As reviewed by Martins and Peixoto (2012), Diaz et al. (2002) assessed hydrocarbon biodegradation in a mangrove microbial consortium immobilized onto polypropylene fibers. They verified that alkane biodegradation increased from <40% at 0 salinity to 65% at >40 salinity and remained there through 140 salinity, then declined back to <30% at 180 salinity, thus demonstrating an optimum salt concentration for biodegradation by these hypersaline-adapted microbes, above which biodegradation slows. In contrast, in studies with heavy crude oil-contaminated marine sediments, Minai-Tehrani et al. (2009) reported that higher salt concentrations (sediment pore water having > 10 salinity) inhibited total crude oil and PAH biodegradation. Degradation of the PAHs phenanthrene, anthracene and pyrene was greater at a salinity of 1, and fluoranthene and chrysene degradation was better at 0 salinity. *Based on the discussion above, it appears that one cannot delineate an optimum salinity range for hydrocarbon biodegradation since such activity depends on the particular adapted microbial community that is dominant in a given environment.*

3.1.6 pH

Because seawater is slightly more buffered than freshwater, the pH of seawater is generally more stable and slightly alkaline (Bossert and Bartha 1984), whereas the pH of freshwater and soil environments is more variable. Organic soils in wetlands are often acidic, as are some surface waters where the salinity is near zero, such as Muskoka in Ontario where 92% of the lakes have an alkalinity value[6] of less than 20 mg/l, which means that they are susceptible to acidification through acid deposition (Muskoka Watershed Council 2007). The pH of mineral soils is more neutral to alkaline. Most heterotrophic bacteria (those that use organic material, including hydrocarbons, for growth) favour a neutral pH (~6.5 – 7.5) (Leahy and Colwell 1990), while fungi are generally more tolerant of acidic conditions (pH <6.5). Therefore, bacteria are the dominant hydrocarbon-degrading microbes in many circumneutral environments, such as aquatic ecosystems, but fungal biodegradation may increase in importance in acid-stressed environments.

> Oil biodegradation occurs over a range of pH values, but is generally optimum at near-neutral to slightly alkaline conditions (pH 6.5-8).

3.2 Oil Impacts on Different Aquatic Environments

3.2.1 Sand and gravel shorelines

The behaviour of spilled oil on sand and gravel shoreline environments primarily depends on the properties of the shoreline, such as the porosity of the substrate, the morphology of the shoreline (slope, topographical variability, sinuosity, stability) and the energy of the waves impinging on the shoreline. Differences will also occur in the fate of oil along marine, estuarine and freshwater shorelines, largely due

[6] *Alkalinity is a measure of the capacity of an aqueous solution to neutralize acid; it is not the same as pH.*

to differences in biological diversity and biomass, as well as dissolved oxygen and nutrient (N and P) replenishment, as discussed above.

> Interactions between oil and fine mineral particles play an important role in natural oil cleansing in marine shorelines.

This interaction of oil and fine particles reduces the adhesion of oil to intertidal shoreline substrates through the formation of oil-mineral aggregates (OMAs; Chapter 2) that are easily dispersed by tidal action and currents. More importantly, suspended OMAs (also, described as clay-oil flocculation) enhance the availability of oil for biodegradation (Figure 2.3), and thus oil biodegradation rates may be accelerated by this process (Bragg and Owens 1995; Lee et al. 1997a, b).

> Persistence of nutrients on marine beaches is dependent on tidal and wave action.

Definitive research conducted on two beaches in Scarborough, ME (Wrenn et al. 1997a, b) clarified the role of wave and tidal energetics and geomorphology on oil biodegradation. They pointed out that beaches with strong wave action will tend to more rapidly lose nutrients needed to maintain or enhance oil biodegradation and that salinity layers are created between the fresh groundwater and the tidal seawater in both high and low wave-action beaches. These tracer studies showed that the washout rate of nutrients from the oil-impacted intertidal zone is strongly affected by the wave activity of the contaminated beach. *Wave action in the upper intertidal zone causes nutrients from the surface layers of the beach to be diluted directly into the water column, resulting in their immediate loss from the bioremediation zone. Washout due to tidal activity alone, however, is relatively slow, and nutrients will likely remain in contact with oiled beach material long enough to allow effective biostimulation on low-energy beaches.* In the two beaches studied (a high and a low energy beach), the ‘sandwiching phenomenon’ (a layer of lower salinity water located between two higher salinity water layers) was observed, which was confirmed by Boufadel et al. (1999) in a mesocosm study. Both the mesocosm and field studies are helpful in providing guidelines for the application of bioremediation strategies, such as biostimulation based on the optimal application of nutrients on marine beaches, which are discussed later in Chapter 6.

Recommendation: The interaction between residual oil in the water with suspended particulate matter of organic origin (e.g., phytoplankton, detritus, extracellular released products) and inorganic origin (e.g., mineral fines) (OMA and clay flocs) on the environmental persistence of spilled oil (sinking, oil biodegradation rates, etc) requires further study. This is a missing point on the calculation of the oil’s mass balance following a spill.

3.2.1.1 Porosity of the substrate

> The rate and depth of oil penetration depend primarily on the porosity of the substrate.

Higher wave exposure enhances both physical removal and weathering processes. Wave-swept rocky shores tend to recover from oil spills within a matter of months, whereas marshes may act as a petroleum sink for many years. Tidal pumping promotes oil penetration into the sediments. Carls et al. (2003) showed that tidal pumping causes dissolved hydrocarbons in beach pore waters to move laterally into streams cut through beach sediments. *On coarse-grained shorelines like cobble and sandy beaches, oil can penetrate more deeply and remain longer (when it is trapped below the limit of wave action; Figure 2.3), compared to finer grained sediments such as silt and clay*. However, oil is more easily removed from coarse-grained sediments by water flushing. Interactions of oil with tidal action, waves and shoreline substrate may also form asphalt-like oil-sediment mats that are resistant to further biological and photochemical weathering. Thus, porosity may control oxygen availability and hence control natural biodegradation rates. More detailed discussion of oil interacting with armoured beaches is presented in Chapter 2.

3.2.1.2 Shoreline morphology

> Shoreline morphology influences oil fate via effects on the nature and extent of transport of the oil both longitudinally along the shoreline and inland.

Steep shorelines (particularly if exposed to wind and wave action) will experience significant erosional processes; therefore, oil deposition would tend to develop in a narrow band within the zone of wave action where it would be subject to repeated cycles of re-suspension and deposition. Steep shorelines usually have little or no vegetative cover, thus further decreasing the likelihood that oil will remain onshore for substantial lengths of time. Shorelines with low sinuosity (i.e., running in a straight line) will tend to have sandbar formation offshore, producing the potential for oil to be deposited on the sandbars as well as along the shore itself. Shorelines with higher sinuosity (curving with embayments) will produce lower-energy conditions on lee-sides of the curvatures, where oil deposition would be more likely to occur. High topographical variability along a shoreline (e.g. rocky outcrops, stream mouths, dunes and human infrastructure, such as docks, weirs and break-fronts) will create variable exposure to wind and wave action, creating, in turn, variable oil deposition. Unstable shorelines subject to erosion will experience changes in position and composition annually, thus affecting the rate at which deposited oil is either re-suspended in the water column, pushed deeper and/or higher up the shore, or transported in bulk via major bank failures.

3.2.1.3 Wave exposure

Higher wave exposure enhances both physical removal and weathering processes. Wave-swept sand and gravel shores will often be unstable, as discussed above, resulting in a dynamic and somewhat unpredictable sequence of deposition and suspension. The combination of wind and wave exposure with low sinuosity and low stability would be the most likely to produce deposition/re-suspension cycles. The ultimate fate of spilled oil under these conditions would depend upon the type of oil and rate of weathering.

Rocky shores with high wave exposure tend to recover from oil spills within a matter of months, particularly when the shoreline has a steep slope and vegetation cover is minimal (IPIECA 1995). In the marine environment, more gradually-sloping rocky shores with heavy vegetation cover (e.g., *Fucus*, a ubiquitous brown seaweed) and tide pools may experience some stranding of oil in the upper intertidal zones. In freshwater lakes, rocky shores are often bare or limited to a lichen/moss vegetative cover; therefore, oil would be less likely to strand (depending upon the density of the lichen/moss cover).

3.2.2 Estuarine shorelines

> Estuarine shorelines are complex, dynamic and diverse; therefore, the deposition and weathering of spilled oil in these environments will be highly site-specific and difficult to predict.

Slopes are highly variable and range from gently sloping **(Figure 3.2)** land to steep cliffs. The waterline is not constant due to tides and storm surges, creating a ‘shore zone’. The variability in slope, energy climate, sediment composition and other physical characteristics (including the presence of woody debris) creates highly-variable transport and weathering conditions for spilled oil. Rates of weathering will also depend upon the nature of vegetative communities. Estuarine vegetation includes eelgrass beds, salt marshes and swamp forests. Mud flats are common. Engineered structures are common along estuarine shorelines (e.g., bulkheads and riprap revetments), adding to the complexity. Thus, there can be multiple stranding sites for spilled oil in estuaries.

Figure 3.2 Pugwash River Estuary, Nova Scotia

3.2.3 Riverine shorelines

The behaviour of spilled oil on river shorelines will be affected by the stream order[7], seasonal hydrology, channel morphology, the tendency for hyporheic flow and the nature and extent of the riparian zone. A spill into a lower-order stream (e.g., a small headwater stream) with a steep, rocky shoreline will behave differently from a spill into a higher-order stream with a broad floodplain and lower slope. The timing of the spill relative to seasonal flow will also be an important determinant. During the spring freshet, a spill would be rapidly transported downstream and along the upper margins of the stream channel, where it could become stranded once river flow drops. A spill that occurs during low-flow conditions (particularly when the river is fully or partially ice-covered) may tend to remain in a smaller area; however, its ultimate fate would depend on further transport and weathering processes once ice melts and flows increase. Channel morphology will affect the deposition and weathering of spilled oil via the potential for stranding on mid-channel bars or in side-channels. Higher-order streams will be more likely to have complex channel morphology. Hyporheic flow (Figure 2.3) along stream margins (via surface-to-near-surface groundwater connection) is common, and spilled oil could enter this flow system, then adsorb to particles along the flow-path. Hyporheic flows also occur vertically across the channel, feeding water into the hyporheic zone under the river. These downward flows may re-emerge immediately following an obstruction or further downstream, creating transport pathways through sediments for dissolved and particulate oil, trapping oil in sediments, and providing sources of dissolved oil to interstitial water of streambeds and bottom waters where flows re-emerge. The width and vegetative cover of the riparian zone along the river shoreline will also affect the transport and weathering of spilled oil. A spill that occurs during high-flow conditions will likely enter the riparian zone and could become stranded on

[7] *Order is reflection of the size (and sometimes complexity) of a river or stream network, from small (brook or stream) to large (major river)*

vegetation or on the finer, organic substrates common to these zones. Riparian zones can contain oxbow lakes and wetlands, which could become sinks for spilled oil.

<u>Recommendation:</u> More research is required on the persistence of oil in riverine, lacustrine and mud flat environments. Such research would benefit risk assessments and aid response operations. Research also needs to focus on mixing and physical dispersion in high gradient, high energy rivers and hyporheic zones connected to groundwater resources.

3.2.4 Rocky cliffs and beaches

On coastlines where the land surface is at a relatively steep angle below the water table, the abrasive action of continuous marine waves may create steep cliffs, and slopes constantly being eroded. As coastal cliffs collapse, the shoreline recedes inland. The speed at which this happens depends, in particular, on the strength of the surf, the height of the cliff, the frequency of storm surges, the hardness of the bedrock and, in the Arctic, the importance of permafrost to bond shore sediments Rocky cliffs are typically not considered a high ecological risk from oil spills unless they provide habitat to wildlife. These sites are frequently left to self-clean by natural physical processes (e.g. scour by waves, etc.) as the oil is not readily absorbed into rocks.

3.2.5 Lakes

> The behaviour of spilled oil in lakes is affected by lake size, basin morphology, exposure to prevailing winds, internal wind-driven lake currents (e.g., seiches) and season of the spill.

Oil spilled into small lakes would likely rapidly spread to cover a large proportion of the lake surface. Residual oil remaining after evaporative loss in small lakes would likely be deposited along the windward shoreline, but if the lake is well protected with steep shores, some residual oil could remain in the narrow littoral zone immediately offshore. Oil spilled into larger lakes would be pushed and mixed by wind and wave action. The eventual location of residual oil after the initial evaporative loss would depend upon the nature of the windward shoreline (particularly slope and substrate size), the nature of the littoral zone immediately offshore (if there are large littoral macrophyte[8] beds, the oil could be captured within those beds), and the effect of lake currents. Seiches[9] can push residual oil up the shoreline on the windward side, where it could become stranded on vegetation or fine shoreline sediments. Oil spilled during seasonal lake turnover[10] in the spring and fall could be subject to mixing deeper into the water column where dissolved oxygen concentrations are low.

As an example of oil spilled onto a lake, on August 3, 2005, a Canadian National Railway train derailed near Wabamun Lake in central Alberta. The derailment released 712,500 L of Bunker C oil and 88,000 L of pole-treating oil from the rail cars, across the shoreline and into the adjacent Wabamun Lake. Workers removed much of the oil via vacuum trucks and by hand. Sorbent booms were ineffective in containing the Bunker C oil. Some containment booms were deployed, but insufficient numbers were available. Eventually, the size of the spill forced the engagement of a response organization with experience and equipment suitable for a larger response effort. The cleanup took years. Although the heavily-used recreational lake was re-opened a year after the spill, the Alberta government was still issuing health warnings about tar balls (Figure 2.3) and oil sheen two years later (Goodman 2009).

[8] *Macrophytes are aquatic plants that may be emergent, submergent or floating*
[9] *Seiches are standing waves in an enclosed or partly-enclosed water body*
[10] *Turnover is a seasonal phenomenon of water movement from top to bottom according to temperature (density), more common in large, deep lakes than shallow lakes*

To estimate the hydrocarbon-degrading capabilities of microbes naturally present in oil-contaminated Lake Wabamun sediment, laboratory tests were conducted with spilled Bunker C oil recovered from the lake and the reference oil, Alberta Sweet Mix Blend (ASMB), in microcosms at 22 °C for four weeks or at 4 °C for eight weeks (Foght 2006; Wang et al. 2011). The results showed that Lake Wabamun sediment microbes were capable of degrading a significant proportion of the ASMB reference oil at both incubation temperatures. However, biodegradation of Bunker C was far less significant than ASMB, with smaller masses of hydrocarbons being degraded under both incubation conditions. For example, only 126 mg Total Petroleum Hydrocarbons per gram of Bunker C were degraded compared with 263 mg/g ASMB in parallel ASMB cultures (fresh sediment, 22 °C for four weeks). Under the best incubation conditions, biodegradation accounted for loss of only ~12-13% by weight of the Bunker C oil added to the cultures. This shows that only a small proportion of LMW hydrocarbons is biodegradable with a high proportion of components (including high molecular weight components, such as asphaltenes and resins) either not readily biodegradable or not detectable by gas chromatography (Appendix A) in the spilled Bunker C oil. *This persistence is most likely due to the recalcitrance of the major constituents of Bunker C oil.*

Oil spilled into the Great Lakes would be subject to high-energy phenomena similar to some marine situations, but without tidal effects. Lake currents would be expected to play a major role in behaviour and persistence. An offshore spill adjacent to strong alongshore lake currents could be widely dispersed in a short period of time. *Areas that are chronically contaminated with low levels of hydrocarbons (e.g., commercial ports and recreational marinas) might be expected to harbour larger numbers of microbes adapted to oil degradation and therefore might be able to respond more quickly to an oil spill than pristine areas where biodegradation could be delayed.*

3.2.6 Wetlands

> Wetlands, including marshes, swamps, fens, muskeg and mud flats, are sensitive to oil spills because of their complex and rich ecosystem diversity and their ability to collect and filter runoff from surrounding environments. Saline wetlands are common in some parts of Canada, particularly the prairies, but the behaviour of spilled oil in these systems has not yet been rigorously studied.

The physical and chemical characteristics of freshwater and saltwater wetlands that affect the dispersion and weathering of oil include small areas of shallow water, finer sediments with high organic content, high vegetation cover and high biochemical oxygen demand (leading to anaerobic conditions). Oil spilled into these systems will not be widely dispersed by wind. Rather, it will tend to be stranded on fine sediments or on vegetation. Transport out of the wetland would be via small stream discharge points.

Saline wetlands (**Figure 3.3**) are highly productive and are often ringed by broad salt flats with salt-tolerant vegetation. They are important habitats for waterfowl. Biodegradation of residual oil spilled into these systems would depend upon the presence and ability of salt-tolerant microbes (Section 3.1.5) to degrade the oil. In addition, if the oil becomes entrained within the anaerobic sediments commonly found within the wetland, the biodegradation rate of the hydrocarbons may be significantly reduced.

Figure 3.3 Aerial view of replicate plots of an experimental oil spill on a saltwater wetland in Nova Scotia, Canada, in 2001 *(joint project between DFO-Canada and U.S. EPA).*

3.2.7 Permafrost

Strategies are needed to deal with the likelihood of spills occurring in remote Arctic regions as exploration and production activities increase. The U.S. EPA (2013) published a short report on the impact of climate change on Alaskan permafrost[11]. Over the past 50 years, temperatures across Alaska have increased by an average of 1.9 °C. Winter warming was even greater, rising by an average of 3.5 °C and is projected to increase an additional 1.9 to 3.9 °C by the middle of this century. Thawing permafrost associated with climate change may cause major impacts on transportation, forests, ecosystems and the economy in the future. Over the past 50 years, thawing permafrost and increased evaporation have caused a substantial decline in the area of Alaska's closed-basin lakes (lakes without stream inputs and outputs). These surface waters and wetlands provide breeding habitat for millions of waterfowl and shorebirds that winter in lower latitudes (Karl et al. 2009). Furthermore, as temperatures rise and permafrost thaws, the softening soil can interfere with tree root systems (causing trees to sink into the ground) and infrastructure supporting oil and gas pipelines, etc., possibly affecting pipeline integrity. *With the exception of a few recent reports (e.g., Yang et al. 2014), little is known about the impacts of oil on permafrost ecosystems and related surface meltwaters, for example, loss of permafrost slope stability due to black-body heating by solar radiation.*

Recommendation: Research is needed to further our understanding of the effects of spilled oil on permafrost ecosystems and how best to develop appropriate response strategies that mitigate damage without doing further harm.

The ADAPT program (Arctic Development and Adaptation to Permafrost in Transition) was designated to fund innovative Canadian research in the field of permafrost change. The ADAPT mission is to utilize this research to develop a structure of "Integrated Permafrost System Science" to understand and predict consequences of rapid changes on ecosystems and economics.

3.2.8 Ice-covered Arctic marine environments

The extent of sea ice is declining throughout the Arctic Ocean and adjacent seas. Some sea ice persists from year to year (known as perennial sea ice), often getting thicker where it forms pressure ridges (e.g., the stamukhi zones between the 10-20 m isobaths). Over the past several decades, the perennial sea ice

[11]Permafrost is ground that remains frozen for two or more consecutive years.

has declined dramatically to be replaced by seasonal (first year) ice. Ocean currents and winds have also played an important role, pushing perennial sea ice out of the Arctic basin. The average sea ice extent in September has decreased by 11.5% per decade over the past 30 years.

Oil spills in these sensitive areas as they warm through global climate change could be devastating to the changing ecosystems and exacerbate the effects of melting snow and ice.

A number of recent reviews have highlighted the results of landmark field studies conducted within the Arctic by Canadian, Norwegian and American scientists on the environmental processes that affect oil behaviour and weathering in open water and in ice, and the effectiveness of current and emerging spill response countermeasures (Dickins 2011; NRC 2014).

In January 2012, members of the international oil and gas industry launched a major collaborative effort to enhance Arctic oil spill capabilities under the auspices of the International Association of Oil and Gas Producers (IOGP). This collaboration, called the Arctic Oil Spill Response Technology Joint Industry Programme (JIP), is aimed at expanding industry knowledge and proficiencies in Arctic oil spill response (http://www.arcticresponsetechnology.org/about-the-jip).The JIP is currently conducting a series of research projects in laboratory conditions on six key areas of research: dispersants, environmental effects, trajectory modeling, remote sensing, mechanical recovery and in situ burning.

Recommendation: In light of the Gulf of Mexico oil spill incident, a need has been identified to advance knowledge of, and ability to deal with, subsurface blowouts in ice-covered marine environments. While the National Energy Board has identified the need for additional precautionary measures in these important environments (e.g., same-season relief well capacity), further research is needed to aid in development of oil detection and response strategies.

Ecological exposure to oil from drilling causes adverse chronic effects on species composition and diversity. *Acute exposures from spills can be severely damaging to fisheries, marine mammals, waterfowl, corals and coastal wildlife by affecting feeding, activity, avoidance, growth and reproduction (Semanov et al. 1997). An important component of Arctic marine productivity is the under-ice community that develops in response to sunlight penetrating sea ice (Chapter 4). This community would be highly exposed to oil discharged from a subsurface blowout. Marine mammals would likewise be at high risk given that they are forced to breathe at small holes in the ice where oil would concentrate (Chapter 4).* The primary sources of oil in the Arctic marine ecosystem are from drilling activities and spills during transport. The risk of crude oil and/or fuel spills in the Arctic Ocean has increased with announcements in 2015 of imminent deep sea Arctic drilling in the Chukchi Sea between Alaska and Russia and the first commercial cargo shipment navigating the Canadian Northwest Passage in 2013.

Oil spilled in the marginal ice zone and polynyas[12] during high primary production periods could cause extensive damage, especially in shallow waters important to organisms at all trophic levels in the food chain. For example, during the summer season, runoff from the Mackenzie River forms a warm, low-salinity 'thermal bar' along the coast of Beaufort Sea. Anadromous fish species congregate in these highly productive waters to feed, grow and mature before returning to rivers in the autumn to spawn, and these regions form crucial summer habitat for Beaufort beluga populations; these living resources and others are depended on for food by native northerners. Onshore winds would carry surface oil into these shoreline zones, exposing resident species to hydrocarbons at important phases in their life cycles. Existing response infrastructures are located at far distances, oil is less accessible when the sea is ice-covered, and conditions may be equally challenging when open water provides conditions for large waves, storm surges and coastal inundation. Topping this off is the slow rate of biodegradation at these cold temperatures (Section 3.1.2), which could lead to persistence of the spilled hydrocarbons for

[12] *A polynya is an area of open water within the sea ice pack*

decades. For years many scientists have agreed that the Arctic environment will require special precautions to minimize the risks of accidental oil spills (NRC 2014).

Uncertainty is high regarding the effect of oil in ice-covered environments. Oil tends to become trapped between ice floes, under ice and within brine channels, resulting in a lengthening of the contamination and exposure times (Figure 2.3). It is likely that recovery from a spill would require years for affected littoral and benthic communities to return to health.

Drilling for hydrocarbons in the Arctic demands improved methods to detect and monitor the behaviour of spills on, in and under ice and within the water column in the event of a subsurface blowout. In addition, oil interactions with permafrost and spring melt are important unknowns in terms of access to sites for spill response, rapid spreading of oil during freshet, slow rates of weathering and how hydrocarbons interact with ice and suspended particulate matter.

In pack ice, oil accumulates at the water surface, flowing around any ice present. Oil can also collect under the ice, which usually has rough topography associated with pressure ridges. At sea- ice concentrations less than 30%, oil behaves as in open water (Venkatesh et al. 1990), but at higher ice concentrations, the oil drifts with the ice. The equilibrium oil thickness in slush or brash ice[13] is nearly four-fold higher than on cold water. As a result, the oil-contaminated area at higher ice concentrations is several orders of magnitude smaller, but the oil layer is thicker. Thus, the presence of pack ice significantly slows oil spreading. *This means that a smaller area is affected, but the impact on that area is greater and may overwhelm the microbial community. Recent research (Greer et al. 2015) has discovered the presence of oil-degrading microbial biofilms at the bottom of sea ice, but the prevalence and persistence of such structures is unknown.*

As it weathers, the fate of oil in ice is affected by density, viscosity, surface and interfacial tensions and water content. As described in Chapter 2, typical weathering processes include evaporation, dissolution, emulsification with water to form water-in-oil gels, photodegradation and dispersion. Singsaas et al. (1994) found that the rates of evaporation, dispersion and emulsification were retarded in pack ice. They reported that the primary factors that reduced the weathering rate when compared to open water and temperate conditions were wave damping, limited spreading of oil bounded by sea ice and low temperature.

Immediate surface evaporation results in losses of small alkanes (C_5-C_{10}) and monoaromatic compounds, such as BTEX (benzenes, toluenes, ethylbenzene and xylenes). Several experiments with refined gasoline and diesel (Serova 1992; Ivanov et al. 2005) have found nearly complete evaporation on the surface of ice during the summer season. The highest evaporative loss occurs in the presence of uncompacted snow, while increasing snow density and thickness reduces evaporation (Belore and Buist 1988).

To determine the importance of dissolution, Faksness and Brandvik (2008a, b) subjected six oils (five crude oils and a heavy fuel oil) to freezing in sea ice during the winter and quantified the migration of water-soluble components from the oil into the ice. They found that the content of water-soluble compounds in the ice decreased with ice depth, and the concentrations changed over time, confirming that the water-soluble components had been transported from the overlying oil through the brine channels in the ice to the underlying water. The field experiments showed that both ice thickness and air temperature prior to an oil spill are important for the distribution of water-soluble components in ice.

Moussification, or the formation of water-in-oil emulsions, forms by water-drop entrainment during mixing (Figure 2.5). This is an important weathering process both in cold and warm water. Emulsification increases the volume of the slick and reduces the biodegradation rate. *The formation of stable water-in-oil*

[13] *Brash ice is an accumulation of the wreckage of other forms of ice made up of fragments not > 2 m across.*

emulsions hampers various oil spill cleanup efforts by increasing volume for containment, lowering combustibility for in situ burning, and increasing viscosity so that chemical dispersion is more difficult.

Photooxidation (Chapter 2) and biodegradation are important transformation processes that occur with petroleum products released into the marine environment (Garrett et al. 1998; Dutta and Harayama 2000; Prince et al. 2003). Whereas photooxidation is highly seasonal in the Arctic, biodegradation rates should be relatively constant in Arctic sea water. Garret et al. (1998) demonstrated that *photooxidation and biodegradation operate on different aromatic hydrocarbon components in crude oils*. Whereas biodegradation and evaporation/dissolution result in the depletion of unsubstituted aromatic compounds relative to their alkylated homologues, photooxidation selectively attacks the alkylated aromatic compounds (Prince 1993; Prince and Clark 2004).

Finally, with respect to sedimentation (Figure 2.3), most oils do not sink as their specific gravity is less than that of seawater. However, when suspended inorganic particulate matter interacts with oil, the conglomerate formed may be negatively buoyant. This natural process may occur in near-shore environments with a high suspended particle load such as that associated with glacial tills in the Arctic. Oil sedimentation is usually considered to be disadvantageous for the overall removal of oil from the environment because oil in the sediment phase tends to be limited by oxygen supply, and anaerobic biodegradation of hydrocarbons is a slow, poorly understood process (Section 3.1.3), particularly when combined with low temperatures.

3.2.9 Offshore Surface Spills at Sea and in Large Freshwater Lakes (e.g., Great Lakes).

3.2.9.1 Spreading

> At Arctic temperatures, the presence of snow and ice can substantially affect the spreading of oil.

The spreading of oil on water is one of the most important processes during the first hours of a spill, provided that the oil pour point (the temperature at which it becomes semi-solid and loses its flow characteristics) is lower than the ambient temperature. The principal forces influencing the spreading of oil (Figure 2.3) include gravity, inertia, friction, viscosity and surface tension. These processes increase the overall surface area of the spill, thus enhancing mass transfer via evaporation, dissolution and later biodegradation. Oil accumulated at the water surface can be pushed by the wind, generally slightly to right of the wind vector in the northern hemisphere. Wind, currents and tides, the three main contributors to transport of oil following an oil spill, may be used to project where the oil might go and what it might encounter in its path.

3.2.9.2 Evaporation

> In terms of environmental impacts, evaporation is the most important weathering process during the early stages of an oil spill.

Evaporation (Figure 2.3) is responsible for the removal of a large fraction of the oil including the more acutely toxic, lower molecular weight components. For oil on water, evaporation removes virtually all the normal alkanes smaller than C_{15} within one to ten days. Gros et al. (2015) reported > 50% of ≤ C_{17} hydrocarbons disappearing within 25 hours from an experimental 4,300 L North Sea oil slick of < 10 km^2 area and < 10 µm thickness. For oil sheen, > 50% losses of ≤ C_{16} hydrocarbons were observed after 1 hour. Volatile aromatic compounds, such as the monoaromatics benzene and toluene, can also be rapidly removed from an oil slick through evaporation. However, these volatile oil components may be more persistent when oil is stranded in sediments. The volatile components make up 20-50% of most crude oils, about 75% of No. 2 fuel oil, and about 100% of gasoline and kerosene. As a result, the physical properties of the remaining slick change significantly (e.g., increased density and viscosity). Major factors influencing the rate of evaporation include composition and physical properties of the oil, wave action, wind velocity and water temperature (Jordan and Payne 1980). Evaporation leaves behind the heavier components of the oil, which may undergo further weathering or may sink to the ocean floor. For example, spills of lighter refined petroleum-based products, such as kerosene and gasoline, contain a high proportion of flammable light ends, which may evaporate completely within a few hours, thereby reducing the toxic effects to the aqueous environment. Heavier oils leave a thicker, more viscous residue, which may have serious physical and chemical impacts on the environment.

3.2.9.3 Dissolution

> The extent of dissolution depends on the composition and state of the oil and occurs most quickly when the oil is finely dispersed in the water column.

Although dissolution (Figure 2.3) is less important than evaporation from the viewpoint of mass loss during an oil spill, dissolved hydrocarbon concentrations in water are particularly important due to their potential influence on the success of bioremediation and the effect of toxicity on biological systems. Light aromatic compounds, such as benzene and toluene, are the most soluble in seawater, and the most acutely toxic. However, these compounds are also first to be lost through evaporation, a process which is 10-100 times faster than dissolution, and oil contains only small amounts of them which tends to mitigate dissolution. Even so, the impact of LMW aromatics on the environment is much greater than simple mass balance considerations would imply (NRC 1985). Dissolution rates are also influenced by photochemical and biological processes. The larger components of oil (4-6 ring PAHs, alkanes $>C_{20}$, etc.) are quite insoluble in aqueous solution, so they tend to persist longer in the environment.

3.2.9.4 Emulsification

> An emulsion is formed when two liquids combine, with one becoming suspended in the other.

Emulsification (Figures 2.3 and 2.5), or formation of oil-in-water emulsions, involves the incorporation of small droplets of oil into the water column, resulting in an increase in surface area of the oil. Emulsification occurs by physical mixing promoted by turbulence at the sea surface. The emulsion thus formed is usually very viscous and more persistent than the original oil and is often referred to as mousse because of its appearance. The formation of these emulsions causes the volume of oil to increase three- to four-fold, which slows and delays other processes that would allow the oil to dissipate. Conventional oils with an asphaltene content greater than 0.5% tend to form stable emulsions that may persist for many months after the initial spill has occurred (WSP Canada, Inc. 2014). *However, as reported in Chapter 2, dilbits do not emulsify as easily as conventional oils. Dilbits, if spilled into turbulent water, can form entrained or unstable emulsions, which break down into water and oil within minutes or a few hours at most, once the sea energy dissipates (Fingas 2015).* Oils containing a lower percentage of asphaltenes are less likely to form emulsions and are more likely to disperse.

<u>Recommendation</u>: Research is needed to further our understanding of the properties of dilbit that preclude it from being less subject to emulsification than other crude oils.

In general, oil-in-water emulsions are not stable, but water-in-oil emulsions are. Water-in-oil emulsions containing 50 to 80% water are most common and have a reddish-brown colour and grease-like consistency. Such emulsions are highly resistant to biodegradation. However, oil-in-water emulsions can be maintained by continuous agitation, interaction with suspended particulates, and the addition of chemical dispersants, discussed further in Chapter 6. Chemical dispersion may influence oil biodegradation rates by increasing the contact area between oil and microorganisms or by increasing the dissolution rates of the more soluble oil components. Emulsification is less likely to occur in fresh water, even for spills of heavier oils, because significant mixing energy often does not persist long enough to generate the stable emulsions seen at sea. Moreover, brine composition (alkalinity in particular because of a buffering effect) is intimately tied to the pH in determining the stabilizing properties of the interfacial films (Strasser 1968). Brines with high [Ca^{+2}] and a high Ca^{+2}/Mg^{+2} ratio form nonrelaxing, rigid films around the water droplets, resulting in stable emulsions (Jones et al. 1978). Higher concentration of divalent ions and high pH result in reduced emulsion stability. Where emulsions do occur, they may separate into oil and water again if heated by solar radiation under calm conditions or when stranded on shorelines.

3.2.9.5 Photooxidation

> In sunlight, oils react chemically with oxygen either breaking down into soluble products or forming persistent compounds called tars.

Oxidation is promoted by sunlight (Figure. 2.3) and the extent to which oxidation occurs depends on the type of oil and the form in which it is exposed to sunlight. However, this process is very slow and, even in strong sunlight, thin films of oil break down at no more than 0.1% per day. The formation of tar balls is caused by the oxidation of thick layers of high viscosity oils or emulsions. This process, also called aggregation, forms an outer protective coating containing heavy compounds, resulting in an increased persistence of the oil in the environment. Tar balls, which are often found on shorelines and have a solid outer crust surrounding a softer, less weathered interior, are a typical product of this process. Oil aggregates may exist from a month to a year in enclosed seas and up to several years in the open ocean. They complete their cycle by slowly degrading in the water column, on the shore if washed there by currents or (if they lose buoyancy) on the sea bottom.

3.2.9.6 Sedimentation/sinking

> Some heavy refined products have a specific gravity ≥ 1.0 and so will sink in fresh or brackish water.

Since seawater has a specific gravity of approximately 1.03, only heavy oils are dense enough, or weather sufficiently, to result in sinking in the marine environment (Figure 2.3). Sinking usually occurs due to the adhesion of sediment particles and/or dense organic matter to the oil. Shallow waters are often laden with suspended solids (such as planktonic organisms or clay/silt particles) providing favourable conditions for sedimentation. This is especially evident in estuaries, which are characterized by having relatively high concentrations of suspended particulate matter that aid in the sedimentation of oil droplets (NRC 2003). Valentine et al. (2014) reported a 3,200 km^2 region in the vicinity of the Macondo well contaminated with excess hopane attributed to deposition from the Deepwater Horizon (DWH) blowout. The pattern of deposition was consistent with both a ‘bathtub ring’ of oil impinging on the continental slope and a fallout plume of dirty marine snow where suspended oil particles sank to the sediment. Another report from the DWH spill by Gutierrez et al. (2013) implicated the role of exopolysaccharides from enriched strains of hydrocarbon degraders in contributing to the formation of oil aggregates during the spill (Figure 2.3). Oil stranded on sandy shorelines often becomes mixed with sand and other sediments. If this mixture is subsequently washed off the beach back into the sea it may then sink. In addition, if the oil catches fire after it has been spilled, the residues that sometimes form may be sufficiently dense to sink.

3.3 Importance of Oil Type in Relation to the Environment

3.3.1 Light oils (diesel, heating oil, light crudes)

These types of oil (Section 2.3.2) are characterized as being moderately volatile and leave a residue (up to one-third of spill amount) after a few days. They contain moderate concentrations of highly toxic (soluble) compounds, especially distilled products. They may result in long-term contamination of intertidal resources and have the potential for acute subtidal impacts (dissolution, mixing and sorption onto suspended sediments). Cleanup can be very effective.

3.3.2 Medium crude oils (most crude oils)

These oils (Section 2.3.3) will evaporate moderately within 24 hours, have a maximum water soluble fraction of 10-100 ppm, can cause severe and long-lasting contamination of intertidal areas, and can be highly toxic to waterfowl and fur-bearing animals. They are chemically dispersible and can be cleaned up effectively if response is fast.

3.3.3 Heavy oils

Heavy oils (Sections 2.3.7) include bitumen and dilbit and refined fuel oils such as No. 6 fuel oil and Bunker C. They do not readily evaporate or dissolve in aqueous solution (water soluble fraction is <10 ppm), can contaminate intertidal areas heavily with long-lasting effects, cause severe impacts to waterfowl and fur-bearing mammals through coating and ingestion, and can sink readily into sediments, exerting adverse effects on benthic communities. *They weather slowly and are difficult to chemically disperse. Shoreline cleanup is difficult under all conditions.*

A major report was published in 2013 by the Canadian government that provided a comprehensive, in-depth review of the properties, composition and marine spill behaviour, fate and transport of two diluted bitumen products from the Canadian oil sands, namely, Access Western Blend (AWB) and Cold Lake Blend (CLB). These two products were chosen to represent all dilbits in use in Canada because they were the highest volume products transported by pipeline in Canada in 2012 and 2013 (Government of Canada 2013). The report documented results from laboratory and wave tank studies of the properties and composition of fresh and weathered AWB and CLB. Included were measurements of the potential of the two products to evaporate, photo-oxidize, and sink in saltwater, as well as how well the dilbits behaved when treated with dispersants. The major results of the in-depth investigation are summarized below:

- Both dilbit products floated on seawater even after exposure to visible light and mixing with water;
- The dilbits sank when they came in contact with fine particulate matter in seawater and mixed by high energy wave action;
- When Corexit 9500 was used in an attempt to disperse the dilbit in seawater mixed by high energy breaking waves, little to no dispersion occurred even when fine particulates were added to aid the dispersion; and
- The two dilbit products did not evaporate as well as conventional crudes and fuel oils, but their behaviours were similar in other ways, such as emulsion formation and how they interacted with sediments.

It should be noted that dispersant testing in these wave tank studies was conducted at only one temperature, 8.3 °C. At that temperature, dispersants are less effective against heavy fuel oils than at higher temperatures (Srinivasan et al. 2007). Government of Canada (2013) did recognize this restriction in its conclusions: *"The physical properties (e.g., density, viscosity and adhesiveness) of these products limit the effectiveness of currently-available spill treating agents, thus restricting remediation and* *potentially contributing to the persistence of the products in marine environments where seawater temperature is < 8 °C."*

<u>Recommendation:</u> More research is urgently needed to determine the highest-risk combination of environmental characteristics when dealing with dilbit. Based on current knowledge and logic, for example, under what circumstances is it most likely that a dilbit product would sink? Under what conditions would weathering of dilbit be the slowest?

More research is needed to further our understanding of the behaviour of dilbit and other heavy fuel oils in a range of environmental settings, including near-shore marine, offshore marine, estuarine, freshwater lakes, rivers and wetlands, and environmental conditions, including combinations of climate, water chemistry and biological communities. This new information would help to optimize the selection of current spill response strategies and to support the development and validation of emerging technologies, including biodegradation of mousse, water-in-oil and oil-in-water emulsions. Details on the factors that influence moussification are needed for a better understanding of its properties and its treatment. The same needs pertain to tar balls.

Research is needed to further our understanding on why dilbit is less subject to emulsification than other crude oils. Knowledge gained might help in developing response strategies for all heavy oils.

3.4 Summary of Research Needs and Recommendations

3.4.1 High Priority Research Needs

3.4.1.1 Arctic Ecosystems

Research is needed to further our understanding of the effects of spilled oil on permafrost ecosystems, where challenges include limited site access, rapid spreading of oil during freshet, slow rates of weathering, and limited knowledge on the interaction of oil with ice and suspended particulate matter. New research would show how best to develop appropriate response strategies that mitigate the damage without causing further harm. In addition, little has been done to advance our knowledge of how to deal with subsurface blowouts in ice-covered marine environments. Similarly, with the recent re-invigoration of drilling for oil over the Arctic Ocean shelves and slopes, improved methods will be needed to detect and monitor the behaviour of spills on, in and under ice and within the water column in the event of such a subsurface deep sea blowout. While the National Energy Board has identified the need for additional precautionary measures (e.g., same-season relief well capacity), a number of laboratory studies have been initiated to further research, but field trials are needed to aid in development of oil detection and response strategies in these important environments.

3.4.2 Medium Priority Research Needs

3.4.2.1 Persistence of Oil in Non-Marine Environments

Most literature on oil persistence concerns marine environments. More information on oil persistence in riverine, lacustrine and mud flat environments, as well as sediments, would be beneficial for risk assessments and response operations. Although much progress has been made over the last decade in our knowledge of oil biodegradation, anaerobic biodegradation of hydrocarbons is less understood. This is important to oil that has sunk into the sediment, whether it be riverine, lacustrine, estuarine or marine, where it could persist for decades.

3.4.2.2 High Risk Characteristics and Treatability of Dilbit

Although the Canadian government has already begun work on the treatability of dilbit, more research is needed to rapidly determine the highest-risk combination of environmental characteristics when dealing with dilbit. Based on current knowledge and logic, for example, under what circumstances is it most likely that a dilbit product would sink? Under what conditions would weathering of dilbit be the slowest? Related to that, the need exists to further our understanding of the behaviour of dilbit and other heavy fuel oils in a range of environments, including near-shore marine, offshore marine, estuarine, freshwater lakes, rivers and wetlands under various combinations of climate, water chemistry and biological community conditions. New information is required for contingency plans to optimize the selection of current spill response strategies and to support the development and validation of emerging technologies, including biodegradation of mousse. Details on the factors that influence moussification are needed for a better understanding of its properties and its treatment. The same needs pertain to tarballs.

3.4.3 Long Term Research Needs

3.4.3.1 Oil-Suspended Particulate Matter Aggregates and Dilbit Emulsification

The interaction between residual oil in the water with suspended particulate matter of organic origin (e.g., phytoplankton, detritus, extracellular released products) and inorganic origin (e.g., mineral fines) on the environmental persistence of spilled oil (sinking, oil biodegradation rates, etc.) requires further study. Formation of aggregates is presently neglected in the calculation of the oil mass balance following a spill. Research is needed to further our understanding of the properties of dilbit that preclude it from being less subject to emulsification than other crude oils. Knowledge gained might help in developing response strategies for all heavy oils.

CHAPTER 4: OIL TOXICITY AND ECOLOGICAL EFFECTS

Abstract

Chapter 4 reviews the literature on the toxicity of oil to marine and freshwater species to identify the primary toxic effects of oil, the mechanisms of toxicity, factors that affect measured or predicted toxicity, the ecological impacts of oil spills, and gaps in knowledge that obstruct the understanding of oil spill impacts and how to manage them.

Spilled oil can be rapidly lethal to fish, birds, mammals and shoreline organisms due to the readily dissolved components of oil and the physical effects of smothering and destruction of the thermal insulation and buoyancy provided by fur and feathers. Chronic and sublethal effects are associated with the less soluble components of oil such as the polycylic aromatic hydrocarbons (PAHs), and some effects may be expressed long after brief exposures. Biomagnification of hydrocarbons in food webs is not an issue because fish, birds and mammals can quickly metabolize and excrete petroleum hydrocarbons, although metabolism of PAHs often creates metabolites more toxic than the parent compound.

Data on the toxicity of oil to aquatic species underpin ecological risk assessments (ERAs) of potential oil spills and environmental impact assessments (EIAs) of actual spills. The literature on oil toxicity is rich, but uneven. The most commonly reported data are from laboratory tests of oil toxicity to selected aquatic species, particularly embryonic life stages that are most sensitive to oil. However, not all data are useful. Many studies, particularly those with algae and plants, were designed to answer highly-focused questions about specific oil spills, and it is often difficult to draw general conclusions that can be applied to new circumstances.

ERAs and EIAs also rely heavily on modeling to predict the acute and chronic toxicity of hydrocarbon mixtures from chemical properties such as lipid solubility (e.g., the Target Lipid Model or TLM). The advantages of modeling are very compelling, considering the cost and time needed to run toxicity tests for every type of oil that might possibly be spilled, or every water sample collected during an oil spill. However, statistical error limits about model predictions are rarely quantified or reported in ERAs and EIAs, despite uncertainty due to untested model assumptions about the stability of oil concentrations in water, the transformations of hydrocarbons by photooxidation or metabolic oxygenation, single or multiple mechanisms of hydrocarbon toxicity, the presence of oil in different phases, additive interactions and the relationship between acute and chronic toxicity.

The toxicity of oil to aquatic species depends on the extent of exposure to the toxic components of oil. In general, light oils rich in low molecular weight narcotic compounds, such as benzene, toluene, ethyl benzene and xylene are more acutely lethal than medium and heavy oils. Heavy fuel oils with high proportions of 3- to 5-ringed alkyl PAHs are more chronically toxic than light oils due to the disruption of embryonic development by alkyl PAHs. The concentrations of polar and heterocyclic compounds in toxicity test solutions are rarely measured, so that potential effects unique to these compounds (e.g., endocrine disruption) are not routinely assessed. Recent spills of diluted bitumen (dilbit) have raised concerns about toxicity because it is often described as a ‘dirty oil’. Nevertheless, only minor fish kills have been caused by diluted bitumen (dilbit) spills, and a single report of dilbit toxicity demonstrated that it causes the typical signs of chronic embryo toxicity at concentrations consistent with its alkyl PAH content. However, there are too few data on toxicity to state with certainty that dilbit is more or less toxic than conventional oils. Dilbit does differ from other oils in its behaviour when spilled, with a more rapid loss of volatiles during weathering and a greater propensity to sink in fresh water. Thus, impacts of spills may represent the unique interactions between the environmental behaviour of dilbit and the exposures of species that select sediment habitats where dilbit accumulates.

ERAs and EIAs may underestimate the potential impacts of oil spills because the relationships between oil exposure and toxicity are not always clear. Analyses of oil solutions in lab experiments and field surveys often combine dissolved oil and particulate oil in one measurement. However, the role of oil droplets as an exposure pathway is ill-defined, and there are significant analytical challenges in discriminating droplet and dissolved oil fractions. Oil concentrations in water change rapidly, and the spatial and temporal characterization of hydrocarbon concentrations in toxicity tests and during oil spills is often inadequate. In coastal and freshwater ecosystems, little is known about the interactive toxicity of oil with chemicals from municipal, industrial and agricultural effluents. Likewise, the interactions between oil toxicity and susceptibility to infection by pathogens are not well understood. As a consequence the impacts associated with an oil spill may be greater than expected.

Although, oil spills on land and to fresh waters are frequent in Canada, too little is known about the fate and effects of oil spilled to freshwater ecosystems. Most information about impacts is derived from marine spills assuming that oil fate, behaviour and effects are similar in both systems. Although the scale of oil spills from trains and pipelines is much smaller than spills from supertankers, the relative impacts may be as great or greater. There is less scope for dilution and degradation of oil in freshwater ecosystems, so that higher concentrations of oil in water may be maintained for longer periods. Shorelines and sediments of freshwater systems are always in close proximity to floating oil, which may accumulate in thick layers, and there is little time to react before spilled oil contaminates sensitive shorelines or aquatic species. Freshwater species are less able to avoid spill sites, and migrating or spawning species may congregate at high densities where oil accumulates. The fate of much of the oil spilled to freshwater ecosystems is often unknown, which raises questions about potential interactions of surface oil with sediments and groundwater flows out of and into streams and lakes (hyporheic flows). Contamination of sediments contributes to the exposure and effects on aquatic species that typically inhabit sediments, particularly the early life stages of fish that spawn in sediments.

In both marine and freshwater systems, oil spill cleanup can be as damaging as the spilled oil. Habitat damage is caused by the removal of oiled vegetation from the water or from riparian lands, clearing of vegetation to permit access to oiled sites, soil compaction by heavy machinery, erosion of shorelines and siltation and de-stabilization of streams by removal of oiled woody debris. Habitat damage can reduce the abundance and productivity of species using the habitat and allow the invasion of species tolerant of the new conditions. Shoreline erosion, once started, may propagate with high water levels or storm action, so that damage is ongoing and increasing in severity.

Chemical dispersion of marine oil slicks reduces the amount of oil contacting shorelines and surface species such as aquatic birds. Dispersion increases the rate at which oil is removed from the surface, is diluted and is available for microbial degradation. However, the dispersants may increase the impact of oil spills by increasing the exposure of subsurface species. In the top 10 m of water, concentrations of dispersed oil may be increased to levels toxic to fish and invertebrate embryos. While the intent of oil dispersion is to dilute the oil to concentrations below toxicity threshold limits, even brief exposures can cause delayed effects that are evident in the weeks, months and years following a spill. The net environmental benefits of dispersion represent the trade-offs between protecting easily-identified surface resources and much-less-obvious sub-surface resources and coastal/near-shore environments. Reports that dispersants and oil cause synergistic toxicity are incorrect. Dispersion simply increases the concentration of oil to which organisms are exposed. Dispersants themselves are moderately toxic to aquatic species when free in solution, but appear to be unavailable and non-toxic when mixed with oil. Thus, dispersant toxicity will depend on how accurately it is applied to oil, whether it is completely mixed with oil, and the concentration of 'free' dispersant in surface water if applications by spraying from aircraft miss the target. The environmental impacts of subsurface dispersant applications at the 2010 Gulf of Mexico DWH blowout are still being evaluated in ongoing studies. In Canada, there are concerns about the potential impacts of chemically-dispersed oil on east coast fisheries. Evidence–based net environmental benefit analysis is essential to support decisions about appropriate oil spill response options, including dispersants.

Although it is clear from laboratory studies that oil is highly toxic to aquatic species, oil spills are often followed by years of debate on actual impacts. Cause-effect relationships are often obscured by a lack of baseline data on affected species and by a high variability in population characteristics and productivity. Variations in oil exposure and effects on a given population are associated with movements into and out of affected areas, avoidance of oil exposure, fisheries closures, delayed effects of toxicity and density-dependent changes in reproduction and survival. Cause-effect is also obscured when chemical, biochemical or molecular indicators of oil exposure and effects in live or dead specimens are not included in monitoring programs. Without these indicators, it is difficult to eliminate alternative causes of disease and mortality. Post-spill monitoring is often perfunctory and ecosystem recovery is defined by how quickly organisms re-colonize spill sites and not by how quickly ecosystem function and productivity are restored. Overall, there is a lack of solid epidemiological sampling designs and a potential bias towards 'false negatives', i.e., concluding that oil spills caused no or mild effects on aquatic species, when in fact important effects occurred but were not detected. Impact on human use of natural resources are also not considered in a systematic way, and there is growing interest in assessing oil spill impacts on 'ecosystem services', i.e., *"the benefits provided by ecosystems to humans that contribute to making human life both possible and worth living".*

Oil exploration and development in northern and Arctic regions has raised concerns about the potential for unique sensitivities of Arctic species to oil spills. Based on a limited array of toxicity comparisons, Arctic fish and invertebrate species do not appear any more or less sensitive than more temperate species when tested at equivalent temperatures. Thus, data from temperate species could be used for a first approximation of risks of oil spills to Arctic ecosystems. However, the behaviour and fate of oil in Arctic ecosystems can be strongly affected by low temperatures, ice cover and the interactions of Arctic species with ice. For example, marine mammals are forced to breathe at small gaps in ice sheets, where floating oil may accumulate. Differences in oil spill impacts between Arctic and temperate regions may be driven more by factors that affect the exposure of organisms to oil than by differences in sensitivity to oil.

The capacity to identify, measure and manage a wide array of potential effects of oil spill is often limited by a paucity of appropriate tools and data. This chapter provides a series of specific research needs throughout the text, and these needs are summarized as follows.

Research is needed:

- At 'spills of opportunity' and experimental oil spills to identify effects on aquatic species at the level of populations, communities and ecosystems due to the acute and long-term toxicity of spilled oil;
- On how the behaviour and fate of fresh and weathered oil in different ecosystems interacts with the habitat selection and unique life history traits of aquatic species to control species-specific oil exposure and toxicity. These interactions are particularly important for diluted bitumen (dilbit) relative to conventional oils, and northern and Arctic ecosystems relative to temperate ecosystems;
- To understand how different oil types (e.g., dilbit) and spill-control agents (e.g., chemical dispersants) affect aquatic species under different environmental conditions, including interactions with contaminants from municipal, industrial and agricultural effluents;
- On mechanically- and chemically-dispersed oil to determine how oil droplets affect the exposure and toxicity of oil to different species and life stages of aquatic organisms. These studies include a need to develop analytical methods to reliably discriminate droplet oil from dissolved oil. Studies on the distribution and effects of dispersed oil under exposure conditions similar to those that may be encountered during response operations (including subsurface injection of dispersants) are of particular importance;

- On strategies and protocols to recover spilled oil that avoid or minimize habitat damage, methods to restore damaged aquatic and riparian habitats and models to define the balance between the environmental costs of natural remediation and oil spill cleanup;
- On methods for finding and measuring spilled oil in different compartments of freshwater and marine ecosystems, for measuring exposure and toxicity of oil to aquatic species *in situ*, and for assessing the structure and function of ecosystems that reflect the extent and time to recovery following oil spills;
- On the contamination of ground water due to soil contamination and the entrainment of oil droplets into bed sediments of rivers by surface water-ground water exchanges;
- To develop standardized oil toxicity test methods for all classes of aquatic organisms to enable reliable comparisons of toxicity among oils, species and different environmental conditions (e.g., salinity, temperature), including rapid changes in oil concentrations in water; and
- To refine models that predict acute and chronic toxicity to aquatic species, particularly to assess the uncertainty caused by violating the assumptions underlying these models and to reduce the variance of model predictions.

Introduction

A primary concern of oil spill responders is to understand and limit the effects of spilled oil on ecosystems, natural resources and the economies and communities that depend on them. These concerns are the main drivers of prospective or retrospective ecological risk assessments (ERAs) or environmental impact assessments (EIAs) which are conducted to understand and mitigate the impacts of future developments (e.g., oil pipelines) and to investigate the effect of oil spills or chronic oiling from urban or industrial sources. Knowledge of the ecological impacts of spilled oil is derived from observational studies following actual spills and experimental laboratory studies, primarily toxicity testing with individual species. While laboratory studies of oil toxicity to species of invertebrates, fish and birds are abundant and detailed, research on oil spill effects on marine mammals, populations of organisms and ecosystem structure and function is often sparse or non-existent. The unevenness of understanding is due to differences in the questions being asked and the logistical difficulties and costs of conducting larger-scale research, including outdoor mesocosm experiments and full-scale field experiments.

The nature of concerns regarding oil spills is also changing. Past perceptions of oil spills were based on high-profile shipping disasters, where large volumes of oil were spilled with widespread acute effects on wildlife and shoreline oiling. Perspectives have changed due to the extensive research following the 1989 *Exxon Valdez* oil spill (EVOS) in Prince William Sound, AK. There is now a greater awareness of the potential persistence of oil, the ongoing exposure of aquatic species due to their behaviour and life habits, and the delayed and cumulative effects of exposure to oil and to other stressors. Concerns are growing for the potential effects of spills in extreme environments as exploration and development expand into Arctic ecosystems and into very deep offshore waters. Similar concerns relate to potential impacts during extreme seasonal conditions (winter, flooding, droughts, etc.) and impacts in remote wilderness areas that are not readily accessible for spill response. The expansion of mid-continent oil production in North America has highlighted the increasing frequency of freshwater oil spills and the question of whether knowledge of marine spills can be applied directly to managing spills to fresh waters. Recent spills of ultra-light oil, heavy fuel oils (HFOs) and diluted bitumen raise questions about the fate, behaviour and impacts of oil with extreme properties and whether the understanding of conventional oils can be applied successfully to predicting impacts of these oils when spilled.

This chapter provides an overview of what is known about oil toxicity and ecological impacts of oil spills to aquatic environments. The discussion of terrestrial effects is limited to the water-land interface, i.e., to susceptible shorelines, including salt marshes or wetlands where spilled oil is blown ashore, and riparian lands of rivers and lakes where spilled oil may be deposited by flooding. For shorelines and riparian lands, there are also concerns about potential habitat destruction by the oil spill response itself. This chapter is based on several comprehensive reviews (Engelhardt 1983; Leighton 1993; NRC 2005; Hodson et al. 2011; Lewis and Pryor 2013; Beyer et al. 2015; Logan et al. 2015) to avoid repeating summaries that have already been published. Information from these reviews is presented in a synthesized form but, where appropriate, some original papers are explained in detail to illustrate a point. Where still valid, research recommendations from these reports are repeated. Data from primary publications are summarized in **Appendix D, Table D.1**, which was first assembled by Hodson et al. (2011), enlarged by Logan et al. (2015), and enlarged and re-formatted for this review. The numbers of citations to original papers reflects the upsurge of interest following the 2010 Deepwater Horizon (DWH) oil spill, and this report is heavily weighted towards recent studies with fish, the most numerous in the literature.

4.1 Effects of Oil on Aquatic Organisms

The effects of oil on aquatic species start with exposure to oil or its components. Exposure may be derived from:

Biomagnification – a food chain or food web phenomenon whereby a substance or element increases in concentration at successive trophic levels. Biomagnification occurs when a substance is persistent and is accumulated from the diet faster than it is lost due to excretion or metabolism.

- External coatings of oil, particularly in air-breathing species that must surface frequently and cannot avoid contact with surface slicks of oil;
- Inhaled aerosols of particulate oil and volatile hydrocarbons by air-breathing aquatic turtles, birds and mammals that contact surface oil (Engelhardt 1983);
- Oil ingested by aquatic birds and mammals that groom after being contaminated, that forage on beaches or intertidal zones contaminated by oil, or that ingest oil associated with algae or with organic or inorganic particulates (Engelhardt 1983; NRC 2005). Although invertebrates do not metabolize or excrete petroleum hydrocarbons quickly, and can contribute to the dietary exposure of predators, petroleum hydrocarbons do not typically biomagnify in food webs. *Unlike persistent chlorinated compounds, most hydrocarbons can be readily metabolized and excreted by fish, bird and, mammals. However, rates of uptake, metabolism and excretion will vary among species and with environmental factors, such as temperature.*
- The dissolved components of oil that partition from water to lipids across respiratory membranes of aquatic species that breathe via gills (invertebrates, fish), and across cell membranes of microbes and algae.

The toxicity of oil to each species varies with exposure, and exposure is a function of oil type, environmental conditions and the life history and physiology of each species. Details about exposure and factors controlling the rates of exposure for different species will be discussed in the reviews of oil toxicity that follow.

4.1.1 Immediate effects of an oil spill

The first and most obvious effect of an oil spill is the contact of oil with shorelines and organisms that inhabit the water's surface, including birds, marine mammals and reptiles. Birds are highly vulnerable because they spend most of their time on water (diving birds) or shorelines (wading birds). Birds and fur-bearing animals, such as seals, sea otters and sea lions, are immediately affected because oil sticks so readily to feathers and fur. When waterfowl and fur-bearing animals come in contact with oil they usually succumb by loss of buoyancy and hypothermia because oil destroys the insulating properties of plumage and fur. Smooth-skinned mammals, such as dolphins and whales, are generally less affected by direct contact with oil. Ingestion of oil, often from grooming to remove oil from fur or feathers, causes anemia, pneumonia, intestinal irritation, kidney damage, altered blood chemistry, decreased growth and decreased production and viability of eggs. Among reptiles, turtles are considered the most susceptible to surface oiling, oiling of nests on beaches or direct ingestion of oiled prey. Possible effects of oil on turtles can include egg and hatchling mortality, a reduction of hatchling size and weight and an increase in respiration rate (RPI 1991).

Mortality due to hypothermia is not instantaneous. Lightly-oiled animals can sometimes recover by grooming to remove small traces of oil, and many animals can be rescued and cleaned. Rates of recovery will depend on: the extent of oiling; the capacity of different species to tolerate the stresses of capture, cleaning, recovery in captivity and re-introduction to the wild; the dose of oil consumed by grooming before rescue; and the size and technical capacity of the rescue effort (Clumpner 2015). Clumpner (2015) identified a need for professional organizations to quickly rescue and treat affected animals.

The littoral zones of aquatic ecosystems extend from the high water mark of shorelines to relatively shallow waters along shore, including the intertidal areas of marine ecosystems. The littoral zone is quite sensitive to stranded oil because it serves as permanent and seasonal habitat for many aquatic species uniquely adapted to periodic exposure to air (e.g., during tidal cycles), turbulence and a wide range of temperatures. Oil may smother sessile species of invertebrates or plants that inhabit the littoral zone when winds, tides or currents bring oil ashore. If the coating of oil is sufficiently thick, it prevents access to sunlight, oxygen, soluble plant nutrients (e.g., N, P), planktonic organisms for filter feeders and removal of waste by flushing with water. It will also impede the movements of organisms to feed, reproduce and avoid predation. This is especially important in low energy environments, where layers of oil are not removed by wave action. For salt marsh plants, oiling of the lower portion of plants and roots is more damaging than coating of leaves and stems, especially if oiling occurs outside the growing season. More damage is experienced if there is repeated contamination of sediments in areas where the oil may persist. Shorebirds and wading birds can be affected by oil in the intertidal area. Land animals, such as raccoons, that scavenge for food in intertidal areas and use them for shelter may ingest oil while eating exposed prey and may become coated in oil while exploring exposed flats and grass beds. The challenge for shoreline cleanup is to remove the oil without killing the organisms that are coated. In most cases, this is impossible, and often the best that can be done is to remove the oil quickly and completely to allow re-colonization of the affected area by healthy organisms from adjacent un-oiled habitats.

4.1.2 Plants

Lewis and Pryor (2013) provided a comprehensive review of publications on the toxicity of 41 crude oils and 56 dispersants to 85 species of unicellular and multicellular algae, 28 wetland plants, 13 mangroves and nine seagrasses. *However, the authors concluded that the database was inadequate to support ERAs of oil toxicity to algae and plants, primarily because the high diversity of methods and measurements (e.g., 107 different response parameters) prevented generalizations*. Effect concentrations varied by six orders of magnitude (0.002 to 10,000 mg/L) and the most sensitive response was embryo fertilization of *Fucus*. Few useful endpoints were derived for risk assessments because most studies were in response to large marine spills and were experimentally diverse. For dispersants, most studies were of formulations that are no longer used, although there have been a few studies of Corexit® EC9500A and Corexit® EC9527A. For example, EC9527A was about 10-40 times less toxic than EC9500A to germination rates of the brown macroalga, *Phyllospora comosa*.

Although oil toxicity to phytoplankton species has been reported frequently (e.g., Garr et al. 2014), it has been difficult to determine if major oil spills cause irreversible damage. Effects on plankton are often mitigated by the rapid dispersion and weathering of oil, recruitment of unexposed organisms from adjacent areas due to currents and mixing, and rapid growth rates.

The primary interactions between oil and phytoplankton may be the physical adherence of oil onto their surface (Lee et al. 1985) and the capacity of algae to absorb hydrocarbons and mediate oil transport within the ecosystem as a result of filter feeding and/or sedimentation processes (Beyer et al. 2015).

Shoreline and riparian plants are another matter. An experimental application of weathered medium-light MESA (Medium South American crude oil) to a Nova Scotia salt marsh suppressed the growth of the predominant plant species, *Spartina alterniflora* (Lee et al. 2003a). Although natural recovery occurred within the same growth season, there was a secondary longer-term change in the plant community; *Salicornia*, a more tolerant and opportunistic plant species, increased in relative abundance. Oil toxicity to salt marsh plants also occurred following the DWH oil spill (Beyer et al. 2015). For some species, only the emergent portion of the plant was affected, and vegetative cover was restored following cleanup. However, where oil penetrated sediments, the roots died and marsh and coastal shorelines were subject to accelerated erosion. This effect was halted only when plants recovered and re-invaded several years after initial oiling. *The role of chemical dispersants in facilitating the transport of oil into marsh sediments is unknown (Lewis and Pryor 2013).* Following the EVOS, aggressive cleaning of shorelines caused significant impacts on abundance and reproduction of the marine macrophyte, *Fucus sp.*, even though it was relatively insensitive to oil (Van Tamelin and Stekoll 1996). The loss of this dominant plant caused a major reduction in habitat and food for associated populations of coastal invertebrates and fish. Full recovery of *Fucus* production required four years or more in the most affected areas.

The effects of oil on freshwater plants are much less studied (Lewis and Pryor 2013), although oil tolerance has been observed in species of bulrushes. Transplants of the three-square bulrush sedge (*Scirpus pungens*) collected from the shores of the St. Lawrence River survived, grew and produced new shoots in sediments contaminated with MESA over a range of concentrations comparable to those associated with oil spills (Longpré et al., 2000). Similarly, a spill of a heavy fuel (HFO 7102) into Wabamun Lake, AB, had little direct effect on the abundance and productivity of softstem bulrush, *Schoenoplectus tabernaemontani* (Thormann and Bayley 2008; Wernick et al. 2009). About 149,500 L entered the lake after accumulating particles of soil and vegetation (Debruyn et al. 2007; Hollebone et al. 2011). Most remained close to shore, contaminating reed beds and sinking to the sediments as tar balls (Hollebone et al. 2011). Bulrush biomass, cover, height and seed head production were unaffected despite heavy oiling and residual contamination of sediments. Nevertheless, there was a major impact on bulrushes caused by the cutting of oiled bulrushes at the sediment surface and the flushing and/or vacuuming of contaminated sediments (Thormann and Bayley 2008). The amount of oiled plants was reduced successfully, but so was the density and biomass of plant rhizomes. The severity of impacts increased with water depth and included lower rates of seed germination, seedling growth, rhizome survival and re-growth. As the predominant shoreline plant, the bulrush provided habitat for nesting aquatic birds, including western grebes (*Aechmophorus occidentalis*), and reproduction of forage fish species and northern pike (*Esox lucius*). Overall, the physical damage to bulrushes of cleanup operations severely reduced the quality of habitat for key aquatic species for several years. Residual tar balls, some of which leaked fresh oil, also persisted for up to 18 months (Hollebone et al. 2011).

Following the June 2012 spill of light sour crude to the Red Deer River, AB, Rood and Hillman (2013) assessed the response of vegetation to floodplain and shoreline oiling and subsequent natural recovery at a previously-established field site. Over the summer period, young balsam poplar trees lost leaves that had been oiled, and growth was checked. However, as the oil weathered and dried on the trees, new shoots emerged on contaminated stems and from roots underneath contaminated surface soils. The overall, effects on trees were limited and due primarily to oil coatings that blocked carbon dioxide uptake and water transpiration. This study demonstrated that leaving oiled vegetation undisturbed to recover on its own prevented habitat damage due to cleanup and avoided colonization of damaged riparian lands by invasive plants. However, the report was limited to one field season only, and no data were presented on impacts on other types of vegetation or animals typical of the riparian zone.

In northern freshwater ecosystems, Hellebust et al. (1975) demonstrated that experimental spills of Norman Wells crude oil to a lake in the MacKenzie River valley caused little effect on planktonic algae in open water other than a blue-green algal bloom. However, the growth of attached filamentous algae was inhibited in open waters, as was the growth and development of sedge species (emergent vegetation) in wetlands at the edge of the lake and in oiled plots back from the edge of the lake. Effects were characterized by the death of roots and emergent tissue of *Carex* species, and a lack of chlorophyll and growth of *Equisetum sp* (horse tails) and moss (*Scorpidium scorpiodes*). Initial effects were caused by the thick layer of oil that limited light penetration, but later effects were associated with the redistribution of oil to the root zone of macrophytes and the accumulation of oil on substrates that supported periphyton. *Wetland macrophytes were highly sensitive to oil, particularly at the margins of open water, with implications for overall productivity of wetlands and the destruction of habitat for aquatic or semi-aquatic animal species.*

Recommendation: **Toxicity tests with plants should be conducted to define clear exposure-response relationships, median effective (EC50) and threshold concentrations, and tissue concentrations associated with effects. Field studies are needed to determine the comparative fate, behaviour and effects of oil in wetlands with varied hydraulic regimes (bogs, fens, marshes, swamps), including areas of permafrost. Habitat restoration methods for shoreline vegetation need to be developed to ensure the rapid recovery of shoreline ecosystems and the optimum balance between oil cleanup and habitat protection.**

4.1.3 Invertebrates

The toxicity of crude and refined oils to invertebrates is derived directly from laboratory toxicity testing, and indirectly from field studies of individual species or changes in structure of exposed invertebrate communities (usually benthic invertebrates because they are relatively immobile and provide spatial patterns of response). There is a reasonable database of acute median lethal concentrations (LC50) for freshwater and marine species, but variations in sensitivity among species with different habitats, life histories and developmental stages (i.e., embryos vs. adults) are not fully understood. For example, Lee et al. (2000) found differences in sensitivity between the mystery snail (*Viviparus georgianus*) and the mimic pondsnail (*Pseudosuccinea columella*) in a controlled oil spill experiment at a wetland site along the St. Lawrence River (Ste. Croix, QC) that were attributed to feeding habits. *V. georgianus*, a detritivore, assimilated contaminants directly from sediments, while *P. columella*, a herbivore, assimilated contaminants indirectly, presumably from oiled vegetation. Although laboratory tests may provide an objective and precise measure of toxicity, toxicity is not absolute and varies with species, life stage and test conditions (Section 4.3), as well as the properties of the oil tested. *For acute lethality, species sensitivity distributions implied that marine invertebrates were no more or less sensitive to a variety of test oils than fish species* (Barron et al. 2013; details in section 4.2.1). As observed for other aquatic species, dissolved petroleum hydrocarbons appear more bioavailable to invertebrates than particulate or droplet oil (reviewed by Dupuis and Ucan-Marin 2015).

Effects on invertebrate species and communities were evident following the EVOS. The dominant taxa in intertidal communities affected by the spilled oil and cleanup procedures included: limpets, barnacles (three species), mussels, snails (two species) and oligochaetes (worms) (Highsmith et al. 1996; Hooten and Highsmith 1996). Effects were caused by oil toxicity, smothering and the loss of habitat when *Fucus* beds were destroyed by cleanup activities. Cleanup procedures, such as washing, steaming or mechanical removal, destroyed some animals, such as grazers (e.g., periwinkles), or their food supply (biofilms on rocks). Two groups, barnacles and oligochaetes, increased in abundance because they rapidly colonized space left by missing species and they consumed oil-degrading microbes. Potential impacts on other organisms would include a reduction in food supply for consumers of intertidal plants and invertebrates, such as shorebirds, diving ducks, otters and even bears. Recovery was incomplete two years following the spill and contamination of mussel beds, including the mussels themselves, persisted more than three years after the spill (Babcock et al. 1996).

Following the DWH spill, laboratory experiments demonstrated the acute toxicity of mechanically- and chemically-dispersed MC-252 (Macondo) oil to crabs (*Rhithropanopeus harrisii*, *Callinectes sapidus*) (Anderson et al. 2014) and mysid shrimp (*Americamysis bahia*) (Hemmer et al. 2011). In contrast, field studies during the spill found surprisingly few effects on invertebrates, with no reports of mass mortalities on oiled shorelines or in coastal waters (reviewed by Beyer et al. 2015). Growth rates of shrimp were reduced in coastal embayments affected by the spill (Rozas et al. 2014), likely due to the closure of shrimp fisheries which increased their abundance (van der Ham and de Mutsart 2014) and depleted their food supply (Beyer et al. 2015). Although caged filter-feeding mussels and oysters were exposed to oil-contaminated particulates during the spill, there was no evidence of assimilation of oil-derived carbon in samples collected after the spill, as indicated by stable isotope ratios in shell and soft tissues (Carmichael et al. 2012b; Fry and Anderson 2014).

Oil dispersants enhanced the exposure, uptake and toxicity of oil to invertebrates, but the opposite was true for fiddler crabs (*Uca minax*) perhaps because of complex relationships among oil droplet size, methods of dispersion and species-specific pharmacokinetics (Chase et al. 2013). For example, in a laboratory exposure of the copepod *Calanus finnmarchicus* to oil droplets from physically- and chemically-dispersed Troll oil, filtration rates were inversely proportional to oil concentrations (Nordtug et al. 2015), due to avoidance, clogging of copepod filtering structures or toxicity. Nevertheless, the filtering rates were sufficiently high that zooplankton could conceivably enhance the rate of removal of oil from water (Nordtug et al. 2015).

As with fish species, invertebrate embryo development is particularly sensitive to oil exposure. Exposure of adult sea-ice amphipods (*Gammarus wilkitzkii*) to a continuous flow of water from an oiled bead column caused little effect on adults but led to a high frequency of abnormalities in embryos carried in their brood pouch (Camus and Olsen 2008). The fertilization success of oyster eggs (*Crassostrea virginica*) was diminished by oil exposure, as were trocophore and D-stage development, with subsequent increased rates of deformities, reduced overall survival and reduced activity of survivors (Laramore et al. 2014). These data suggest that trends and conclusions from studies with fish embryos (Section 4.1.4.2) may also apply to invertebrate embryos.

The potential impacts of oil spills on terrestrial invertebrate species that interact with emergent vegetation in salt marshes are not well studied (Beyer et al. 2015), a research need also relevant to freshwater riparian lands affected by oil spills (e.g., the Kalamazoo River spill, Chapter 8).

Recommendation: Research is needed on interactions between the physiology, life history and habitat characteristics of invertebrates and susceptibility to oil exposure and toxicity.

4.1.4 Fish

The toxicity of oil to fish is treated in greater detail than for other aquatic species, primarily because more research has been done. Many of the interactions between the chemistry of oil and its toxicity to fish may also apply to other species.

4.1.4.1 Acute toxicity

Fish are at risk of acute exposure to oil in the 24 to 48-hour period following a discrete spill to large marine or freshwater ecosystems. However, fish kills are typically brief and localized because of the rapid loss of the acutely lethal low molecular weight (LMW) components of oil due to dilution and weathering. In contrast, acute mortality can be extensive when there is an ongoing point source of oil, e.g., in a high-gradient river where oil is distributed rapidly but not highly diluted before weathering occurs (e.g., pipeline break, Pine River, BC, reviewed in Hodson et al. 2011).

The acute lethality of oil is associated primarily with LMW components, such as monoaromatics (e.g., BTEX), diaromatics (naphthalene and alkyl naphthalenes) and short-chain alkanes (< C12) (NRC 2005). Metals, such as aluminum, copper, nickel, vanadium and mercury, occur in most crude oils, with concentrations increasing from light to heavier crudes (reviewed by Dupuis and Ucan-Marin 2015). However, these metals have not been associated with the acute toxicity of oil to aquatic biota, either because concentrations are sub-toxic, or the metals are not sufficiently bioavailable in acute exposures. Environmental contamination by metals, particularly mercury and vanadium, is evident near oil production facilities (Lee 1983; Kelly et al. 2010). The sources are predominantly extraction processes, and in the case of the Alberta oil sands, airborne and waterborne particulates released by the erosion of surface soils during bitumen mining.

Sublethal effects of acute exposure are also evident and include biochemical signs of exposure to polycyclic aromatic hydrocarbons (PAHs) (e.g., Ramachandran et al. 2004a), avoidance of oil solutions and suppression of feeding behaviour (Lari et al. 2015) and delayed effects of embryo toxicity, such as impaired swimming of juvenile fish (e.g. Mager et al. 2014; Section 4.7.1.2). However, most publications on acute exposures concern only the lethality of petroleum hydrocarbons and modeling for risk and impact assessments.

The acute lethality of oil is usually attributed to LMW hydrophobic petroleum hydrocarbons that partition into lipid membranes and cause mortality by narcosis, a general term for an array of effects on lipid membrane receptors and functions (Campagna et al. 2003). Narcotics include non-polar compounds (e.g., benzene, naphthalene) and polar compounds (e.g., heterocyclic hydrocarbons; Table 2.1), which differ somewhat in their water solubility, bioavailability and toxicity. Larger compounds, such as alkyl PAHs (alkyl PAHs) with three or more rings, contribute less to acute toxicity because they are taken up more slowly than LMW compounds (McGrath and Di Toro 2009). Narcotics are sufficiently water soluble to reach maximum concentrations in water in contact with fresh, un-weathered oil within two hours (NRC 2005), but *most are lost from water within two days by volatilization, biodegradation and dilution (Chapter 2). As a consequence, lethal concentrations in water are not sustained unless there is an ongoing discharge of oil (NRC 2005).*

K_{ow} (octanol-water partition coefficient): the ratio of the concentrations of a compound in *n*-octanol (a water-insoluble phase that mimics tissue lipids and floats on water) to the concentrations in underlying water, at equilibrium.

BCF - The bioconcentration factor or ratio of concentrations in tissue to concentrations in water.

The acute toxicity of hydrocarbons to aquatic biota can be estimated from octanol-water partition coefficients (K_{ow}) (McCarty and Mackay 1993). Aquatic organisms exposed to solutions of hydrocarbons accumulate them in proportion to K_{ow} **(Figure 4.1)**. Mortality occurs when tissue concentrations reach a ‘critical body residue’ or median lethal dose (CBR or LD50) of approximately 5 mM in tissue lipid (McCarty and Mackay 1993). There are linear relationships between K_{ow} and BCFs, or LD50s across an array of hydrocarbons (**Figure 4.1**), so that LC50s for individual hydrocarbons can be estimated mathematically from K_{ow}. Curvilinearity reflects reduced rates of chemical uptake due to the increased miscibility of compounds with water at lower values of K_{ow}, and steric interference of diffusion of larger compounds through membranes at higher values of K_{ow}. Within the linear range of K_{ow} models, mixtures of hydrocarbons appear to act additively when expressed as toxic units (TU), allowing the estimation of the toxicity of mixtures from the partial TU contributions of each component of the mixture.

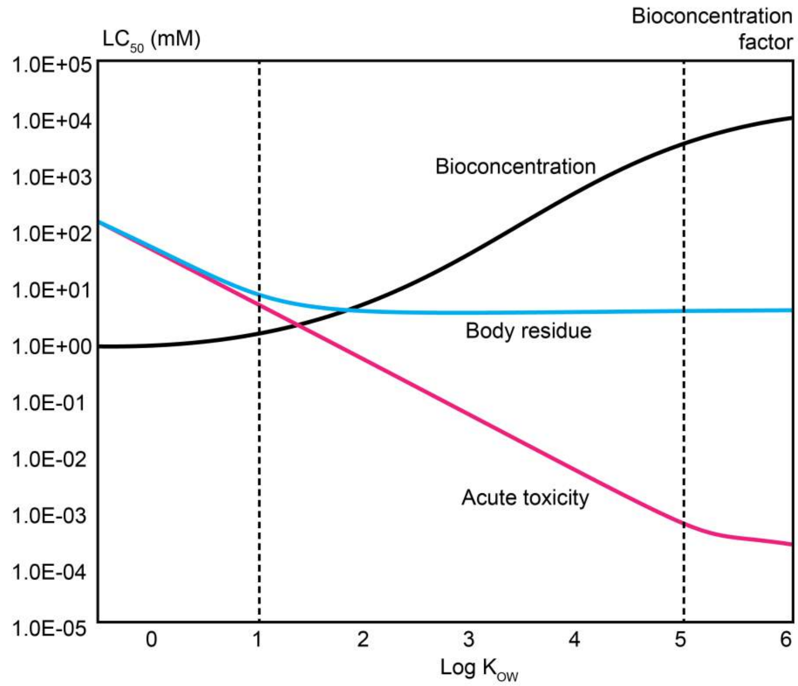


***Figure 4.1**. The general relationships among the octanol-water partition coefficients (K_{ow}) of neutral organic compounds and their bioaccumulation and acute toxicity (narcosis) to fish. The horizontal portion of the 'body residue' regression represents the critical body residue or median lethal dose (LD50) of 5 mM common to most narcotics. Adapted with permission from McCarty, L.S., and D. Mackay. 1993. Enhancing ecotoxicological modeling and assessment. Body residues and modes of toxic action. Environmental Science &.Technology 27:1718-1728. Copyright (1993) American Chemical Society.*

Toxic Unit (TU): The ratio between the concentration of a compound in water and its LC50. When water concentrations exceed the LC50 (> 1.0 TU), test organisms will die rapidly; when less than the LC50 (<1.0 TU), mortality occurs more slowly and fewer organisms die.
- Two compounds act additively when 0.5 TU of compound A plus 0.5 TU of compound B (or 0.3 of A and 0.7 of B) cause 50% mortality of exposed organisms.
- Two compounds are termed synergists when toxicity appears more-than-additive.
- Two compounds are termed antagonists when toxicity appears less-than-additive.

These predictable relationships among properties of hydrocarbons form the basis for mathematical models to estimate the total dose received, the dose-rate and the acute lethality of mixtures of hydrocarbons from the concentrations measured in water. These include the target lipid model (TLM) (Di Toro et al. 2000; McGrath and Di Toro 2009); the Oil Toxicity and Exposure model (OILTOXEX)(French-McCay 2002); the PETROTOX model (Redman et al. 2014); and ecological models for the Barents Sea (Olsen et al. 2013). These models provide a very convenient tool for estimating exposure of aquatic organisms to hydrocarbons, and the risk of acute lethality following oil spills. However, they are less successful in predicting sublethal toxicity associated with highly specific mechanisms of action (MOAs) such as interactions of PAHs with specific cardiac receptors (Section 4.1.4.2).

A primary obstacle to modeling the acute lethality of actual spills is often the inadequate characterization of the toxic components of oil or water samples (NRC 2005). The models are also based on a variety of assumptions (text box) and cannot be validated before spills. Validation following a spill is challenging due to the problem of finding dead organisms and characterizing their exposure to oil. Variance about regressions relating log LC50 to log K_{ow} is also large, with predicted values often one- to two-orders of magnitude above or below measured values (McGrath and Di Toro 2009), and model errors are rarely incorporated into quantitative uncertainty estimates in ecological risk assessments. The original LC50 values from which the models were first derived (e.g., Di Toro et al. 2000; French-McCay 2002) were also generated prior to 2000 from a heterogeneous array of chlorinated and non-chlorinated compounds and may not be representative of all petroleum hydrocarbons, especially for compounds with K_{ow} values greater than 5.3 (See section 4.3).

Assumptions inherent in models of oil mixture toxicity based on K_{ow} and narcosis

- All chemicals in the TLM model share a single common mode of action (MoA) of narcosis;
- Hydrocarbon concentrations in water are constant with time;
- Tissue lipid concentrations are at equilibrium with water concentrations;
- Metabolism of hydrocarbons does not change tissue concentrations or rate of exposure;
- Metabolites of hydrocarbons do not differ in their toxicity from parent compounds;
- Concentrations of compounds in mixtures are adequately characterized;
- The K_{ow} values of chemicals used to develop models encompass the range of K_{ow} values for petroleum hydrocarbons that contribute to acute lethality of oil;
- The models can predict the toxicity of hydrocarbons with log K_{ow} > 6, beyond the linear range of the statistical relationship (0-5.3) (McCarty and Mackay 2003);
- Models developed with data from un-substituted PAHs apply to alkyl PAHs;
- There are no synergistic or antagonistic interactions in mixtures, only additivity;
- There are no mixture interactions with other compounds in water, natural or anthropogenic; and
- Only dissolved hydrocarbons are present in the aqueous phase; non-aqueous phase oil (droplets) is not present.

Recommendation: Models predicting the acute lethality of oil should be refined to narrow confidence limits about model predictions by restricting toxicity data for model development to petroleum hydrocarbons and to single test species.

4.1.4.2 Chronic and sublethal toxicity

Chronic and sublethal effects of oil on fish are associated with either chronic exposures (e.g., oil stranded in sediments) or with the delayed or lingering effects of acute exposures. Effects range from the first genetic and molecular responses of cells to impacts on rates of reproduction, growth, disease and survival. Exposures to oil may be via respiratory uptake of hydrocarbons from water (most common), direct contact with droplets (an emerging area of research), the diet or maternal transfer to eggs (not well studied). Most studies of waterborne oil reference the concentrations of total PAHs (TPAHs) and/or total petroleum hydrocarbons (TPHs) in test solutions that affect 50% of test organisms. The EC50 and LC50 values for chronic exposures range from 0.3–60 µg/L TPAH and 0.03 – 11 mg/L TPH (**Figure 4.2, Appendix D, Table D.1**; Hodson et al. 2011; Logan et al. 2015). These concentrations are well within the range of concentrations anticipated in surface waters near slicks of un-dispersed oil or in plumes of chemically-dispersed oil and only brief exposures (one to 96 hours) to these concentrations can cause embryo toxicity (McIntosh et al. 2010; Section 4.2.3). The variance among studies reflects differences in species sensitivity, the mix of toxic components unique to each oil (Section 4.2.2), and the methods of preparing, testing and characterizing solutions of oil (Section 4.3).

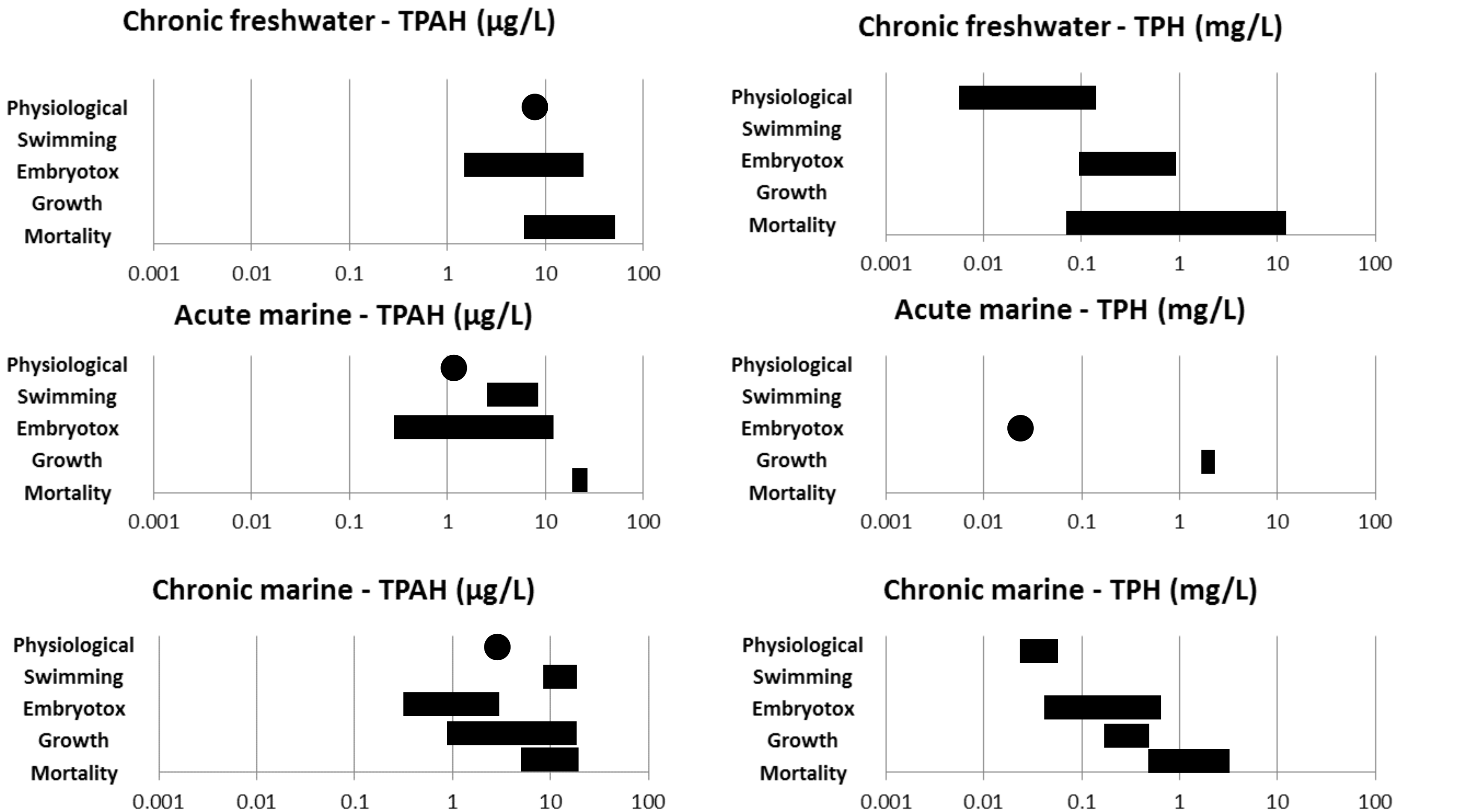


Figure 4.2 *Sublethal (EC50 values) and lethal (LC50 values) concentrations of total polycyclic aromatic hydrocarbons (TPAH) and total petroleum hydrocarbons (TPH) reported for fish subject to acute (1-96 h) or chronic (>96 h) exposures to oil. The black rectangles represent the range of concentrations reported to cause a given effect, and the solid circles indicate only one measurement was available. Data were drawn from studies reporting measured concentrations (**Appendix D, Table D.1**: Kocan et al. 1996; Marty et al. 1997; Carls et al. 1999, 2008; Little et al. 2000; Brand et al. 2001; Couillard et al. 2005; Greer et al. 2012; Gulec and Holdway 2000; Pollino and Holdway 2002; Perkins et al. 2005; Shen et al. 2010; Olsvik et al. 2011; Wu et al. 2012; Gardiner et al. 2013; Incardona et al. 2014; Mager et al. 2014; Martin et al. 2014; Dussauze et al. 2015; Madison et al. 2015; Sørhus et al. 2015).*

For juvenile or adult fish, the overall effect of oil exposure is to reduce fish production at spill sites (Reviewed by Dupuis and Ucan-Marin 2015). Oil toxicity may include reduced rates of growth and increased rates of infectious disease (Section 4.1.4.4), mutations and possibly cancer (Section 4.1.4.5) and disruption of sexual maturation and reproduction.

Reproductive effects include lower concentrations of sex steroids, such as plasma estradiol, slower gonadal growth and delayed time to sexual maturity (reviewed in Brown-Peterson et al. 2014). These effects are more typical of chronic rather than delayed toxicity, and may involve endocrine disruption by hydrocarbons that mimic steroid hormones, or increased rates of hormone metabolism by enzymes that oxygenate hydrocarbons. Establishing links between oil exposure and effects on reproduction is complex because effects depend on the stage of maturation when fish are first exposed (Truscott et al. 1983). *Identifying and interpreting the effects of oil spills on reproductive performance of fish will be complicated by a high variability in their sensitivity to endocrine disruption—timing is critical!*

Research following the EVOS highlighted the high sensitivity of fish embryos to oil exposure, as judged from the low concentrations of hydrocarbons causing toxicity (e.g., Carls et al. 1999; Appendix D, Table D.1). Ecologically, embryo sensitivity is also imparted by their inability to avoid exposure to hydrocarbons. Embryo-toxicity is often considered an effect of chronic exposure, i.e., an exposure that constitutes a significant portion of an organisms' life span or development stage. However, there are instances of delayed effects, where a response typical of a chronic exposure occurs long after a brief or acute exposure (Section 4.2.4). *Delayed effects may not be obvious at the time of a spill, but may become evident as changes in rates of recruitment, growth, reproduction, disease or mortality in the months or years following a spill, depending on the life history of the species exposed***.** In this review, chronic toxicity will refer to effects of exposures that exceed 96 hours or effects of acute exposures that are evident 96 hours or more following exposure.

Embryo toxicity due to exposure to oil or to individual PAH is characterized by blue sac disease, a syndrome that includes: pericardial and yolk sac edema; cardiotoxicity; craniofacial, ocular and spinal deformities; degeneration of muscle somites, peripheral neurons and endothelial cells; fin erosion; failure of swim bladders to inflate; altered behaviour and swimming ability; and induction of cytochrome P-450 (CYP1A) enzymes (e.g., Schein et al. 2009; deSoysa et al. 2012; Incardona et al. 2013; details in Section 4.1.4.4). Not all of these signs of toxicity are evident in embryos of each species exposed to oil, but all species exhibit many of these signs.

> **Cytochrome P450:** The cytochrome P450 gene (*cyp1a*) codes for CYP1A proteins, enzymes that oxygenate PAHs as the first step in their excretion. 'CYP1A induction' refers to the increased synthesis of CYP1A proteins when the *cyp1a* gene is up-regulated after specific PAHs or alkyl PAHs bind to the intracellular aryl hydrocarbon receptor protein (Billiard et al. 2002).

The high sensitivity of embryos to oil toxicity is due to the large number of genes that are up-regulated or activated only during embryonic development. It is critically important that these genes be activated in the proper sequence, to the proper extent and at the proper time for normal development. However, PAHs, the components of crude oil associated with embryo toxicity (Section 4.1.4.3), can bind to protein receptors in cells to interfere with protein function or to activate a broad spectrum of genes. Thus, oil exposure interferes with the carefully orchestrated sequence of events essential for normal development of tissues such as the heart, leading to impaired cardiac function (e.g., Incardona et al. 2004, 2009; Hicken et al. 2011).

The up- and down-regulation of a large number of genes represent the primary reactions to oil exposure, indicating that hydrocarbons have interacted directly with cellular receptors to initiate gene transcription. Activation of one gene can cause the secondary activation of many more, because they are often linked directly or indirectly. One of the most commonly reported responses to exposure to crude oil and to chlorinated hydrocarbons such as PCBs, is activation or up-regulation of the *cyp1a* gene, a member of a large family of cytochrome P450 genes (e.g., Olsvik et al. 2011, 2012; Sørhus et al. 2015). There are many genes involved in embryo development that are 'downstream' of *cyp1a* and that are also activated with exposure to PAHs. Activation of these genes at an inappropriate stage in embryonic development may be one cause of PAH and dioxin-like toxicity (Billiard et al. 2008).

The CYP1A proteins are enzymes that oxygenate double bonds in PAHs as the first step in their excretion. Thus, increases in CYP1A enzyme activity following gene activation cause a rapid increase in the rate of excretion of PAHs. For example, the half-life of tissue retene (7-isopropyl-1-methylphananthrene, a C-4 alkylphenanthrene) in rainbow trout is estimated as <14 hours at 15 °C (Fragoso et al. 1999). High rates of oxygenation of PAHs can prevent acute lethality by facilitating the clearance of PAHs from tissues (Hicken et al. 2011). *Not all PAHs will induce CYP1A enzymes (Basu et al. 2001; Billiard et al. 2002), but all PAHs accumulated by fish exposed to oil are subject to oxygenation by CYP1A enzymes because mixtures of PAHs in oil include those that cause induction.* In vertebrate species exposed to PAHs in oil, the up-regulation of *cyp1a* can increase CYP1A enzyme activity by up to 1,000-fold, in parallel with increasing toxicity (Brinkworth et al. 2003; Colavecchia et al. 2007; Madison et al. 2015). Thus, CYP1A induction provides a reliable indicator of PAH exposure and potential effects in vertebrates; invertebrate species do not express *cyp1a* genes and excrete PAHs more slowly than vertebrates.

The oxygenation of PAHs can also release reactive oxygen species (ROS) and reactive metabolites of PAHs into the cell (reviewed by Crowe et al. 2014). There are frequent reports that genes involved in combating oxidative stress, suppressing mutations associated with the effects of ROS on DNA, and responding to general cellular stress are up-regulated in oil-exposed fish embryos (e.g., Olsvik et al. 2011; Madison et al. 2015). Exposure of cod larvae (*Gadus morhua*) to mechanically-dispersed oil caused the expression of genes related to drug metabolism, endocrine system development and function and lipid metabolism, with the highest response for *cyp1a* (Olsvik et al. 2011). Genes related to bone resorption were up-regulated while those related to bone formation were down-regulated, consistent with craniofacial and spinal deformities frequently reported in oil-exposed embryos.

Unlike acute lethality, there are multiple MOA that contribute to embryo toxicity, but they are not mutually exclusive. Craniofacial deformities reflect the disruption of the normal transformation of neural crest cells to specific cell and tissue types (de Soysa et al. 2012). Cardiac toxicity represents unique interactions of PAHs with cardiac receptors, so that the heart does not develop to its proper form and function (Incardona et al. 2004, 2006, 2013; Hicken et al. 2011; Scott et al. 2011). These interactions were evident *in vitro* as impaired ion regulation, cell signaling and contractile rhythmicity in oil-exposed cardio-myocytes of blue-fin (*Thunnus thynnus*) and yellow-fin (*Thunnus albacores*) tuna (Brette et al. 2014). Cellular effects corresponded to changes in cardiac function in whole embryos when oil-exposure impaired atrial-ventricular signaling and coordination (Incardona et al. 2009). Edema and circulatory failure of embryos may follow impaired cardiac function or be due to oxidative damage to lipid membranes in endothelial cells of blood vessels following CYP1A metabolism of PAHs. CYP1A induction was evident early in embryonic development and was prominent in gills, liver, kidney, eyes and endothelial cells of blood vessels of fish embryos exposed to retene (Brinkworth et al. 2003), bituminous sediments (Colavecchia et al. 2007) or oil (Incardona et al. 2013).

The predominant MOA underlying chronic toxicity varies with the PAH being tested. For example, the embryo toxicity of pyrene depends on its interaction with the arylhydrocarbon receptor protein and CYP1A induction (Incardona et al. 2006). In contrast, phenanthrene, retene and dibenzothiophene are toxic even when CYP1A protein synthesis is blocked (Incardona et al. 2004, 2005; Scott et al. 2011). In fathead minnow and white sucker embryos exposed to bituminous sediments, CYP1A enzymes were induced in every tissue showing histopathology, and the extent of induction was correlated to rates of mortality and pathology (Colavecchia et al. 2007). Although correlations imply a direct role of CYP1A enzyme activity in toxic effects, they may simply reflect PAH concentrations in each tissue.

The metabolism of PAHs can also increase their toxicity and carcinogenicity (Section 4.1.4.5). Inhibition of CYP1A induction demonstrated that metabolites of retene appear more toxic to trout embryos than the un-metabolized parent compound (Hodson et al. 2007b; Scott and Hodson 2008; Scott et al. 2009). Similarly, phenolic derivatives of 1-methylphenanthrene were up to four-fold more toxic to Japanese medaka (*Oryzia latipes*) embryos than un-substituted 1-methylphenanthrene (Fallahtafti et al. 2012). The pattern of –OH substitution affected toxicity, and may reflect the propensity for biotransformation of phenolic derivatives to *p*-quinones. Unlike acute lethality, chronic toxicity was unrelated to solubility or K_{ow} because all four OH-substituted congeners had the same modeled K_{ow}. Similarly, co-exposure of trout embryos to phenanthrene (does not induce CYP1A) and to an inducer of CYP1A enzymes caused greater toxicity to trout embryos than exposure to phenanthrene alone (Hawkins et al. 2002), consistent with the idea that metabolites were the toxic forms of PAHs. The MOA of alkyl PAHs likely includes oxidative stress because the severity of embryo toxicity and signs of oxidative stress were reduced when rainbow trout (*Oncorhynchus mykiss*) embryos were co-exposed to retene and Vitamin E, an antioxidant (Bauder et al. 2005). *The balance between the accelerated rates of excretion of PAHs and the production of excess reactive intermediates will determine whether oxidative stress and pathology occur and will depend, in turn, on the extent and duration of oil exposure and accumulation of TPAHs*.

Research and monitoring of the effects on fish of the DWH spill focused largely on embryo toxicity in laboratory or mesocosm experiments. The MC-252 oil caused similar cardiotoxicity as Alaska North Slope (ANS) crude oil, and pathology and up-regulation of *cyp1a* genes by both oils were correlated to concentrations of TPAH (Incardona et al. 2013). Oiled sediments from affected coastal embayments caused the same toxic effects on zebrafish embryos as reference sediments spiked with MC-252 oil (Raimondo et al. 2014) and were consistent with effects caused by chemically-dispersed oil, with a threshold sediment concentration of TPAH between 2 to 27 mg/kg. Gulf killifish (*Fundulus grandis*) embryos exposed to sediments from coastal areas contaminated by the DWH oil spill responded with the typical signs of embryo toxicity (Dubansky et al. 2013) Similarly, killifish from areas contaminated by oil showed the down-regulation of 1,070 genes and the up-regulation of 1,251 relative to un-oiled reference areas (Garcia et al. 2012) and many gene responses indicated physiological and reproductive impairment (Whitehead et al. 2012). The genomic responses were reproducible in laboratory exposures of killifish (Pilcher et al. 2014) and spotted sea-trout (*Cynoscion nebulosus*) (Brewton et al. 2013) to MC-252 oil, with clear activation of excretory pathways (e.g., *cyp1a*). Activation of *cyp1a* was associated with growth depression in sea-trout (Brewton et al. 2013) and with gene expression in killifish indicative of changes in gene transcription, cell cycle progression, RNA processing, DNA damage, oxidative stress and apoptosis (Crowe et al. 2014; Pilcher et al. 2014). Impacts on the reproductive biology of spotted sea-trout sampled from oil-contaminated coastal embayments of Louisiana and Mississippi were reported by Brown-Peterson et al. (2014). Impacts included delayed maturation, smaller relative gonad sizes and a reduced frequency of spawning, but no biological or chemical indicators of exposure to oil were reported.

In general, there is a good understanding of the waterborne concentrations of TPHs, TPAHs and specific un-substituted and alkyl-substituted PAHs causing chronic toxicity, and sufficient data to support risk assessments of oil spills.

<u>Recommendation:</u> Additional research is needed to reduce the uncertainties in translating laboratory data for risk and impact assessments. In particular, relationships need to be established among waterborne concentrations of hydrocarbons, tissue concentrations, genomic responses and toxic effects. Furthermore, mechanisms of action and critical exposure periods for impacts on the reproductive biology of sexually maturing fish need to determined, as does the role of PAH metabolism in toxicity of oil to fish.

4.1.4.3 Hydrocarbons causing chronic toxicity

To establish the connection between exposure and environmental impacts of spilled oil, it is essential to know which constituents of oil cause toxicity and at what concentrations. *The components of oil that cause chronic toxicity to fish embryos are considered to be alkyl PAHs (Table 2.1), including heterocyclics such as alkyl dibenzothiophenes* (Rhodes et al. 2005). TPAHs comprise about 0.2 to 6.5% by weight of oil, depending on its source and type, and alkyl PAHs comprise 80-95% of TPAHs in crude and refined oils (Wang et al. 2003). *Alkyl PAHs partition from oil to water more slowly than monoaromatics, reaching peak concentrations within four to 12 hours (NRC 2005). Because of their lower volatility, alkyl PAHs persist in water longer than monoaromatics and are dissipated primarily by advection and diffusion. Over weeks or months, alkyl PAHs stranded on substrates will continue to partition from oil into water* (NRC 2005), as was evident from a comparison of the cardiotoxicity to zebrafish (*Danio rerio*) embryos of two crude oils (Jung et al. 2013).

A number of indirect approaches have been used to identify the components of oil causing chronic toxicity to fish embryos. Correlations between concentrations of alkyl PAHs in test solutions and the chronic toxicity of ANS crude oil (**Table 2.2**, Appendix B) to fish embryo development were reported by Carls et al. (1999). Using a toxic units approach, Barron et al. (2004) evaluated four mechanistic models of the chronic toxicity of the constituents of oil test solutions to pink salmon (*Oncorhynchus gorbuscha*) and Pacific herring (*Clupea pallasi*) embryos and concluded that toxicity was best described by summing the toxic unit contributions of alkyl phenanthrene concentrations.

More direct evidence was provided by studies of the chronic embryo toxicity of individual PAH congeners that produced the same syndrome of blue sac disease as did exposure to crude and refined oils. The PAHs tested are commonly found in oil and included 3- to 5-ringed un-substituted PAH (Hawkins et al. 2002; Incardona et al. 2004, 2006, 2011; Rhodes et al. 2005), alkyl phenanthrenes (Billiard et al. 1999; Kiparissis et al. 2003; Turcotte et al. 2011), hydroxylated derivatives of alkyl phenanthrenes (Fallahtafti et al. 2012), alkyl chrysenes and alkyl benzo[a]anthracenes (Lin et al. 2015), and dibenzothiophene and dimethyl dibenzothiophene (Rhodes et al. 2005). Effects-driven-chemical-fractionation (EDCF) of crude oil (Hodson et al. 2007a) and heavy fuel oil (Adams et al. 2014b; Bornstein et al. 2014) linked embryo toxicity to fractions and sub-fractions of oil that contained 3- to 5-ringed alkyl PAHs. Alkyl PAHs were progressively enriched in serial fractions of HFO in parallel with increased toxicity, and comprised up to 25% of total hydrocarbons in toxic fractions. Fractions dominated by LMW compounds, including BTEX and alkyl naphthalenes (2-ringed PAH), or by high molecular weight (HMW) aliphatics (waxes), resins or asphaltenes (Table 2.1) were non-toxic at the concentrations tested.

Overall, many of the chronic effects of oil on fish embryos can be attributed to 3- to 5-ringed alkyl PAHs. The chronic toxicity of PAHs to fish has been associated with their binding to the AhR protein (Section 4.1.4.2). However, other components of oil may also be AhR agonists, as indicated by *in vitro* reporter gene assays of hydrocarbons extracted from aquatic worms exposed to SARA fractions (Section 2.1.1) of eight different crude and fuel oils (Vrabie et al. 2012). The AhR agonists were aromatic, hydrophobic, resin-like compounds primarily in mid- to high-boiling point fractions, and some were resistant to biotransformation *in vitro*. There were too many compounds in isolated fractions to identify specific agonists, although these characteristics correspond to some un-substituted and alkylated PAHs and heterocyclic aromatic compounds.

In all EDCF studies, most components of toxic fractions were unidentified and may have included polar compounds not typically analyzed in detail in oil. Polar compounds in a biodegraded Norwegian Sea crude oil and in 14 fractions of WAF solutions created by high performance liquid chromatography (HPLC) separation were identified as agents affecting rainbow trout liver cells in culture (Melbye et al. 2009). Responses included induction of CYP1A and vitellogenin (egg yolk protein, an indicator of estrogen-like compounds), as well as cytotoxicity. The main contributors to all three responses were the water-soluble components of the polar fraction that contained 70% of the hydrocarbons, while fractions enriched with PAHs and alkyl PAHs were less potent. However, ketone and quinone derivatives of a wide array of 3- to 6-ringed non-alkyl PAHs showed significant potency for activating the *cyp1a* gene in mammalian cell assays (Misaki et al. 2007). In contrast, a survey of the endocrine-disrupting potential of 11 crude and refined oils using *in vitro* mammalian cell assays demonstrated that all contained compounds with some estrogenic or androgenic potency, but potencies were 10^4 to 10^7-fold lower than those of the reference compounds estradiol and testosterone (Vrabie et al. 2010, 2011). Although polar compounds, such as phenols, are typically associated with endocrine effects, no equivalent fractionation studies have been conducted to identify whether components of oil cause endocrine disruption *in vivo*.

Similarly, the toxicological significance of the oxygenated hydrocarbons measured in MC-252 oil (Table 2.2) over an 18-month period of weathering following the DWH oil spill is unknown (Aeppli et al. 2012). However, aromatic and polar compounds extracted from biodegraded ANS crude oil were chronically toxic to embryos of inland silversides (*Menidia beryllina*) (Middaugh et al. 2002). Extracts of the saturate fraction were non-toxic at the concentrations tested, but the fractions recombined represented the additive effects of the aromatic and polar compounds. This experiment did not analyze oxygenated compounds or the toxicity of untreated oil, but they demonstrate the presence of significant concentrations of residual toxic compounds in biodegraded oil. It is essential that oil toxicity tests include as complete an analysis of test solutions as possible, including polar fractions. Routine analyses by GC-MS identify about 40-50 different PAHs or families of alkyl PAHs, in addition to BTEX and saturates.

<u>Recommendation:</u> Research is needed to identify petroleum hydrocarbons associated with different toxic effects.

Models have been developed for ERAs to predict the chronic toxicity of oil (e.g., TLM) (McGrath and Di Toro 2009). However, chronic toxicity is not modeled directly. Instead, acute lethality (LC50) is calculated by the model, and chronic toxicity is estimated from the average ratio of concentrations causing acute and chronic toxicity (acute-chronic ratio or ACR) for algae, invertebrates and fish. However, observed ACR values ranged 10-fold higher and lower than the average, likely because of large differences in the physiology and biochemistry among widely differing plants and animals used as test species. *All of the assumptions underpinning the acute lethality model (Section 4.1.4.1) are inherent in the chronic toxicity model, with additional critical assumptions about chronic toxicity that weaken its application to risk assessment (text box). Not surprisingly, the TLM model does not predict the chronic toxicity of petroleum hydrocarbons very accurately, and a further 'correction factor' of 2.0 must be used to compensate for the average under-estimate of toxicity, which in itself is variable* (McGrath and Di Toro 2009). While these models have been applied to the results of published toxicity tests with a variety of species and a variety of chemical mixtures (McGrath and Di Toro 2009), the results were not very satisfactory, primarily because the case studies examined were not designed for this purpose.

Assumptions inherent in models of acute lethality applied to chronic toxicity

- The MOAs for chronic toxicity and acute lethality are the same (narcosis), regardless of a wide array of sublethal effects caused by oil (Section 4.1.4.2) and large differences in the genetics and physiologies among algae, invertebrates and fish; and
- A single mean ACR derived from tests with algae, invertebrates and fish predicts the chronic toxicity of all PAH to fish embryos.

Although current models carry a high risk that predicted toxic effects could be under- or over-estimated by a wide margin, the advantages of modeling mixture toxicity for ERAs and EIAs are very compelling, considering the cost and time needed to run chronic toxicity tests for every oil that might possibly be *spilled or every oil sample collected at a spill.* Recently, Redman et al. (2014) used the PETROTOX model to estimate the chronic toxicity of HFO and fractions of HFO created for an EDCF using the reported concentrations of PAHs in each fraction. There was a good correspondence between toxicity predicted from the PETROTOX model and toxicity measured directly (Adams et al. 2014b), although more research is needed to identify sources of error in both the model and the EDCF.

Recommendation: Models of chronic toxicity must be developed from results of chronic toxicity tests and not from acute toxicity tests via application factors.

4.1.4.4 Physiological and pathological responses

The molecular responses of fish exposed to oil in laboratory experiments (Section 4.1.4.2) suggest that there should be equivalent responses in fish surviving an oil spill and related changes in physiological functions that could affect the performance of those fish. Following the 2007 oil spill from the *Hebei Spirit* off the coast of Korea, Jung et al. (2011, 2012) measured the activity of liver CYP1A enzymes and the concentrations of PAH metabolites in bile of two benthic species, marbled flounder (*Pseudopleuronectes yokohamae*) and flatfish (*Paralichthys olivaceus*), sampled in 2008 and 2009. These biomarkers[1] provided clear evidence that fish were accumulating and responding to PAHs from the oil spill in a spatial pattern that corresponded to measured concentrations of PAHs in sediments. The consistent responses relative to fish from a reference area during the two years following the spill indicated the persistence of bioavailable hydrocarbons in sediments.

Balk et al. (2011) also observed similar CYP1A and bile metabolite responses of Atlantic cod and Atlantic haddock (*Melanogrammus aeglefinus*) sampled from the North Sea close to oil drilling and production platforms. Fish captured close to the platforms also showed enhanced activities of antioxidant enzymes, changes to fatty acid composition, increased concentrations of arachidonic acids and reduced concentrations of Vitamin E (antioxidant), indicating not only accumulation and metabolism of petroleum hydrocarbons but also signs of oxidative stress. Elevated concentrations of DNA adducts in haddock suggested a reaction of PAH metabolites with double bonds in DNA, mutagenicity and a potential for carcinogenicity. Oxidative stress was also suggested by increased non-enzymatic antioxidant capacity in serum of Gulf killifish (*Fundulus grandis*) exposed to MC-252 oil (Crowe et al. 2014).

Effects of PAHs and oil exposure on the development and function of the embryonic heart should impair the capacity of survivors to swim, capture prey and avoid predation. Effects on embryonic circulation persist into the juvenile stages of fish, a latent effect evident long after exposures to oil. Embryos of mahi-mahi (*Coryphaena hippurus*) that survived 48 hour exposures to weathered MC-252 oil (1.2 µg/L TPAH) showed a reduced critical swimming speed in swim tunnels when tested 24 days after exposure (Mager et al. 2014). Fish exposed to oil (30 µg/L TPAH) for 24 hours as juveniles were 30-fold less sensitive than fish exposed as embryos. For both groups, no changes occurred in metabolic rate or respiratory efficiency (Mager et al. 2014). Delayed effects on capacity to swim were also observed in adult zebrafish 10 to 11 months after exposure as embryos to ANS oil (24-36 µg/L TPAH), a concentration that caused 10-15% mortality of embryos during exposure (Hicken et al. 2011).

Exposure of fish to crude oil is also associated with impaired immunocompetence and an increased susceptibility to disease, likely due to the effects of PAHs on cellular and humoral immune responses (Reynaud and Deschaux 2006). However, relating the prevalence of disease to oil exposure in field studies is complicated by the number of uncontrolled environmental stressors that act on fish simultaneously or in different sequences and that can affect immune responses. For example, a variety of hypotheses were examined to explain the crash in abundance of Pacific herring in Prince William Sound following the 1989 EVOS (Pearson et al. 1999), including: a direct effect of oil exposure on survival and

[1] *Not to be confused with the term ;biomarkers' used to describe internal hydrocarbon standards in oil analyses; Chapter 2*

recruitment of larvae; an indirect effect of oil on the food web supporting herring; the population outgrew its food supply; an epizootic of viral hemorrhagic septicemia (VHS) was triggered by environmental conditions, an over-abundance of herring, impaired immune function, and the stress of oil exposure; overharvesting; and natural chaotic population dynamics. Pearson et al. (1999) concluded that there was no clear link between the decline in herring abundance and oil exposure and that an array of natural factors contributed to the decline. This view was reinforced by Marty et al. (2003) who could not establish a temporal link between epizootics and the 1989 oil spill. In contrast, Thorne and Thomas (2007) related post-spill epizootics in herring with their surfacing behaviour and interaction with oil slicks at the time of the spill, genetic abnormalities that corresponded to oil toxicity and trends in fishery statistics and distribution of herring predators (sea lions). They concluded that the collapse of the herring fishery was a five-year event triggered by the oil spill.

The immune response to pathogens is also complex and can lead to different interpretations of cause and effect, depending on circumstance. For example, when juvenile Pacific herring were exposed to different concentrations of oil in water and their immune systems were challenged by subsequent exposures to a pathogenic bacterium that causes vibriosus, their response depended on duration of oil exposure (Kennedy and Farrell 2008). After one day of exposure, resistance to infection was enhanced, while the opposite occurred after 57 days of exposure. Resistance was associated with a short-term physiological stress response while long-term sensitivity was associated with impaired ion regulation.

Fish diseases can also enhance sensitivity to oil exposure. The cumulative mortality of juvenile flounder (*Pseudopleuronectes americanus*) increased with an eight-week exposure to sediments contaminated with Hibernia crude oil (100 to 2,200 μg/g). At each sediment concentration, mortality was greater in fish infected by the hemoprotozoan, *Trypanosoma murmanensis*, relative to un-parasitized controls (Khan 1991).

During the DWH oil spill, unusual external lesions on red snapper (*Lutjanus campechanus*) in the northern Gulf of Mexico were associated with several pathogenic bacteria. Arias et al. (2013) proposed a causal association between lesion prevalence and exposure to oil. They assumed that the affected fish were immunocompromised by oil exposure, corresponding to previous experience with other fish species (reviewed by Dupuis and Ucan-Morin 2015). However, no evidence was collected of actual exposure to oil, so this proposed cause-effect relationship was not well supported.

<u>Recommendation:</u> Research is needed on the cause of epidemics in fish and the interactions among pathogens, environmental stressors, exposure to oil and prevalence and severity of disease, including chemical and biological markers of oil exposure and effects.

4.1.4.5 Gene mutations and cancer

Mutagenicity and carcinogenicity are often linked to metabolism of specific PAHs. It is well-established that oxygenation of benzo[a]pyrene (BaP; Table 2.1), a pro-carcinogen, by CYP1A enzymes can generate an array of non-carcinogenic and carcinogenic metabolites (e.g., diol-epoxides of BaP) (reviewed by Shugart 1995). Carcinogenic metabolites cause gene mutations by covalent bonding to cellular DNA and interfering with normal replication.

Non-alkylated, pro-carcinogenic PAHs, such as BaP are found at measurable concentrations in crude and refined oils (Yang et al. 2011) but they comprise much less than 15% of total PAHs (Wang et al. 2003). Although methyl phenanthrenes are demonstrated mutagens in cell culture assays (Lavoie et al. 1981, 1982), the mutagenicity of most alkyl PAHs is not well characterized, primarily because few of the thousands of congeners of alkyl PAHs are commercially-available for testing. No papers were found that report carcinogenicity of alkyl PAHs to fish.

<u>Recommendation:</u> Research is needed to assess the mutagenicity and carcinogenicity of alkyl PAHs to fish.

There has been a variety of studies reporting mutagenicity in fish and invertebrates following marine oil spills (e.g., Bolognesi et al. 2006), but none so far have associated elevated rates of cancer in fish with exposure to oil. Cancers are most evident in benthic species (sessile, in constant contact with bottom sediments, feed on benthic organisms), such as English sole (*Pleuronectes vetulus*; marine) (Myers et al. 2003) and brown bullhead (*Ameiurus nebulosus*; freshwater) (Baumann et al. 1996). Benthic species experience a longer and more intense exposure to potential carcinogens than those in the pelagic zone. The absence of PAH-related cancers in fish following oil spills may reflect the slow onset of chemically-induced cancers (months to years; Baumann et al. 1996), the even slower appearance of frank tumours and the lack of long-term monitoring of fish populations at sites of major oil spills. Interpretation of data on cancer prevalence in fish is also confounded by:

- The age of fish sampled at contaminated and reference sites (prevalence increases with age);
- Co-exposure to other carcinogens not derived from oil;
- Migration of fish to and from sites of exposure; and
- Cell proliferation in response to infections by viruses, bacteria and parasites (Baumann et al. 1996).

In contrast, at sites where high concentrations of pyrogenic PAHs predominate in sediments due to urban and industrial development, there is clear evidence of cancer in locally-resident fish (Myers et al. 2003). Cancer is characterized by premature mortality of older fish and corresponding changes in the age structure of the population. However, overall abundance may not change because sexual maturation and reproduction precede mortality (Collier et al. 1992; Bauman et al. 1996). The discovery of tumours in fish exposed to pyrogenic PAHs may be related to the higher concentrations of carcinogenic PAHs, such as BaP and nitrogen heterocycles, and to the long-term intensive studies typical of sites affected by urban and industrial pollution.

<u>Recommendation:</u> Long-term monitoring of impacts following an oil spill should include histological examinations of fish to assess the prevalence of cancer and other diseases in relation to oil exposure.

4.1.4.6 Population and ecosystem consequences of oil toxicity

The effect of oil exposure on cardiac development, structure and function in fish embryos with subsequent impairment of swimming stamina (reviewed in Section 4.1.4.4) indicates that population level effects on fish will follow an oil spill due to a decreased ability of juveniles to capture prey and avoid predation. The ecological relevance of embryo toxicity is the potential for reduced rates of growth, survival, abundance and productivity. These effects would not be predicted from standard embryo toxicity tests because they are delayed and evident only when the fish are free-swimming, months or years following exposure. For example, Heintz et al. (2000) observed a 15% reduction compared to controls in the rate of return of pink salmon released to the Pacific Ocean following sublethal exposures to oil as embryos. In contrast, pink salmon exposed to sublethal concentrations of oil as juvenile fish showed no change in returns as adults, compared to controls (Birtwell et al. 1999). The different outcomes of these two similar studies are consistent with the observed high sensitivity to oil of the developing heart of embryos and the much lower sensitivity of juveniles (Mager et al. 2014).

The behaviour and migration of salmon can also be affected by exposure of adults. Although Brannon et al. (1986) found no change in the ability of healthy adult chinook salmon to return to their home stream after a brief (one hour) exposure to Prudhoe Bay crude oil (PBCO), adult coho salmon (*Oncorhyncus kisutch*) avoided a salmon ladder contaminated with oil (Weber et al. 1981). The numbers climbing the ladder decreased in linear proportion to increasing oil concentrations. *Avoidance is good news from the perspective of survival, but bad news if salmon do not complete their spawning migration and reproduce.*

<u>Recommendation:</u> Further research is needed to determine whether poor returns of adult pink salmon that survived exposure to oil as embryos are related to changes in survival at sea, swimming capacity or response to environmental cues that guide migration.

Despite the apparent high sensitivity of pink salmon embryos to oil exposure in the lab (Heintz et al. 1999), *in situ* (reviewed in Ballachey et al. 2014) and during migration following exposure to oil as embryos (Heintz et al. 2000), the case for an effect of the EVOS on pink salmon populations in Prince William Sound remains controversial. Population modeling (Geiger et al. 1996; Heintz, 2007) suggested significant impacts of low-level exposures to oil-derived PAHs. However, the technical basis for characterizing impacts and linking oil exposure to effects on recruitment and abundance was questioned by Brannon et al. (2012), mainly because of the complexity of ecological interactions with the population dynamics of salmon and the absence of clear evidence of a decline in natural production of salmon (Brannon et al. 2006). Hatcheries and tributaries to Prince William Sound produced so many juvenile fish annually that deficits in production in tributaries affected by the spill were not easily detected. However, the opposite would occur if an oil spill coincided with the spawning of a rare or threatened species, such as the eulachon (*Thaleichthys pacificus*), in the estuaries of west coast rivers (Hodson et al. 2011).

For the DWH oil spill, there were surprisingly few reports of impacts on wild fish at sea or along the coast of the Gulf of Mexico despite numerous laboratory studies demonstrating effects of oil exposure on fish embryos and adults. Recruitment of fish to coastal marshes of Alabama appeared unaffected, as indicated by no change in marsh-associated resident or transient nekton (all actively-swimming aquatic species) over a two-year period following the spill (Moody et al. 2013). However, there were no indicators of potential exposures to oil, other than location. Similarly, the survival of fish embryos in coastal seagrass habitat appeared unchanged in 2010 following the DWH oil spill, in comparison with a previous five-year dataset (Fodrie and Heck 2011). Recruitment of red snapper on artificial reefs was more strongly correlated to dissolved oxygen concentrations and the presence of predators (age-1 fish) than to exposure to oil, and there was no evidence of year-class failure (Szedlmayer and Mudrak 2014). Similarly, a comparison between satellite-based estimates of oil distribution and the modeled spawning habitats of blue-fin tuna indicated that less than 10% of offshore spawning grounds, and 12% of the larval distribution area, would overlap with the distribution of oil slicks (Muhling et al. 2012), suggesting little impact on recruitment.

Fodrie et al. (2014) reviewed the lack of correspondence between observed effects on fish populations and expectations of impacts from laboratory toxicity studies. They cited several major factors that obscure population-level responses: high spatio-temporal variability in population demographics; movement of fish into and out of affected areas (natural 're-stocking'); fisheries closures that removed a major source of harvest mortality and that compensated for oil-related losses of fish; food web compensation (enhanced productivity due to input of oil-derived carbon); and delayed effects over several generations. Other factors could dampen population responses, such as behavioural avoidance of oil exposure, rapid dilution of oil in the open ocean (particularly following chemical dispersion) and population compensation, such as density-dependent changes in egg, juvenile and adult survival. As well, expectations of effects may be heightened by potential high-sensitivity bias in laboratory tests, depending on experimental designs. Without an obvious fish kill following a spill, as was the case with the Pine River in northern British Columbia (see below) or Asher Creek, MO (reviewed by Dupuis and Ucan-Marin 2015), it is very difficult to make an unambiguous case for sublethal, delayed or long-lasting effects. *Nevertheless, numerous laboratory studies (Appendix D, Table D.1) leave little doubt about the potential toxicity of spilled oil. Difficulties in making the case for oil spill impacts in situ do not mean that population effects do not occur; rather, highly variable population dynamics prevent firm conclusions. Overall, a potential bias in studies of effects on fish populations appears to favour 'false negatives' (no effects perceived on* *fish populations when there were effects) rather than 'false positives' (effects perceived that were non-existent or due to other factors)*. These uncertainties need to be resolved and the capacity to define population-level impacts improved.

<u>Recommendation:</u> (adapted in part from Fodrie et al. 2014): Research is needed to: 1) establish an observation network to provide pre-spill baseline data on physical, chemical and biological characteristics of aquatic ecosystems, including fish population, abundance and productivity, particularly in areas where spills are likely; 2) determine individual-level measures of genomic, physiological and demographic responses in baseline surveys as indicators of overall health, rates of disease and exposure to oil and other contaminants (e.g., Stagg et al. 2000); 3) develop a better understanding of the basic ecology and early life-history of fishes including movement, diet, habitat use and longevity and; 4) establish the links between hydrocarbon exposure of individuals and their molecular and cellular responses to signs of toxicity and pathology.

In freshwater ecosystems, EIAs and studies of the rate of recovery of oiled ecosystems are also limited by a lack of data, appropriate assessment methods, and the challenges of sunken oil. There are few field studies of the effects of spilled oil on freshwater fish, other than counts of the dead and dying immediately following a spill. The weakness of short-term census data is that counts of dead fish are often inaccurate because of a low counting efficiency in wilderness areas that are hard to access. Following a spill of sour crude into the Pine River, BC, in 2000, only a partial count of dead fish (1,600) was reported because the river was difficult to access quickly. Dead fish either decayed or were consumed by scavengers before they could be counted. As a consequence, estimates of the total kill varied widely, from 25,000 to 250,000 (Hodson et al. 2011).

Monitoring of time-to-recovery of oiled ecosystems relies too heavily on standing stocks of fish. Without measuring fish population demographics, community structure, movements and productivity (e.g., rates of reproduction and recruitment), actual recovery cannot be separated from 're-stocking' by fish from un-oiled regions of a watershed. Only small amounts of sunken residual oil in sediments could significantly reduce embryo survival and recruitment of sediment-spawning fish species. Following the 2005 spill of HFO 7102 to Wabamun Lake, AB (Section 4.1.2), most residual oil was trapped in shoreline reed beds (Hollebone et al. 2011), but some was measured in offshore spawning shoals of lake whitefish (*Coregonus clupeaformis*) (Short 2008). Debruyn et al. (2007) measured the survival and prevalence of deformities typical of oil exposure of whitefish embryos held in egg containers installed on contaminated and reference shoals in November 2005, four months after the spill. In April 2006, the prevalence of severe skeletal deformities typical of oil exposure was significantly higher among hatched survivors at the exposed site than at a reference site. The rates of pathology were correlated to the amount of TPAHs accumulated by passive samplers installed adjacent to the egg containers.

<u>Recommendation:</u> Research is needed to: 1) develop methods to find and measure residual oil in reed bets and bed sediments of lakes and rivers; 2) assess oil exposure and toxicity of residual oil to embryos of fish species with different spawning media (e.g., sediments, vegitation, water column); and 3) measure the density, survival and recruitment of naturally-spawned fish embryos in oil-contaminated ecosystems.

Some of these research needs may be met by studies of actual 'spills of opportunity'. The current understanding of the ecological effects of oil in marine and coastal environments is derived largely from studies of the 1989 EVOS. Innovative research on the distribution, effects, and persistence of oil in Prince William Sound is cited throughout this chapter and clearly informs current research on the 2010 DWH spill. For Canada, the legacy of the extensive research on these two spills is a much stronger capacity for ERAs and EIAs and the opportunity to advance our knowledge by building on a solid technical base of understanding.

Much could also be learned if there were small areas of contaminated sites 'set aside' for natural attenuation of spilled oil. A well-known example is a segment of contaminated shoreline untouched 30 years following the *Arrow* spill of Bunker C in Nova Scotia (Lee et al. 2003a). *However, the greatest potential for understanding ecological effects of oil pollution may be studies of oil spilled to experimental marine and freshwater ecosystems. Small-scale experimental spills allow the fewest practical limitations to field investigations and the greatest opportunity for research where gradients of natural environmental stressors can be controlled. To date, the few experimental spills in Canada have been extremely informative (e.g., Sergy and Blackhall 1987; Hodson et al. 2002; Venosa et al. 2002; Garcia Blanco et al. 2007), but their scopes were limited by the questions being asked. Additional experimental spills are needed to keep pace with Canada's rapidly expanding oil transportation network and the risks to a wide array of ecosystem types.*

4.1.5 Reptiles and amphibians

No species of sea turtles nest in Canada, but five of the world's seven species are sighted on an occasional basis on both the east and west coast, including green (*Chelonia mydas*), Atlantic loggerhead (*Caretta caretta*) (and a hybrid of the two), Atlantic ridley (*Lepidochelys kempii*), olive ridley (*L. olivacea*) and leatherback (*Dermochelys coriacea*) turtles (www.thecanadianencyclopedia.ca/en/article/turtle/). *While several studies of turtles in the northern Gulf of Mexico were published before and after the DWH oil spill, no links were established among the status of different species, indicators of health and exposure to oil* (Beyer et al. 2015). However, all studies identified a high risk of severe damage to populations should there be contact with oil and emphasized the need for conservation efforts to sustain populations that are under pressure from a variety of anthropogenic stressors.

Native species of turtles, other reptiles (43 species total) and amphibians (46 species) inhabit terrestrial and freshwater habitats of southern Canada, with their northern distribution limited by the boreal forest. No species inhabit the tundra zone (www.thecanadianencyclopedia.com/en/). Oil spills to aquatic ecosystems and riparian lands will create significant risks of exposure of reptiles and amphibians to petroleum hydrocarbons, as well as potential impacts on their habitats from oil spill cleanup. Turtles may be coated with oil or inhale volatiles or aerosols of oil when they surface and the eggs of species that spawn on shore may be exposed to stranded oil. Numerous studies have demonstrated that turtles, particularly long-lived predatory species at a high trophic level, bioaccumulate persistent organic pollutants and develop dose-dependent deformities (Rowe et al. 2009). However, the evidence for effects of petroleum hydrocarbons, particularly PAHs, on turtles is less established. Bell et al. (2006) reported deformities in snapping turtles (*Chelydra serpentina*) and painted turtles (*Chrysemys picta*) from a wildlife refuge in Pennsylvania that was heavily contaminated by past industrial activity with metals, PAHs and other organic compounds. The prevalence and severity of deformities far exceeded those at a reference site, and were equivalent to or greater than those reported at other contaminated sites. Although measured concentrations of PAHs in turtles at the contaminated site were far greater than at the reference site, the cause of deformities was not conclusive because the study had insufficient resources to analyze metals and other organic compounds. At this same refuge, the survival, home-range and water temperature preference of four species of freshwater turtles contaminated by an oil spill were unaffected relative to un-oiled turtles, despite their capture, rehabilitation by cleaning and release (Saba and Spotila 2003). There was a similar experience following the 2010 spill of dilbit to Talmadge Creek and the Kalamazoo River. Large numbers of juvenile and adult turtles were rescued, cleaned and released (USFWS 2015) and because some were captured and released up to five times, it was concluded that they were unharmed by the experience.

Although the short-term effects of oiling on free-swimming turtles appear negligible, there were no studies of the chronic effects of the dilbit spill or of the effects on the embryonic stages of turtles exposed to dilbit on the exterior of egg shells. For Arabian Light crude oil, eggs of snapping turtles showed a very low sensitivity to un-dispersed oil (WAF) or to chemically-dispersed oil (chemically-enhanced WAF or

CEWAF) (Rowe et al. 2009). After single doses of WAF or CEWAF were percolated through nests containing viable eggs, there were no significant effects on hatching success, weight, length, lipid content, DNA damage or overall survival post-hatch. The absence of effects corresponded to tissue concentrations that were less than those observed in deformed turtles from a contaminated site (Bell et al. 2006). In contrast, eggs of loggerhead turtles buried in nests on a Florida beach were killed by a spill of fuel oil, although the cause may have been suffocation, not toxicity (reviewed in Rowe et al. 2009).

The unique adaptations and life histories of some species, such as beach nesting by marine turtles, may create unique sensitivities to oil exposure and effects. A potential cause of mass die-off of marine iguanas (*Amblyrhynchus cristatus*) following a diesel spill in the Galapagos Islands may have been due to effects on algae, their primary diet, or on their unique gut symbionts (Wikelski et al. 2011). In fresh water, amphibians (frogs, salamanders) that spawn in clear, shallow ponds may be subject to photo-enhanced toxicity (Section 4.2.5). The toxicity of a diluent recovered from contaminated groundwater in California to tadpoles of the southern leopard frog (*Rana sphencephala*), increased by three-fold in the presence of UV-B at wavelengths and intensities typical of California (Little et al. 1998).

These limited studies reviewed are insufficient to draw firm conclusions about the relative risks of toxicity to turtles and amphibians exposed to oil. The influence of variables, such as exposure regimes (single doses vs. repeated doses or continuous exposures), species characteristics (e.g., the nature of the egg shell and chorion and permeability to hydrocarbon uptake) and the relative toxicity of LMW and HMW PAHs, remain unknown. Of particular importance in Canada are the interactions between oil exposure and the natural stressors acting on turtles that are at the northern limit of their range. Extremes of temperature and short seasons for growth and reproduction could aggravate even minor effects of oil toxicity.

Recommendation: Research is needed on the toxicity of oil to embryonic and juvenile turtles and amphibians to determine which species characteristics contribute most to sensitivity to oil and which exposure routes are most harmful.

4.1.6 Birds

*Aquatic birds are at risk of acute mortality following a spill if their feathers become contaminated***.** Bird feathers have a function in flight, water repellency and thermoregulation, and all three functions are significantly impaired by contact with oil. In severe cases, birds are unable to fly, at risk of drowning because of loss of buoyancy and at risk of hypothermia and starvation due to heat loss, accelerated metabolism to generate heat and a reduced ability to feed. Issues of thermoregulation are particularly acute if birds are:

- Oiled during winter months (marine coastal zones, Great Lakes);
- In areas influenced by currents of cold Arctic water (e.g., Gulf of St. Lawrence);
- At higher latitudes (seasonal use of Arctic islands for breeding and nesting); or
- On migration flyways in spring and fall.

Oil spills in areas frequented by aquatic birds often kill hundreds of thousands of birds. For example, the mean mortality (with 95% confidence limits) of over-wintering birds in the Gulf of Mexico during the DWH oil spill was estimated as 600,000 birds (320,000 to 1,200,000) using a carcass sampling model, and 800,000 birds (160,000 to 1,900,000 using an exposure probability model (Haney et al. 2014a, b). The most affected species were predicted to be laughing gulls (*Leucophaeus atricilla*, 32% of the population), royal terns (*Thalasseus maximus*, 15%), brown pelicans (*Pelecanus occidentalis*, 12%) and northern gannet (*Morus bassanus*, 8%). A potential source of bias in the sampling model was the low probability of recovering carcasses of oiled birds during coastal surveys. In a stranded bird survey, most of the 7,229 dead birds collected were found near the coast adjacent to New Orleans and the stricken oil platform (Tran et al. 2014), reflecting the source and distribution of oil during the spill. Shorebirds may be similarly affected and in the Gulf of Mexico it was estimated that 28 species, comprising more than 1,000,000 birds, were at risk of exposure during the DWH spill (Henkel et al. 2012). For the dunlin (*Calidris alpina*), a shorebird, 8.6% and 0.6% of live birds showed light to trace oiling in 2010/11 and 2011/12, respectively, indicating that as many as 100,000 birds could have been affected by oil (Henkel et al. 2014). This number would be even higher without cleanup operations (Beyer et al. 2015).

Similar effects were evident in northern marine ecosystems affected by oil spills, particularly if the spill coincided with breeding. In Prince William Sound, the estimated number of direct mortalities of seabirds (with 95% confidence limits) following the EVOS was about 375,000 (300,000 to 645,000), based on the numbers of oiled carcasses recovered and an intensive study of the proportion of carcasses that disappeared due to scavengers before being enumerated (Piatt and Anderson 1996). The estimated half-life of beached carcasses was ≈1 day and systematic bird surveys only began two weeks after the spill (Ford et al. 1996). Early in the spill, 100% of recovered carcasses were oiled, but the percentage oiled declined to zero within four months for a wide array of species. While acute mortality of birds, such as the common murre (*Uria aalge*; comprised 70% of beached birds), could be attributed to oil exposure, longer-term effects on abundance were much less certain due to ecosystem-wide changes in abundance and species composition of prey (fish, invertebrates) in Prince William Sound (Piatt and Anderson 1996).

Local effects of oil spills may also have continent-scale impacts. Species such as the northern gannet, common loons (*Gavia immer*) and a variety of shorebirds migrate to and from summer nesting sites in the Arctic, inland lakes and both coasts of Canada. Mortality during incidents such as the DWH oil spill may have continent-wide effects on population dynamics and abundance. Monitoring is needed to establish baseline estimates and trends in abundance and productivity of nesting populations and to assess whether oil spills in over-wintering areas or along major flyways have affected one or more species. For example, after the DWH spill, new software tools, such as Google Fusion Tables and Google Maps, were applied to an existing wildlife database to show whether the distribution of aquatic birds overlapped the area affected by the spill (Tran et al. 2014).

Sublethal oiling of birds can also affect reproduction. Even a few microlitres of oil transferred from the parent to the surface of eggs during incubation can be absorbed and cause deformities and embryo mortality. The median lethal dose (LD50) of weathered MC-252 oil applied to the exterior of mallard eggs (*Anas platyrhynchos*) was 0.5 µL or about 0.5 mg oil/egg (Finch et al. 2011). In contrast, dispersed oil was four to six times less toxic than un-dispersed oil, suggesting that the dispersant mitigated oil toxicity, perhaps by enabling a more rapid loss of oil from the egg's surface. However, Corexit® 9500 by itself at doses of 100 µL/egg caused acute mortality and lower doses reduced hatching success (Finch et al. 2011).

In areas of Prince William Sound affected by the EVOS, reproductive rates appeared lower for birds that feed in open water (e.g., kittiwake [*Rissa tridactyla*]) (Irons 1996) and on shorelines (e.g., black oystercatcher [*Haematopus bachmani*]) (Sharp et al. 1996). Relative to un-oiled areas, winter survival rates of female harlequin ducks (*Histrionicus histrionicus*) were reduced for up to 10 years following the spill (reviewed in Ballachey et al. 2014). Effects on pigeon guillemots (*Cepphus columba*) were less obvious due to the difficulties in finding well-scattered and concealed nests, but a general decline in abundance seemed to be exacerbated by the spill (Oakley and Kuletz 1996).

Understanding the impacts of oil spills on aquatic birds is limited by the small number of comprehensive surveys during oil spills and the difficulties in recovering oiled birds before they disappear. For example, in busy shipping routes off Newfoundland, the disposal of waste oil and contaminated bilge water causes a chronic and continuous loss of seabirds, such as thick-billed murres (*Uria lomvia*), as indicated by winter surveys of 13 beaches on the Avalon Peninsula (Wiese and Ryan 2003). Although deaths related to oiling have been increasing, the total number of birds killed could not be estimated from these data. Only a small fraction of the Newfoundland shoreline adjacent to shipping routes could be surveyed, and the proportion of affected birds that did not strand on shore was unknown. However, trends were validated by significant negative correlations between the percentage of murres oiled and the annual harvest, implying an impact of mortality on overall abundance.

For freshwater spills, data are not readily available for effects on aquatic birds. To cover damage assessment needs, Irons (1996) recommended the immediate collection of data on oil exposure, distribution, abundance and behaviour of birds at spill sites where baseline data is lacking. Dead fish and birds were observed in shoreline reed beds following the 2005 spill of heavy fuel oil to Wabamun Lake, AB (Birtwell 2008; Section 4.1.2), but estimates of total numbers have not been published. *The ecological significance of widespread bird mortality from oiling is also poorly understood*. Experience with the DWH spill indicates that widespread mortality of fish-eating birds may have had 'top-down' effects on the marine ecosystem of the Gulf of Mexico, changing the abundance and age structure of fish populations that supported the birds (Short 2015).

<u>Recommendation:</u> Research is needed to: 1) validate methods for estimating bird numbers and their susceptibility to oil spills; and 2) establish long-term pre-spill baselines of population abundance and an understanding of food web functioning and productivity in areas of Canada at risk of oil spills, particularly where birds over-winter (e.g., the Great Lakes), along major migratory flyways or in nesting colonies.

4.1.7 Mammals

Aquatic mammals are particularly susceptible to floating oil because they must surface at regular intervals to breathe. Some species can sense the presence of oil, and captive bottlenose dolphins (*Tursiops truncates*) have even been trained to detect and avoid oil (Engelhardt 1983), but field observations indicate that most species do not consistently avoid spilled oil; within 24 hours of the EVOS, killer whales were swimming through surface slicks (reviewed by Dupuis and Ucan-Marin 2015). Even if mammals could detect oil, exposure may be unavoidable in Arctic ecosystems if ice can herd floating oil into thick layers in breathing holes and leads between ice floes (Chapter 2). When mammals surface through oil, their skin or fur will be contaminated, and they may inhale liquid oil or oil aerosols during rapid, high-volume respiration, causing lung damage or narcosis and drowning. For filter-feeding baleen whales, exposure includes consumption of oil-contaminated plankton and, in extreme cases, baleen may be clogged by liquid oil (Engelhardt 1983).

Aquatic mammals that rely on fur for insulation face the same issues of acute mortality due to thermoregulatory failure as do birds. Only a light oiling may lead to serious heat loss and the risk of death by hypothermia or starvation. All species are not affected equally. For species that do not have fur (e.g., cetaceans), the significance of direct contamination of skin is less clear and, in fact, oil may not stick as readily to such species (Engelhardt 1983). Seals accumulate oil on fur, but hypothermia may be offset somewhat by thick layers of blubber, although there is no information about newborns. Sea otters (*Enhydra lutris*) do not have blubber for thermal insulation. If oiled, they must increase their time spent foraging to compensate for an increased rate of metabolism due to stress and thermal regulation. However, otters groom compulsively to maintain the water repellency and thermal insulation of their fur and may starve if time spent grooming increases at the expense of time spent foraging (reviewed by Sinclair 2012). Some otter populations in Prince William Sound experienced elevated mortality rates for up to 22 years following the EVOS. Mortality was associated with intermittent exposure to residual oil in intertidal sediments where otters forage for clams (reviewed in Ballachey et al. 2014).

Hydrocarbons consumed by aquatic mammals through grooming or contaminated diets can be metabolized and readily excreted, but some is stored in blubber and other fat deposits. Engelhardt (1983) speculated that stored hydrocarbons may be released into circulation when fat is consumed during periods of physiological stress (e.g., low food availability, migration, lactation), and circulating hydrocarbons may be bioavailable and toxic to the fetus or nursing newborns. Tissue pathology identified by necropsies of animals recovered after oil spills included:

- Irritation of tissues around the eyes;
- Kidney pathology that may reflect the excretion of hydrocarbon metabolites;
- Hemolysis, anemia and erythropoietic dysfunction;
- Liver and kidney dysfunction, including uremia and dehydration;
- Lesions in the upper digestive and gastro-intestinal tracts; and
- Changes to the adrenal cortex suggesting significant responses to stress and increased kidney function (Engelhardt 1983).

Mortality of a variety of sea mammals has been frequently associated with marine oil spills. Sea otters, harbour seals (Phoca vitulina), Stellar sea lions (Eumatopius jubatus), killer whales (Orcinus orca) and humpback whales (Megaptera novaeangliae) were most affected by the Exxon Valdez oil spill. Elevated rates of mortality were evident in the months following the spill in oiled areas compared to un-oiled (Loughlin et al. 1996). Higher concentrations of hydrocarbons in carcasses of otters, harbour seals and sea lions from oiled areas strengthened the connection between oil exposure and effects.

As with fish, links between oil exposure and acute and chronic effects remain controversial because most marine mammals are quite mobile and not easily studied. Mortality may not occur in the immediate vicinity of an oil spill, particularly if oil causes slow starvation due to chronic respiratory damage, disruption of thermal regulation or an inability to feed properly. For example, the estimated carcass recovery rates of cetaceans after the DWH spill were as low as 2% (Williams et al. 2011), which limits the statistical validity of any proposed cause-effect relationships. Without direct evidence of an exposure to oil, it may be impossible to discriminate oil toxicity from multiple other causes of morbidity. During the DWH oil spill, there was a prolonged ‘Unusual Mortality Event’ (UME) of bottlenose dolphin in the Gulf of Mexico (Carmichael et al. 2012a) that began before the oil spill and persisted for months afterwards. The UME overlapped in time and space with the spill, and dolphins were observed swimming and feeding in areas of oil-contaminated waters (Schwacke et al. 2014). Although the UME began before the spill, its prolongation and severity were attributed to oil exposure, implying interacting and delayed toxicity. Thinning of the adrenal cortex (hypoadrenocorticism, suggestive of chronic stress) combined with bacterial pneumonia, the primary cause of death, corresponded to previous observations of poor health in mammals exposed to other oils. Dolphins from oil-exposed areas were five times more likely to have moderate-to-severe lung disease than dolphins from an un-oiled reference site. Venn-Watson et al. (2015) strengthened the case for oil toxicity by examining dead and stranded dolphins collected from oiled and reference sites. They confirmed the high prevalence of bacterial pneumonia and hypoadrenocorticism, but eliminated algal toxins, morbillivirus infection and brucellosis as contributing factors. Similarly, Litz et al. (2014) eliminated morbillivirus and brevitoxicosis as causes of the UME. Although the proposed cause-effect relationship was biologically plausible and the effects corresponded in timing and location to possible oil exposure, the case for oil toxicity was weakened by a lack of data on concentrations of hydrocarbons or hydrocarbon metabolites in tissues, urine or bile. Similarly, there were no measurements of molecular or biochemical markers of hydrocarbon exposure or toxicity, such as elevated concentrations of CYP1A proteins or DNA adducts (Fossi and Marsili 1997). An analysis of external wipes from 13 of 35 beached bottlenose dolphin carcasses collected between May 2010 and November 2012 found residues typical of weathered Macondo oil (Stout 2015), indicating exposure at the time of the spill and ongoing exposure over the next two years. Low concentrations of hydrocarbons in digestive-tract materials were not consistent with dietary exposure. These data support the role of oil exposure in the UME event, but the cause-effect case would be stronger if data on pathology and contamination were linked for each stranded animal.

During the DWH spill, skin biopsies of sperm whales (*Physeter macrocephalus*) sampled from the Gulf of Mexico demonstrated nickel and chromium concentrations two to five times higher than background (Wise et al. 2014). Concern was expressed for potential genotoxicity, but the forms of nickel and chromium in MC-252 oil residues were not measured (the valence state determines carcinogenicity). Overall, the links between tissue metal concentrations and exposure to the DHW spill were not clear, given that the whales travelled widely throughout the Gulf, there are other sources of metals in the Gulf, including the Mississippi River, and other measures of oil exposure (tissue concentrations of petroleum hydrocarbons, biomarkers of oil exposure and effect) were not included.

<u>Recommendation:</u> There is a need for more in-depth research on the accumulation, disposition and effects of petroleum hydrocarbons and metals in marine mammals, and methods to link biomarkers of oil exposure and toxicity to specific sources of oil.

The DWH spill may have also affected marine mammal behaviour, as indicated by acoustic recordings of sperm whales that suggested they had moved away from the spill (Ackleh et al. 2012). Information about marine mammal behaviour may also be key to mitigating potential impacts on many species following spills in Canadian waters. For example, the seasonal abundance, migrations and behaviour of humpback whales in the Bay of Fundy, beluga, fin and blue whales in the Gulf of St. Lawrence, and killer and humpback whales off the British Columbia coast are well established. This baseline information has already influenced decisions on major shipping routes in the Bay of Fundy, in this case to avoid collisions, and on the siting of a major oil terminal in the St. Lawrence River estuary to minimize the potential exposure of beluga whales to oil spills.

<u>Recommendation:</u> Monitoring is needed in areas of existing and proposed oil-related activities to ensure that the seasonal and spatial use of habitat by marine mammals is well described and that risks of oil exposure are minimized.

4.1.8 Ecosystem services

The impacts of oil spills in aquatic ecosystems have been viewed traditionally in terms of oil effects on individual species, populations or ecosystems. Ecosystem services provide a different perspective on oil spill effects, focusing on values to human society that are affected, either negatively or positively, by ecological impacts.

Ecosystem services are "the benefits provided by ecosystems to humans that contribute to making human life both possible and worth living" (NRC 2013) and are derived from functioning ecosystems, i.e., the interactions among plants, animals and microbes as primary and secondary producers, among predators, prey and competitors, and between living species and environmental characteristics such as temperature and habitat. The physical and chemical properties of an environment also provide services, such as modifying climate by storing heat and carbon dioxide. Services can be classified into four categories (NRC 2013):

- *Provisioning services* (e.g., material goods such as food, feed, fuel and fiber);
- *Regulating services* (e.g., climate regulation, flood control and water purification);
- *Cultural services* (e.g., recreational, spiritual and aesthetic services); and
- *Supporting services* (e.g., nutrient cycling, primary production and soil formation).

Ideally, each service can be valued economically, allowing the damage to aquatic ecosystems from an oil spill to be expressed monetarily and in ways that are easily understood by non-ecologists. For example, when access to an ocean beach is blocked by an oil spill for several months during the tourist season, the loss of income from tourism can be accounted for in the overall cost of cleanup. An analysis of ecosystem services can provide a basis for compensating the public for lost opportunities to use the beach and the businesses or individuals who have suffered financial loss following a reduction in the tourist trade.

This concept may generate a much broader appreciation of ecological, social and economic impacts (i.e., on human well-being), the nature of damages included in a post-spill assessment, and the potential options for remediation and restoration. Its implementation will require a broader and more systematic framework for structuring programs of research and monitoring, for developing comprehensive models of how ecosystem services are generated, delivered and affected, and for identifying the trade-offs and balances in protecting some ecosystem services, potentially at the expense of others (Net Environmental Benefits Analysis). More importantly, analyses of ecosystem services will define the data that must be collected to support the approach, the extent and nature of remediation needed to restore services to their pre-spill values and include the cultural and economic values of affected communities, particularly indigenous communities, to create perspective on the question of "How clean is clean enough?"

A US National Research Council (NRC) Technical Panel provided a comprehensive review of the 2010 DWH oil spill to determine if the ecosystem services concept provided an additional and useful approach for assessing resource damage of the oil and of the spill cleanup under the US Natural Resources Damage Assessment process (NRC 2013). After examining four case studies in detail (wetlands, fisheries, marine mammals and the deep Gulf of Mexico), they identified *three primary obstacles to the comprehensive application of the concept:*

1. *A lack of baseline measurement of goods and services produced by the Gulf of Mexico ecosystems just prior to the harmful event. Only for fisheries of commercially-important species are there adequate data for an ecosystem services analysis because the mandate of fisheries agencies is to track abundance, harvest, price and overall economic activity;*
2. *The technical challenge of developing a comprehensive model to predict the ecological impacts of an oil spill and associated economic impacts. Such models can be developed from existing ecological and economic valuation models, but a major obstacle can be a lack of socioeconomic understanding and data that describe complex human dependencies on natural systems; and*
3. *The challenges of realistic and accepted economic valuations of ecosystem services, particularly for services that are not valuated in market activity (e.g., the value of deep sea sediments as a repository for persistent contaminants from oil spills). If ecosystem services cannot be valued easily, there is a risk that these services could be discounted or ignored in the decision-making process (NRC 2013).*

The relevance and value of the NRC (2013) report was derived from the legal requirements for Natural Resources Damage Assessment under the *1990 US Oil Pollution Act* (NRC 2013).

Recommendation: **To benefit from an ecosystem services approach to assessing impacts, research is needed to determine if existing regulatory frameworks for spill response, remediation and monitoring provide an adequate basis for defining and assigning responsibility for its implementation. Comprehensive ecological and socioeconomic models must be developed in collaboration with communities at risk, particularly indigenous communities to evaluate the significance of ecosystem services for marine and freshwater ecosystems.**

4.2 Factors Affecting Oil Toxicity to Fish

4.2.1 Species tested

There are considerable differences among species in their sensitivity to oil, some of which relate to their physiology and life history, some to the environmental characteristics of their habitats (e.g., temperature, salinity) and some to differences among laboratories in test methods, experimental designs and responses *measured.* Compilations of toxicity data across a wide range of species can illustrate the relative sensitivity of an individual species (**Appendix D, Table D.1**), identify the more sensitive species and define a benchmark for protecting the majority of species.

> **Species sensitivity distributions (SSDs) -** compare the cumulative proportion of species (percentile) affected by oil to a toxicity endpoint measured for each species (e.g., the 96 hour LC50). SSDs display the range of concentrations associated with a specific effect and can be used to estimate the concentrations that affect a given percentage of tested species. The 'HC5', or hazardous concentration harming the 5^{th} percentile of species, is often used in ecological risk assessments to establish toxicity benchmarks that should, in theory, protect 95% of all species from the effect represented by the endpoint.

Barron et al. (2013) provided a useful perspective on the relative acute lethality of an array of crude and fuels oils to aquatic species, as well as two dispersants tested without oil. Species sensitivity distributions (SSDs) for 227 measures of acute lethality (LC50s) for 67 fish and invertebrate species typical of warm and cold waters were expressed as measured concentrations of TPHs. Data were selected for a mix of marine and freshwater species based on several criteria, including:

- All life stages except embryos;
- Test duration (invertebrates: 48–96 hours; fish: 96 hours);
- Exposure regime—i.e., gradients of oil concentrations administered as a continuous flow of (rare) or as static tests with daily solution renewal (most common);
- Fresh oil only;
- No chemical dispersants; and
- Oil exposure characterized by measured concentrations of TPH.

HC5 values were derived from a curvilinear regression of percentile responses of 10 to 39 species against log LC50 values (mg/L TPH). *Invertebrate species were distributed evenly throughout the SSDs indicating they were not consistently more or less sensitive than fish species, as expected for a non-specific narcosis MOA typical of acute lethality.* One acknowledged bias in this study was the separation of species tested by oil type. As might be expected, northern oils (e.g., ANS crude) were tested more frequently with coldwater species, while southern oils (South Louisiana crude) were tested more frequently with warmwater species. However, for inland silversides, a warmwater estuarine fish, relative sensitivity in each SSD was not fixed but varied with the oil tested and the mix of species included (Barron et al. 2013), suggesting no consistent bias (see also section 4.2.6).

For the chronic toxicity of oil to fish embryos, SSDs were prepared from the data summarized in **Appendix D, Table D.1**, selecting only those studies reporting chronic lethal (LC50) and sublethal (EC50) toxicity values expressed as measured concentrations of hydrocarbons in test solutions (**Figure 4.3**). Some SSDs are incomplete because there were too few data for chronic LC50s expressed as TPAH concentrations, and too few data reporting chronic EC50s expressed as TPH concentrations. *Nevertheless, HC5 values calculated from the regressions of Figure 4.3, or estimated by eye, ranged over two orders of magnitude, from 0.23 to 3.2 µg/L TPAH or 10 to 190 µg/L TPH (**Table 4.1**), and the SSDs indicated no consistent differences between freshwater or marine species in sensitivity.*

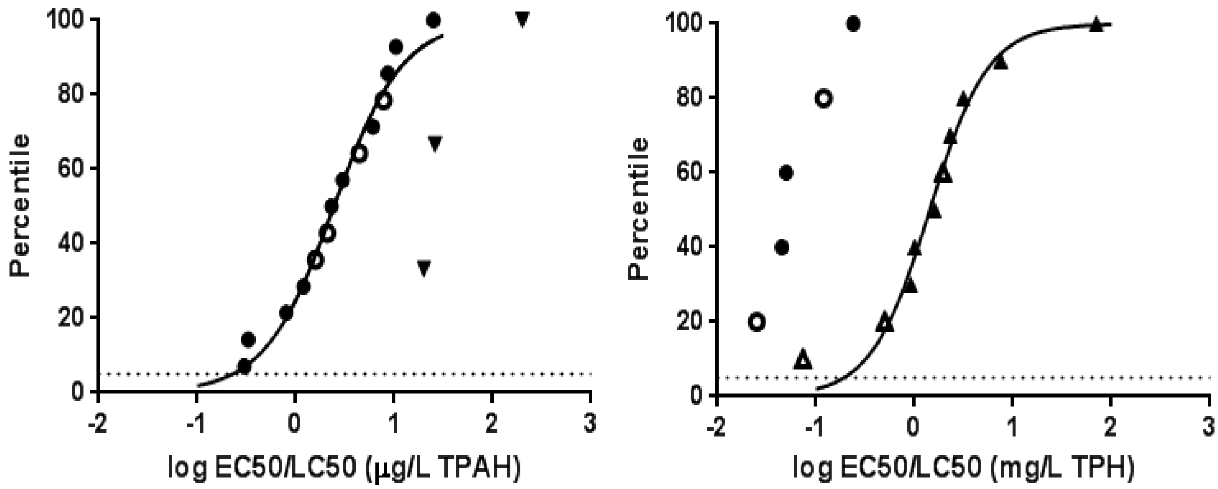


Figure 4.3 *Species sensitivity distributions for the sublethal (circles, EC50 values) and lethal (triangles, LC50 values) toxicities of oil, expressed as total polycyclic aromatic hydrocarbons (TPAH; Panel A) and total petroleum hydrocarbons (TPH; Panel B) to marine (filled symbols) and freshwater species (open symbols). Data were selected as the lowest EC50 or LC50 values for a given species, so that one species did not dominate the analysis. Only datasets with 10 or more species were analyzed statistically with a non-linear regression (GraphPad Prism Ver. 5; GraphPad Software Inc, LaJolla, CA). The horizontal line represents the 5th percentile of species and intersects the regressions at an EC50 or LC50 equivalent to the 'HC5'. Data were drawn from papers summarized in* ***Appendix D, Table D.1*** *(Kocan et al. 1996; Marty et al. 1997; Carls et al. 1999, 2008; Gulec and Holdway 2000; Little et al. 2000; Brand et al. 2001; Pollino and Holdway 2002; Couillard et al. 2005; Perkins et al. 2005; Shen et al. 2010; Olsvik et al. 2011; Greer et al. 2012;; Wu et al. 2012; Gardiner et al. 2013; Incardona et al. 2014; Mager et al. 2014; Martin et al. 2014; Dussauze et al. 2015; Madison et al. 2015; Sørhus et al. 2015).*

The primary limitations of establishing toxicity benchmarks from SSDs are the assumptions that the species included represent the range in sensitivity of all species in all ecosystems under all environmental conditions, and that the SSD truly reflects differences in toxicity among species and not the selection of test species according to their tolerance of lab conditions or differences in test methods among laboratories. *Nevertheless, SSDs provide a reasonable first estimate of toxicity benchmarks, although a comprehensive comparison among species and oils within one testing laboratory would increase the confidence in their application to risk assessments.*

<u>Recommendation:</u> SSDs should be improved by testing a wider array of test species, with toxicity expressed as TPAH and TPH concentrations, or as concentrations of specific hydrocarbons identified as the toxic components of oil.

Table 4.1 *The concentrations of TPAHs and TPHs estimated to be hazardous to 5% of test species, as estimated from species sensitivity distributions of chronic embryo toxicity (**Figure 4.3**)*

	HC5 calculated from regression equations	HC5 estimated from data distributions
TPAH – EC50 (µg/L)	0.23	
TPAH – LC50 (µg/L)		3.2
TPH – EC50 (mg/L)		0.01
TPH – LC50 (mg/L)	0.19	

4.2.2 Type of oil and oil characteristics

As indicated in Section 4.1, *the acute toxicity of crude and refined oils has been attributed to LMW hydrocarbons that cause lethality by narcosis, regardless of life stage, while MMW 3-5-ringed PAH are thought to be the primary components that cause chronic toxicity to fish embryos.* Based on this knowledge, it might be expected that the relative risks of acute and chronic toxicity of different oils could be assessed by simply ranking them in order of the concentrations of their toxic constituents. *For example, very light oils that are rich in monoaromatics and short-chain alkanes should be more acutely lethal than heavy fuel oils with smaller proportions of these hydrocarbons.* While this may generally be true, the SSDs developed by Barron et al (2013) for acute lethality of crude and fuel oils demonstrated that estimated HC5 values varied widely among oils, from 0.29 to 3.5 mg/L TPH. Light and heavy fuel oils were more acutely toxic (0.29 and 0.56 mg/L TPH, respectively) than four crude oils (0.9 to 3.5 mg/L TPH). The lightest oil (South Louisiana crude) was two- to three-times less toxic than the average for all oils, based on measured TPH concentrations. No toxicity data for very light oils, such as Bakken crude, were found.

By the same reasoning, *oils that are enriched in alkyl PAHs (e.g., heavy fuel oils) should cause greater chronic toxicity to fish embryos than oils with low concentrations of alkyl PAHs. Virtually all crude and refined oils tested to date cause a similar array of toxic responses in fish embryos* (**Appendix D, Table D.1**), including light and heavy crudes (Wu et al. 2012), refined products, such as diesel (Schein et al. 2009) and HFO (Incardona et al. 2012a; Martin et al. 2014), and bitumen (Colavecchia et al. 2004, 2006) and products derived from bitumen, such as Orimulsion (Boudreau et al. 2009), and diluted bitumen (Madison et al. 2015). *However, toxicity is highly variable and may be confounded by the relative proportions of different alkyl PAH in each oil*. For example, Martin et al. (2014) measured the toxicity of a crude and heavy fuel oil to trout embryos expressed as measured concentrations of TPAHs in test solutions (**Table 4.2**). If toxicity was determined solely by TPAHs, there should be little difference between the oils in TPAH concentrations causing embryo toxicity. However, HFO was 4 to 5-times more toxic than crude oil, perhaps due to higher proportions of the more embryotoxic 3- to 5-ringed alkyl PAHs, differences in bioavailability of the toxic constituents, or the presence of toxic compounds not typically analyzed in oil, such as polar compounds (e.g., phenolic derivatives of alkyl PAHs, alkyl dibenzothiophenes; reviewed in Section 4.1.4.3).

It is often difficult to express relationships between PAH concentrations in oil and toxicity quantitatively because the physical characteristics of oil (e.g., density, viscosity) modify toxicity by controlling droplet formation and the rate of partitioning of hydrocarbons from oil to water. The proportion of HMW waxes, resins and asphaltenes will control the physical characteristics of oil (Chapter 2), which in turn affect the dispersability of oil in water. Thus, relative to light oils, heavy oils are more difficult to disperse mechanically in water, are less likely to form fine droplets and may appear less toxic than light oils because their toxic constituents partition more slowly to water.

Weathering of oil changes the relative concentrations of different toxic components of oil, so that toxicity may change over time depending on what compounds are lost by volatilization and oil-water partitioning (e.g., Carls et al. 1999). Microbial transformations of hydrocarbons (review, Neff et al. 2013) may also create hydroxylated derivatives that are more toxic than the parent compound (Hodson et al. 2007b; Fallahtafti et al. 2012). Thus, the measured toxicity of fresh oil may over- or underestimate impacts of spilled oil as it weathers (Neff et al 2000). This bias may also occur in lab studies due to the risk of thermal degradation of hydrocarbons if oil is heated to simulate weathering.

<u>Recommendation:</u> Microbial metabolites in weathered oil and their contribution to toxicity need to be determined.

Table 4.2 *A comparison of the concentrations of TPAHs in two test oils to the concentrations in test solutions causing chronic toxicity (25 day EC50 values) to trout embryos (Martin et al. 2014).*

	MESA crude oil	**HFO 6303**
TPAHs in undiluted oil (µg/g)	13,415	42,586
Median effective concentration (25 day EC50) for sublethal embryo toxicity to rainbow trout (µg TPAH/L)	23	5

Recent spills of diluted bitumen (dilbit; e.g., Kalamazoo River, Chapter 8) have raised concerns about unique threats to aquatic environments because the composition and proportions of hydrocarbons in dilbit differ considerably from conventional crude oils. As outlined in Chapter 2, dilbit is prepared from bitumen, a highly-weathered oil depleted in LMW compounds. When bitumen is extracted from the oil sands, many of the polar and water soluble components are removed by water washing, including naphthenic acids (NAs), naturally-occurring, linear and cyclic carboxylic acids found in the acidic fraction of crude oil and raw bitumen. The NAs account for much of the acute toxicity of oil sands process water. Because extracted bitumen is too viscous to flow through pipeline, diluents such as natural gas condensates are added to reduce viscosity, in effect replacing many of the LMW compounds lost during bitumen formation. The amount of diluent added changes to accommodate seasonal temperature effects on viscosity and the chemical composition changes with its commercial source. As a consequence, there may be differences in the chemistry and toxicity of diluent between summer and winter blends, and among batches.

No publications were found describing the acute lethality of fresh or weathered dilbit to fish. Bitumen itself is chronically toxic to fish exposed to bituminous sediments, as demonstrated by blue sac disease in embryos of white sucker (*Catostomus commersoni*) and fathead minnow (*Pimephales promelas*) and endocrine disruption of slimy sculpin (*Cottus cognatus*) (reviewed in Dew et al. 2015). Alkylnaphthalenes, the PAH of lowest chronic toxicity, are mostly lost during the formation of bitumen, so that Access Western Blend (AWB) dilbit contains a lower proportion than conventional crude oils (Yang et al. 2003). Nevertheless, the *concentrations of 3-5-ringed alkyl PAHs in AWB are equivalent to those of conventional oils, suggesting that chronic toxicity should not differ markedly*. There is only one published report on the chronic embryo toxicity of AWB dilbit (Madison et al. 2015). The EC50 for Japanese medaka fell in the 37th percentile of an SSD for an array of crude and refined oils (**Figure 4.3**). This rank suggests that dilbit may be slightly more embryo-toxic than average, but until there are equivalent data for other species, any conclusions about the perceived toxicity of dilbit may be confounded by species differences in sensitivity.

Spills of dilbit also do not suggest any unusual toxicity. Unpublished reports about a 2007 spill of approximately 100,000 L of dilbit to Burrard Inlet indicated that the primary acute effect was oiling of aquatic birds, most of which were rescued (Dew et al. 2015). Other effects were due to spill cleanup, i.e., removal of oiled *Fucus sp* followed by mortalities of species, such as barnacles and limpets that use *Fucus* beds as a habitat. Hydrocarbon contamination was measurable in some species of crab but not others, and contamination of sediments and mussels (*Mytilus edulis*) was still evident four years post-spill. Other long-term ecological effects were not investigated. The impacts of this spill were relatively mild, likely because it occurred in a harbour well-equipped to handle spills, the response was rapid and most dilbit was recovered. Weather and tide conditions also limited the spread of the spilled dilbit and the spill did not coincide with salmon or bird migrations. However, the sediment contamination indicated that some dilbit sank, which may account for much of the unrecovered portion.

In fresh water, the 2010 spill of dilbit from a ruptured pipeline contaminated Talmadge Creek and the Kalamazoo River, MI, caused significant environmental impacts (reviewed in detail Chapter 8). Dilbit that flowed overland to the creek floated initially, but 10-20% sank due to the rapid evaporation of volatile components and the accumulation of soil particles and suspended particulates in the creek and river (reviewed by Dew at al. 2015). As with the Burrard Inlet spill, there were direct effects on animals in the river, including large numbers of oiled turtles, birds and mammals, most of which were treated and survived. Although there were no immediate fish kills, fish abundance and diversity decreased in oiled areas and there were clear signs of oil exposure and effects on fish, as indicated by physiological markers of exposure to petroleum hydrocarbons and poor health. Sediments contaminated with dilbit were toxic to benthic invertebrates, but toxicity varied somewhat with sediment characteristics (reviewed by Dew et al. 2015). However, the biggest impact was the damage to aquatic and riparian habitats by the spill cleanup (reviewed in Sections 4.2.7).

Overall, the direct toxic effects of dilbit in both freshwater and marine ecosystems do not seem dramatically different from those of other oils. However, dilbit does differ from other oils in its behaviour when spilled. The very rapid loss of volatiles during weathering increases viscosity and reduces the susceptibility to mechanical or chemical dispersion, which may limit the partitioning of PAHs into water (Section 4.2.3) and the extent of exposure of aquatic biota.

<u>Recommendation:</u> Research is needed to determine how the behaviour of fresh and weathered dilbit in various aquatic habitats affects exposure and toxicity to aquatic species.

More generally, the risk of toxicity of an array of oils is not absolute, but depends on viscosity and how it controls droplet formation and the partitioning of the toxic components of oil into water. Differences in the resistance to droplet formation can be reduced experimentally by chemical dispersion (Section 4.2.3) to enable comparisons of toxicity among oils with less bias from differences in viscosity. Thus, to compare toxicity among oils for ERAs, toxicity test data should be generated by methods that maximize the surface area of oil exposed to water and the bioavailability of hydrocarbons to test species (reviewed in section 4.3).

4.2.3 Chemically- vs. mechanically-dispersed oil

*Chemical dispersants are used to reduce the amount of oil on the water's surface and the risks of oil to surface species, such as seabirds, marine mammals and turtles, and to shoreline marshes, estuaries and beaches. Dispersion transfers oil into the water column where it can be diluted, dissolved in water, and degraded by microbes. The downside of dispersion is the risk of toxicity from the dispersants themselves and increased exposure of aquatic species to the toxic constituents of oil (NRC 2005). Thus, chemical dispersion may increase the impacts of oil on subsurface aquatic resources by making the components more bioavailable***.** For example, PAHs from four different oils were six to 1,100-fold more bioavailable to juvenile trout from dispersed oil (CEWAF) than from un-dispersed (WAF) (Ramachandran et al. 2004a), depending on the oil tested. Similarly, the toxicity of CEWAF of crude, diesel and heavy fuel oils to trout embryos was greater than the toxicity of WAF when exposures were expressed as the amount of oil added to test systems (Schein et al. 2009; Adams et al. 2014a; Martin et al. 2014). *Following dispersion, the ecological risks of spilled oil will increase because the volume of water contaminated with toxic concentrations of oil may increase by up to 1,100-fold during the period of plume dilution.*

When oil is added to water, the rate of partitioning of hydrocarbons from oil to water is largely a function of droplet size, i.e. the surface-to-volume ratio (Redman 2015). With physical dispersion, oil droplet size and stability in water varies with oil characteristics such as viscosity. Heavier and highly-weathered oils are harder to disperse and appear less toxic to aquatic species. Chemical dispersants reduce the median size of oil droplets and stabilizes droplets in water and can even enhance the dispersion of heavier oils.

Thus, the apparent increase in toxicity following chemical dispersion can be attributed primarily to an increased bioavailability of the toxic constituents of oil.

When toxicity is expressed as oil loadings, large differences in toxicity between solutions of WAF and CEWAF have been interpreted as synergistic interactions between the dispersant and oil toxicity (e.g., Rico-Martinez et al. 2013). This is a common mistake when the recommended practice of measuring hydrocarbon concentrations in test solutions is not followed (NRC 2005; Coelho et al. 2013; Adams et al. 2014a). When concentrations of TPHs or TPAHs are measured in test solutions, differences in toxicity between CEWAF and WAF, among oils, and among CEWAFs prepared with different dispersants, largely disappear (e.g., NRC 2005; Wu et al. 2012; Incardona et al. 2013; Adams et al. 2014; Dussauze et al. 2015; Redman and Parkerton 2015). *Toxicity is determined by the measured amount of oil in solution, not by oil loading.*

Modern dispersants are less acutely lethal than mechanically-dispersed crude oil (WAF), and far less toxic than chemically-dispersed oil (CEWAF) (NRC 2005; Hemmer et al. 2011). Nevertheless, adding a toxic agent to disperse oil that is also toxic might seem counterintuitive.

Under ideal conditions, chemical dispersants are not readily bioavailable to aquatic species. For example, Corexit® 9500 dissolved in water is toxic to fish embryos, but non-toxic when first mixed with mineral oil to create chemically-dispersed mineral oil (Adams et al. 2014a). When properly mixed, most dispersant appeared to be sequestered by the mineral oil and not bioavailable at toxic concentrations. However, for applications under field conditions, often by airplane, there is no guarantee that all of the dispersant will land on oil slicks or be properly mixed with oil. *Where the dispersant misses the slick or fails to mix with oil, the potential for dispersant toxicity to aquatic species in subsurface waters is increased.*

In laboratory tests of chronic embryo toxicity, the presence and effect of free dispersant are indicated by early mortality of eggs, before signs of blue sac disease appear. When mortality occurs later and coincides with the onset of blue sac disease, it is likely caused by PAHs and not by dispersant (Kuhl et al. 2013; Adams et al. 2014a). The array of gene transcriptional responses in fish embryos is also somewhat different between dispersant and dispersed oil (Olsvik et al. 2012), suggesting a direct interaction of dispersant with transcription. *When dispersants are used at oil spills, the unique molecular responses of fish to dispersants coupled with chemical analyses of un-sequestered dispersant could provide tools to diagnose specific dispersant effects in the field*.

In older fish, dispersants may be endocrine disruptors. Nonylphenol ethoxylates, a common constituent, can degrade to nonylphenol, which interacts with the estrogen receptor of vertebrates. However, only two of eight commercially-available dispersants caused weak estrogen-receptor activity in a mammalian cell line, and no androgen receptor activity, although all dispersants were cytotoxic at high concentrations (Judson et al. 2010).

<u>Recommendation:</u> Research is needed to determine whether dispersants and chemically-dispersed oil are endocrine disruptors in sexually-maturing fish *in vivo*.

The intended benefit of chemical dispersion is a more rapid dilution of oil-contaminated water throughout the water column, assuming that mixing energy is sufficient. Models of the fate of WAF and CEWAF of spilled oil along 200 nautical miles of Norwegian coast over a 30-day period showed that the overlap in distribution between toxic concentrations of oil (0.1 to 1.0 µg/L TPAH) and the eggs and larvae of northeastern Arctic cod (*Boreogadus saida*) was reduced somewhat by chemical dispersion (Vikebø et al. 2015). While the results suggest that dispersants could be used to reduce the potential for embryo toxicity, the model was highly site- and species-specific because it included many assumptions about oil and egg/embryo distribution. *Most importantly, the model did not consider the relationships among* *concentration, exposure time, embryo developmental stage and oil toxicity.* Although high concentrations of oil in water may be transitory following dispersion (i.e., less than 24 - 48 hours) (NRC 2005), only brief exposures (one to 2.4 hours) of Atlantic herring (*Clupea harengus*) eggs to realistic concentrations of CEWAF were sufficient to increase rates of deformities and mortalities at hatch and swim-up, 14 days later (McIntosh et al. 2010; Greer et al. 2012). *Thus, transient exposures of embryos to high concentrations of oil at a critically-sensitive stage of embryonic development may be highly toxic*, even though the modeling scenario indicated that 30-day average concentrations were sub-toxic.

<u>Recommendation:</u> Research is needed to define and model the interactions among concentration, exposure time and toxicity for different life stages of fish.

Chemical dispersion of oil also has implications for coral reef species which may be particularly sensitive because of their shallow habitats and complex species interactions. At spill sites, the exposure of coral reefs to oil will increase if chemically-dispersed oil is mixed to depths of one to 10 m. One- to five-day exposures of embryos and larvae of different coral species to CEWAF caused greater toxicity than exposures to WAF, as indicated by reduced rates of fertilization and survival (reviewed by NRC 2005). There were also long-term effects of brief exposures, expressed as elevated rates of mortality and reduced growth and coverage one to two years following a spill. Complete recovery was evident within 10 years. In lab studies, Corexit® 9500 dispersant alone was about 15 times more toxic to corals than to anemones. Sublethal exposures to dispersants or to dispersed oil reduced the feeding behaviour of corals and brief exposures (8 – 24 h) to CEWAF caused delayed mortality and reduced growth, even though survivors rapidly depurated accumulated oil (Shafir et al. 2007; Mitchelmore and Baker 2010). Clearly, dispersants should not be used in the vicinity of coral reefs, a recommendation that corresponds to current practice in shallow waters.

In Canada, corals on both the Pacific and Atlantic coasts inhabit deeper and colder waters (e.g., http://ibis.geog.ubc.ca/biodiversity/efauna/BritishColumbianCorals.html) so that dispersion of surface oil is less likely to cause their exposure to petroleum hydrocarbons. However, the novel use of dispersants to manage the discharge of oil from the wellhead during the DWH oil spill demonstrated that benthic organisms in waters as deep as 1,300 m are at risk of exposure to chemically-dispersed oil.

The NRC (2005) review also questioned the assumption that oil dispersion would protect marine birds by removing oil from the surface. The protection of birds from surface oil depends on the efficiency of oil dispersion, but diving birds could be exposed to subsurface plumes of dispersed oil, and presumably this may extend to marine mammals.

<u>Recommendation:</u> Research is needed to: 1) assess the toxicity of dispersed oil to deepwater corals, ground fish and invertebrate species that have high economic importance (e.g., lobster, crab, scallops); 2) model the distribution of deepwater plumes of dispersed oil in relation to areas of known fisheries productivity, such as the fishing banks of Canada's east coast or unique habitats like the sponge reefs off Canada's west coast; and 3) assess the potential for effects of chemically-dispersed oil on marine bird and mammals.

Decisions on the use of dispersants following an oil spill use a 'Net Environmental Benefit Analysis' (NEBA) to identify the trade-offs between impacts on surface and subsurface resources (NRC 2005). Although the NEBA concept is logical, the effectiveness of its application is dependent the level of information available for comparisons of risk between surface versus subsurface resources and offshore versus shoreline impacts.

<u>Recommendation:</u> To support evidence-based decisions on net environmental benefits, baseline data are needed on abundance of species that frequent areas at risk of oil spills. Where data are inadequate, rapid methods are needed for surveying subsurface aquatic resources at the time of a

spill. The behaviour, fate and effects of dispersed oil should be investigated under field conditions typical of Canadian waters at risk of oil spills and the toxicity of new chemical agents used for sorption, solidifying, burning, herding, specialty cleaning and bioremediation of oil (Chapter 6) assessed (Tamis et al. 2012).

4.2.4 Sediment contamination

The NRC (2005) reviewed a series of studies on experimental chemical dispersion of oil in near-shore areas of tropical, temperate and Arctic ecosystems. While chemical dispersion reduced the amount of residual oil on shorelines, the interactions of dispersed oil with sediments were less clear, particularly with fine-grained sediments that were not the focus of most studies. A recent and very comprehensive review of the interactions among spilled oil, oil dispersants, the rate of formation of oil-mineral aggregates and oil precipitation to sediments demonstrated that dispersant use accelerates oil precipitation to sediments (Gong et al. 2014).

Bottom-dwelling (benthic) organisms will be exposed to dilbit or to oil that has settled into the sediment or is present chronically due to natural seeps. Extensive lethality has been observed when high quantities of oil reach the bottom following spills or well blowouts (Teal and Howarth 1984). Sensitive species give way to opportunistic species in such cases. Oil that has mixed with sediments can persist for very long periods of time, e.g., 30 years after the *Arrow* spill in Nova Scotia (Lee et al. 2003b) and 25 years after the EVOS in Alaska (reviewed by Ballachey et al. 2014). Persistence is due to the slow biodegradation that takes place under the anoxic conditions characteristic of benthic environments. Organisms in constant contact with contaminated sediments (infauna and epifauna) are at a higher risk of adverse impacts, including impaired feeding, growth, development and recruitment, that may alter population dynamics and community structure. In coastal waters, macroalgae (e.g, kelp) may experience decreased reproduction, bleaching and mortality upon exposure to oil, and effects on macroalgae reduce habitats and abundance of other benthic species. As discussed in Section 4.1.4.6, benthic fish species are particularly susceptible to an increased prevalence of cancer following exposure to carcinogenic and mutagenic PAHs typical of pyrogenic PAHs, but there have been no long-term studies of the prevalence of cancer in benthic fish chronically-exposed to spilled oil.

Benthic species may also be subject to hypoxia if there is a high biochemical oxygen demand (BOD) of sediments due to organic enrichment from an oil spill and oil toxicity to benthic species could be underestimated if hypoxia is not taken into account. For example, oil from the DWH spill was more toxic to adult and embryonic sheepshead minnows (*Cyprinodon variegatus*) when tested under hypoxic conditions (2.5 mg/L dissolved oxygen) relative to normoxic conditions (>5.9 mg/L oxygen; >80% saturation) (Hedgpeth and Griffitt 2015).

<u>Recommendation:</u> Benchmarks are needed for petrogenic PAHs in marine and freshwater sediments to guide sediment cleanup following an oil spill.

4.2.5 Photo-enhanced toxicity

The aromatic components of oil (e.g., PAH) may be susceptible to photooxidation due to the interaction of UV light with double bonds (Chapter 2). The photo-modified products of these reactions include phenols or epoxides, which are more water-soluble than the parent compounds. *Thus, photooxidation of PAHs in surface waters to more water-soluble derivatives may contribute to their more rapid dilution to non-toxic concentrations. However, photo-modification may also create hydroxylated derivatives that are more toxic than the parent compound (e.g., Fallahtafti et al. 2012).*

A more important process is photo-enhanced toxicity, i.e., toxicity due to photooxidation *in vivo*, which exposes cells to highly ROS, such as singlet oxygen and hydroxy radicals. Although ROS react quickly and do not persist long enough in water to cause toxicity, the generation of ROS in cells allows their immediate reaction with double bonds in lipids (lipid peroxidation), proteins (inactivation of enzymes) and nucleic acids (mutations). These reactions are reproducible *in vitro*, and toxicity *in vivo* can be predicted from the physical and chemical characteristics of PAHs (Greenberg et al. 1993; Ren et al. 1994). For example, photo-enhanced embryo toxicity is greater for pyrene than for retene (Räsänen, et al. 2011). All species have oxidative defense and DNA repair systems to protect cells from damage by ROS generated by normal oxidative metabolism, but the rate of ROS production in tissues during photo-enhanced toxicity far exceeds the capacity to neutralize them. The result is a rapid destruction of cells, tissue necrosis and mortality of the exposed organism.

The risk of photo-enhanced toxicity will be greatest in the clear waters of the open ocean, in coastal and freshwater ecosystems where turbidity is low and UV light penetrates to the sediments, and at northern latitudes with seasonally long days. Species or life stages most at risk are transparent or semi-transparent (Barron and Ka'aihue 2001), including many zooplankton species (sub-Arctic copepods) (Duesterloh et al. 2002), crab larvae (Alloy et al. 2015) and the embryos of fish that are un-pigmented at hatch (e.g., vendace [Coregonus albula]) (Vehniainen et al. 2003). There is little risk to pigmented embryos (e.g., pike; Esox Lucius) (Hakkinen et al. 2004; Räsänen et al. 2011) or to juvenile and adult fish (Barron et al. 2005).

For marine species, such as Pacific herring, co-exposure to UV light, including normal sunlight, increased the toxicity of WAF and CEWAF of crude oil by up to 48-fold (Barron et al. 2003; NRC 2005), as was the case for freshwater zebrafish embryos exposed to crude oil (ANS, MC-252) and to HFO (Hatlen et al. 2010; Incardona et al. 2012b). WAF alone increased the prevalence of chronic, sublethal cardiotoxicity in exposed embryos, whereas WAF combined with natural sunlight caused more rapid mortality due to severe tissue necrosis. Cardiotoxicity was correlated to concentrations of tricyclic PAHs in test oils, but photo-enhanced toxicity may involve other compounds, such as heterocycles (e.g., carbazoles). UV light caused a greater increase in toxicity of HFO compared to ANS (Hatlen et al. 2010), likely because of higher concentrations of TPAHs involved in photo-transformations.

While there are many studies of photo-enhanced toxicity to fish and aquatic invertebrates, the significance remains controversial because few field studies have confirmed these effects at actual oil spills. Sellin Jeffries et al. (2013) developed a risk model relating PAH concentrations in surface waters following the 1989 EVOS to the depth of UV-A light penetration and the occurrence of embryos of Pacific herring in surface waters. They concluded that less than 1% of the herring embryo biomass would have been present in surface waters containing sufficient PAHs to cause injury by photo-enhanced toxicity. In contrast, field experiments with caged Pacific herring embryos and passive water samplers suggested that the toxicity of HFO spilled by the grounding of the *Cosco-Busan* in San Francisco Bay in November 2007 was enhanced by natural UV light (Incardona et al. 2011). The passive samplers demonstrated the presence of other contaminants derived from urbanized watersheds at both oiled and reference sites. Although hydrocarbons associated with photo-enhanced toxicity were only present at oiled sites, the results do not preclude interactive toxicity among petroleum hydrocarbons, anthropogenic compounds and natural stressors, such as temperatures that fluctuate with tidal cycles.

Recommendation: Additional studies are needed to verify that photo-enhanced toxicity occurs at oil spills, and the extent to which it may interact with other anthropogenic contaminants and natural stressors.

4.2.6 Arctic vs. temperate spills

The interest in oil resources by Arctic coastal nations and the expansion of oil exploration and development along the Mackenzie River Valley and in the Beaufort Sea, raise concerns about the impacts of oil spills in sub-Arctic and Arctic ecosystems, and the toxicity of oil at low temperatures. Recent *reviews of oil spills under Arctic conditions conclude that impacts will depend on the interactions among the unique physical characteristics of the environment (e.g., the presence of sea ice), the chemistry, fate and behaviour of spilled oil at low temperatures (Chapters 2, 3 and 6), and the biology of primary, secondary and tertiary production by species uniquely adapted to Arctic conditions* (Lee et al. 2011; AOSRT 2014).

The perceived risk of oil toxicity to Arctic species is derived primarily from laboratory toxicity studies, most focused on fresh oil. Most field studies of spilled oil in the Arctic, concern Arctic waters of Norway (AOSRT 2014), Chapter 8 and Lee et al. (2011) review the Baffin Island Oil Spill experiment (BIOS) in detail. The AOSRT (2014) review was concerned primarily with marine conditions, and effects on freshwater species were not addressed. However, as indicated in Section 4.2.1, there appears to be little systematic difference between freshwater and marine species in sensitivity to oil exposure, and presumably this extends to Arctic species, although no studies were found that tested this assumption.

The implications for Arctic mammals are covered briefly in Section 4.1.7 and relate mostly to the increased potential for exposure to oil when it is confined to breathing holes in ice. For Arctic invertebrates and fish, effects will depend on the extent of their exposure to oil entrained or dissolved in water or trapped under ice where species congregate. Under-ice algae that grow in light passing through surface ice, support communities of organisms, including periphyton grazers, predatory fish and marine mammals. These under-ice communities would be uniquely sensitive to a subsurface discharge of oil because buoyant oil would accumulate in high concentrations under the ice, where there may be a risk of photo-enhanced toxicity (Lee et al. 2011; Section 4.2.5). As AOSRT (2014) concluded, the exposure of marine Arctic species to oil could correspond to two scenarios: spiked exposures (brief and rapidly declining exposure; see Section 4.3.1) typical of open ocean spills; and prolonged or chronic exposures associated with oil trapped under ice.

Other unique conditions in the coastal shelf of the Beaufort Sea that could enhance the impacts of oil spills have been identified (Carmack and Macdonald, 2002; Lee et al. 2011; ADNR 2014). For example, a thermal bar formed each summer along the shore west of the MacKenzie River creates a zone of low salinity water where river and salt water mix. This zone is highly productive and attracts salinity-tolerant fish species from coastal tributaries. Oil contamination in this zone could have significant impacts on abundance and productivity of both freshwater and marine fish species, and other species such as beluga whales that seasonally occupy critical habitat in the near-shore.

Whether Arctic species are uniquely sensitive to oil due to adaptations to life between -1 and 2 °C remains an open question. Comparisons of toxicity among temperatures will be complicated by the effects of temperature on the kinetics of partitioning of hydrocarbons from oil to water, the pharmacokinetics of bioaccumulation, and the activity of enzymes involved in metabolism and excretion of hydrocarbons. In assessing the risks to fish, consideration must be given to their unique adaptations to Arctic conditions, such as high tissue concentrations of antifreeze proteins. For example, the unusually high sensitivity of Arctic cod to oil exposure may be related to a lack of kidney glomeruli to limit the loss of antifreeze proteins. Excretion of PAH metabolites via the bile instead of the kidneys may prolong their exposure to PAHs by reducing excretion rates. Because *comparative data on hydrocarbon metabolism and toxicity are sparse, tools developed for monitoring oil exposure and effects in temperate species should be interpreted with caution when assessing the potential impacts of oil on Arctic fish species.*

Preliminary studies suggest little difference in oil toxicity between Arctic and temperate species (AOSRT 2014). A comparison of published data on the toxicity of two components of crude oil and 13 crude oils to an array of marine species across five phyla (annelids, arthropods, chordates, echinoderms and molluscs) concluded that there was no systematic difference in acute lethality (<8 day exposures) between temperate and Arctic species (de Hoop et al. 2011). Similarly, biomarker responses of Arctic cod exposed to the water soluble fraction of crude oil (e.g. induction of cytochrome P450 and antioxidant enzymes;

DNA damage) were identical in direction and fell within the range of those observed for temperate species exposed to similar concentrations of oil (Nahrgang et al. 2010). *de Hoop et al. (2011) concluded that data from temperate species could be used for a first approximation of risks of oil spills to Arctic ecosystems.* However, chemically-dispersed oil was less toxic at 2 °C to Arctic species of fish and invertebrates than un-dispersed (Gardiner et al. 2013), in contrast to greater toxicity of CEWAF to temperate species at 10-28 °C (Section 4.2.3). The greater toxicity of WAF than CEWAF at low temperatures may be explained by a more prolonged retention of acutely toxic volatile compounds at cold temperatures compared to warm (Perkins et al. 2005). Understanding the effect of temperature on the relative toxicity of chemically-dispersed oil will require detailed chemical analyses of hydrocarbons in test solutions and tissues of test organisms.

Overall, the differences in oil spill effects between Arctic and temperate regions appear to be driven more by factors that affect exposure of organisms to oil than by differences in toxicity of oil. Recent reviews of oil toxicity in Arctic ecosystems by Olsen et al. (2013) and AOSRT (2014) identified research needs similar to those of temperate ecosystems.

Recommendation: Research on the effects of oil should take into consideration unique aspects of Arctic ecosystems by considering: 1) interactions among low temperature, physiological adaptations of Arctic species to low temperature and the kinetics of hydrocarbon solubility, uptake and excretion; 2) the habitat, life histories and reproductive capacity of regional species at risk; 3) chronic or sublethal endpoints related to growth and embryonic development; 4) heavy fuel oils widely used in Arctic shipping; 5) the efficacy and effects of oil dispersion under Arctic conditions; 6) long-term studies of ecosystem recovery; and 7) inclusion of Arctic communities in the design and conduct of research.

4.2.7 Marine vs. freshwater spills

The history of oil spills is dominated by major shipping accidents at sea or near marine coastal ecosystems. Much of what is known about the potential effects of oil spills is derived from detailed research following incidents, such as the EVOS in Prince William Sound, AK, in 1989, and the more recent DWH spill in the Gulf of Mexico in 2010. However, as reviewed in Chapter 1, the frequency of marine shipping accidents has been declining due to improvements in tanker safety programs and construction standards. In Canada, most recent spills are inland, reflecting the locations where oil is produced, transported and used.

As the result of an aging pipeline infrastructure, major oil spills have occurred in Russia, such as the Komi spill that resulted in the release of 100,000-350,000 tonnes of crude oil and produced water into a river near the town of Usinsk (Owens et al. 1999). As media attention and scientific reporting on these spills have been limited, the public's attention on oil spills in North America has been focused on marine oil spills and the large cleanup efforts involved. It is important to examine the level of environmental impacts, costs and technical challenges that may be encountered following spills to fresh water.

A comparison of the 2010 DWH oil spill from a well blow-out in the Gulf of Mexico and the 2010 spill of Western Canadian Select dilbit (Table 2.2) to the Kalamazoo River, MI, from a pipeline break highlights some important differences between marine and freshwater spills (Hodson and Williams 2012; Chapter 8.7). The most obvious difference was one of scale. The DWH spill discharged about 780,000 m^3 of crude oil over a 12-week period, contaminating an area ranging from 6,500 to 180,000 km^2. By contrast the Kalamazoo River spill lasted only17 hours, the volume lost was 235-fold smaller (3,320 m^3), and only 60 km of river was oiled. At first glance, the potential for ecological impacts would appear much smaller for the Kalamazoo River. However, in both cases, there were significant impacts on aquatic and shoreline ecosystems, significant technical challenges in dispersing or recovering oil, and the cleanup continued for at least four years due to residual oil present as slicks, tar balls and contaminated sediments.

The challenges of cleaning up a freshwater spill were reflected in a substantial difference in the estimated costs of cleanup ($50 US/L spilled for the DWH vs. $300/L spilled for the Kalamazoo River) (Hodson and Williams 2012). The higher 'per litre' costs to clean up the Kalamazoo River spill seems counterintuitive given the difference in size the affected ecosystems. In marine systems, tidal cycles nourish broad shoreline and intertidal ecosystems that are rich in species adapted to daily flooding, exposure to air and input of nutrients. Because of tides, the intertidal area subject to oil contamination, and the number of species affected, is quite large. In contrast, water level fluctuations in freshwater systems are much smaller and less frequent, the shoreline ecosystem is narrower and the shoreline species diversity and density are lower (Sergy and Owens 2011).

Relative to the Gulf of Mexico, the Kalamazoo River is of low volume with a limited dilution capacity and a limited area for oil to spread and disperse. Dilbit remained in thick layers with less opportunity for weathering by photolysis and biodegradation and a greater opportunity for exposure of aquatic biota to toxic hydrocarbons. Although mixing energy from wind or waves was relatively low in the Kalamazoo River, water depths ranged from only a few centimeters to a few meters, increasing the interactions between surface water and sediments. The high ratio of shoreline length-to-water surface area meant that a greater proportion of shoreline was contaminated and seasonal flooding carried oil into forested riparian lands.

Although the DWH spill was much larger than the Kalamazoo River spill, the affected Gulf of Mexico open water ecosystem was proportionately larger (Cleveland 2013), ensuring a very high dilution capacity and opportunity for oil to spread, disperse and degrade. The open sea provided abundant mixing energy due to wind and waves and an extended time before oil reached shore (four to five weeks)(Cleveland 2013), where impacts were similar in nature to those of the Kalamazoo River. Although the great depth of the Gulf (1,500 m at the site of the well blowout) limited interactions between surface oil and sediments, a unique feature of the DWH spill was the physical and chemical dispersion of oil at the wellhead. Approximately, 75% of discharged oil did not reach the surface, forming a subsurface plume at 1,000-1,400 m depth. This plume appears to have contaminated sediments of the Gulf of Mexico over a wide area (Valentine et al. 2014), but the extent and degree of contamination is still a matter of debate and research. In the Kalamazoo River, contamination of shallow (< 10 m) sediments was evident as frequent sheens that resurfaced from the sediments to the relatively calm water surface and considerable effort was expended in trying to recover sunken oil.

In offshore marine waters, oil usually floats because its specific gravity is less than that of salt water (Chapter 2) and low turbidity reduces the likelihood of oil-mineral aggregates that may sink and contaminate sediments. As floating oil spreads, surface slicks thin and weather rapidly, and are subject to more rapid photolysis and biodegradation (Chapter 2). For the DWH spill, winds and currents kept much of the surface oil offshore, enabling recovery by skimming, burning of surface oil and surface chemical dispersion for enhanced dilution and biodegradation. Estimates of the fate of the spilled oil are highly uncertain, but it is likely that only a relatively small proportion (but still a large volume) of the oil reached shore, although weathered oil continues to wash ashore as tar balls or oily materials. For the Kalamazoo River spill, the specific gravity of un-weathered dilbit was close to that of fresh water, increasing the risk of sinking as it weathered and lost its lighter components. The risk of dilbit sinking was increased by the formation of oil-mineral aggregates (Figure 2.2) due to contact with soil before entering the Kalamazoo River and with high concentrations of suspended solids in the water caused by flooding.

Effects of oil on aquatic receptors vary with their relative sensitivity and extent of exposure. No studies have been published that specifically compare the relative sensitivity of marine and freshwater species, although publications on toxicity (**Figure 4.2**, Appendix D, Table D.1) do not suggest any major differences. However, the bioavailability of PAHs to salinity-tolerant fish species exposed to WAF and CEWAF decreased with increasing salinity (Ramachandran et al. 2006), suggesting a greater sensitivity of fish to spilled oil in fresh or low-salinity waters. In marine ecosystems, there is a potential to harm more species than in fresh water due to a higher biodiversity. In contrast the potential impacts of spills on single species may be more severe in freshwater habitats. Avoidance is possible (e.g., in clean tributaries), but habitats are small and physically constrained and there is less oil dilution. *Overall, oil spill effects will be site- and species-specific, depending on how the biology and ecology of each species interact with the potential for oil exposure. In both marine and freshwater ecosystems, impacts will vary with seasonal aggregations of species for spawning, synchronized hatching of eggs, schooling behaviour and habitat selection.*

Oil spill cleanup options (Chapter 7), *such as booming and skimming, burning of surface oil and chemical dispersion, are well established for marine ecosystems and are designed for open water applications. For offshore spills, delays may be significant before oil is blown onto sensitive shorelines, allowing the opportunity to plan and prepare a response to protect those shorelines.* For the DWH spill, the deepwater plume of dispersed oil presented new challenges in understanding potential impacts and how to mitigate them. Although the plume was 'good news' in that the oil was apparently 'gone', subsequent studies identified a 'bathtub ring' of contamination at depths where the plume encountered sediments (i.e., at 1,500 m) (Valentine et al. 2014). The significance of this contamination and the extent of damage to benthic ecosystems is still a subject of active research.

At open ocean spills, cleanup efforts are viewed as mostly positive because oil is physically removed from the surface (skimming, burning, chemical dispersion) to protect surface species and sensitive shorelines. The large-scale of the open ocean also reduces the risk and overall impacts of smoke from burning oil and the transient increase in dispersed oil concentrations in subsurface waters. In freshwater ecosystems, burning and chemical dispersion of oil are not accepted practices because they present toxicity risks to human populations and to small aquatic ecosystems. While booming and skimming work in some circumstances, access of equipment to oil spills may be limited by topography (e.g., canyons), distance (remote wilderness with no road access) or season (spring thawing of ice roads). Strong currents in high-gradient rivers also reduce the effectiveness of booms and skimmers, particularly during spring floods when ice and debris are present. The sinking of dilbit in the Kalamazoo River presented challenges for cleanup technologies and a heightened standard of 'How clean is clean enough?' due to its proximity to rural and urban development. New technologies were developed to capture oil droplets suspended in the water column ('snares') and to refloat oil from contaminated sediments ('poling', 'tillers', water jets, etc.), but their overall effectiveness in terms of cost and percentage of oil recovered are not well established (Chapter 7).

Spill cleanup often causes significant habitat damage, in addition to the physical and chemical effects of oil. The effects of mechanical cleanup of wetlands and marshes along shorelines differ between marine and freshwater ecosystems. Root systems in marine marshes are dense and can bear greater weight than more porous root systems of freshwater marshes (Sergy and Owens 2011), so greater care is needed in freshwater ecosystems to minimize habitat damage. Shorelines and riparian lands are damaged by the construction of access roads and stable pads for large equipment, by removal of oiled vegetation and un-oiled vegetation to access shorelines, the excavation of contaminated soils and the destabilization and erosion of shorelines, marshlands and river channels following excavation. For the Kalamazoo River watershed, riparian lands along both sides of Talmadge Creek (site of the spill) were deforested for access roads and some islands that had been over-washed by oil during flooding were removed completely. Habitat destruction on this scale requires extensive remediation and the impacts on ecosystem structure, function and services (e.g., access by locals for recreation) may be evident for decades. Other examples are reviewed in Chapter 8.

Overall, the scale of oil spills in freshwater ecosystems may be smaller than in marine systems, but the severity of impacts relative to the amount of oil spilled may be greater due to the smaller scope for dilution and degradation of oil, the close proximity of shorelines and sediments, the confinement of aquatic species to the spill sites and high densities of single species during migration or spawning. The *fate of much of the oil spilled to freshwater ecosystems is often unknown, which raises concerns for potential interactions of surface oil with sediments. Entrainment of droplet oil into bed sediments by surface water (hyporheic flows) creates a risk of groundwater contamination and toxicity to early life stages of aquatic species that live in or spawn in sediments. The technical difficulties of cleanup are aggravated by limitations on the use of common tools, such as chemical dispersants and burning, the inaccessibility of some spill sites and the potential for greater damage to sensitive ecosystems than is caused by the oil itself. The pressures on companies that spilled oil, on agencies responsible for regulation and on responders cleaning up the oil to justify their actions, to clean up the spill quickly and to prevent future spills may be that much greater when spills are near urban development.*

<u>Recommendation:</u> Research is needed on the behaviour and effects of oil in freshwater ecosystems to take into account the diverse scales, processes, water movements and biological communities in such systems.

4.2.8 Interactive and cumulative effects

The effects of oil spills on aquatic ecosystems are often viewed in isolation of other stressors, particularly if they occur in the open ocean. However, with shipment of oil through Canada's major ports, waterways and watersheds, and spills from pipelines in areas of urban and industrial development, there is a potential for oil spills to waters already affected by contaminants from other activities or legacy contaminated sites. A few examples include:

- Mining effluents: metals, metalloids (e.g. selenium), mine flotation reagents, acid, suspended solids;
- Pulp mill effluents: organic contaminants, chemical and biochemical oxygen demand (COD and BOD);
- Municipal effluents: pharmaceuticals, personal care products, BOD, nutrients;
- Agriculture: pesticides, nutrients, suspended solids, BOD, pathogens (livestock); and
- Wood preservative plants: creosote, copper, chromium, arsenic.

In addition to the potential for interactive toxicity, organic wastes can alter oil fate and behaviour. High concentrations of dissolved organic material (e.g., pulp mill and municipal effluents) may act as chemical dispersants, promoting the formation of oil droplets and the solubilization of petroleum hydrocarbons. As with chemical dispersants, dispersion by organic wastes may remove surface slicks more rapidly than in pristine waters, diluting oil to non-toxic concentrations and promoting biodegradation. However, in confined and shallow fresh waters, they would also increase the exposure of aquatic species to toxic concentrations of oil without the benefit of open water dilution. Similarly, increased turbidity due to soil erosion (agriculture, mining, forestry) and the discharge of organic particulates in effluents may promote the formation of oil-mineral aggregates and increase contamination of sediments.

Other stressors could include normal events in the life cycle aquatic species. A massive spring die-off of bluegill sunfish (*Lepomis macrochirus*) in Lake Winona, MN, followed a winter spill of Bunker C oil (Fremling 1981). Mortality was delayed until spring spawning, likely due to the combined stresses from oil exposure, loss of condition over the winter, rising temperatures and spawning.

Natural oil seeps or contaminated sediments that occur in oil-rich areas such as the McMurray oil sands formation in the Athabasca River watershed, and methane seeps in the Arctic Ocean may also influence the fate and effects of spilled oil. Natural sources of hydrocarbons create a potential for background or baseline toxicity (e.g., Colavecchia et al. 2004, 2006) and foster microbial communities adapted to biodegradation of oil. The balance between an increase in the 'toxic load' of hydrocarbons and the rate of their removal by microbial degradation under different environmental conditions will be site-specific.

In summary, the cumulative and interactive effects of oil and other contaminants are not well defined and are little studied.

<u>Recommendation:</u> Research is needed to determine interactions between other anthropogenic contaminants and the fate, behaviour and effects of oil in coastal and freshwater ecosystems, and to develop methods that discriminate between the effects of oil and other stressors.

4.3 Limitations of Current Toxicity Test Methods with Oil

The quality of ERAs for proposed petroleum developments and EIAs following oil spills depend entirely on the quality of data used to predict impacts and to incorporate into models. Toxicity data are derived primarily from laboratory tests that describe the quantitative relationships between oil concentrations and the responses of exposed organisms. Ideally, toxicity data should be comparable among laboratories. However, as discussed in Section 4.1.4.1.1, the accuracy and relevance of toxicity benchmarks derived from toxicity data for a diverse array of species developed by a variety of laboratories depend on a number of largely untested assumptions, including that:

- *Concentrations of petroleum hydrocarbons are known and constant during a toxicity test;*
- *The relationship between the amount of oil added to a test solution and the concentration of petroleum hydrocarbons in solution is monotonic;*
- *All petroleum hydrocarbons are freely dissolved in aqueous test solutions;*
- *The constituents of oil as a complex mixture remain in constant proportion to each other across the range of test concentrations and over time; and*
- *The exposure scenarios in laboratory tests match the scenarios of actual oil spills.*

For most published studies of oil toxicity, these assumptions are rarely tested, and when the assumptions have been tested, they are rarely met due to the low water solubility of hydrocarbons. Redman and Parkerton (2015) reviewed the implications for the outcome of toxicity tests with crude oil, and provided recommendations for the optimal test method, cited throughout the following text. *This section provides strong support for improving and standardizing methods for oil toxicity testing and chemical analyses of test solutions. Standardized tests provide a technically sound basis for comparisons of toxicity among species, environmental condition, and different sources of oil, but they do not necessarily provide data that match scenarios of actual spills.*

4.3.1 Constant vs. time-varying exposure concentrations

Because the components of oil are hydrophobic, with log K_{ow} values ranging from <3 to >6.5, the loss of hydrocarbons from test solutions is continuous, and test concentrations are not constant. The more water-soluble LMW components are lost primarily by volatilization and possibly by biodegradation. The less soluble components are lost by adsorption to the walls of exposure vessels, to the test organisms and to surface films. As a consequence, in static toxicity tests without daily renewal of test solutions, there is a continuous decline in concentrations of oil over the course of the experiment. Within 24 to 48 hours, virtually no hydrocarbons are bioavailable to test species (e.g., alkyl PAH) (Kiparissis et al. 2003). These exposures are equivalent to 'spiked exposures' (NRC 2005), the continuous dilution method recommended by CROSERF (*Chemical Response to Oil Spills Ecological Effects Research Forum*; see below).

In tests of solutions of hydrocarbons that are renewed daily (static daily-renewal protocol), the loss of hydrocarbons from solution creates a 24-hour saw-tooth pattern of exposure (Kiparissis et al. 2003). These test conditions are the most commonly reported for oil toxicity tests. However, in interpreting these tests to develop benchmarks, it is unknown if test organisms respond to the nominal concentration (amount added to the test solution), the initial concentration (time = 0 hour), the average concentration over the duration of the test, or some integral of concentration and time (e.g., Toxicity Index (TI) = concentration x time) (NRC 2005). *The issue is further complicated because the rate of loss of hydrophobic compounds from test solutions increases with hydrophobicity (K_{ow}), creating a mixture in which the relative proportions of each constituent are changing constantly. These test conditions create a great deal of uncertainty in risk assessments of oil toxicity, and in comparing toxicity among different oils, different species and different environmental conditions.*

These problems can be resolved, in part, with continuous-flow exposure systems. These include: oil-desorption columns (partitioning of hydrocarbons from oil-coated gravel to flowing interstitial water) (Carls et al. 1999; Martin et al. 2014); re-circulating tanks with pumps to recycle and mix surface oil into the water of exposure tanks (e.g., Dussauze et al. 2015); and continuous addition of fresh oil to flowing water, e.g., using jets to mechanically generate reproducible suspensions of oil droplets in exposure solutions (Nordtug et al. 2011a). Relative to static or daily-renewal protocols, oil-desorption columns slow the rate of decline in oil concentrations. However, they cannot sustain constant concentrations because oil-water partitioning depletes the finite amount of hydrocarbons in the column. The continuous re-circulation of surface oil in toxicity test tanks sustains relatively constant concentrations of hydrocarbons in water. However, concentrations decline somewhat (Dussauze et al. 2015) due to weathering or absorption to the apparatus. The most stable exposure system is the continuous generation of fresh suspensions of oil droplets by oil-water injection (Nordtug et al. 2011a). In tests with haddock embryos, this system provided a relatively constant exposure regime in terms of TPHs and TPAHs, with less than a 25% decline in concentrations over an 18-day test (Sørhus et al. 2015). The primary drawback is the need to dispose of a large amount of oily wastewater. *Although methods for generating a continuous flow of oil-contaminated water are available, they are not yet widely used or characterized under different salinities, temperatures and flow conditions.*

<u>Recommendation:</u> Research is needed to test and validate continuous-flow methods that improve the stability of exposure concentrations throughout oil toxicity tests.

An alternative way to interpret and apply oil toxicity data developed with time-varying exposures is to incorporate pharmacokinetic equations describing rates of hydrocarbon accumulation, metabolism and depuration into models that relate hydrophobicity to tissue doses causing toxicity (Redman and Parkerton 2015) (Section 4.1.4.1). Mathews et al. (2008) tested this approach with the target lipid model (TLM) developed by diToro et al. (2000). Although the results were promising, data for pharmacokinetics of individual hydrocarbons were scarce. Although the potential role of hydrocarbon metabolism by cytochrome P450 enzymes (sections 4.1.4.4 to 4.1.4.6) was acknowledged, metabolism and the toxicity of metabolites were not included in the model. The TLM modified for pharmacokinetics included the same untested assumptions about uptake, MoA and toxicity of hydrocarbons as the original (Sections 4.1.4.1 and 4.1.4.2), and the data sets used to develop and validate the model were not designed for that purpose. The modified model also did not address the effects of environmental (e.g., temperature, salinity) and biological factors (e.g., species) on rates of PAH uptake, metabolism and depuration.

<u>Recommendation:</u> The uptake and depuration rate constants for a wide array of individual PAHs and alkyl PAHs should be measured for a variety of species and life stages of fish, and at different temperatures and salinities.

4.3.2 Exposure time

Acute toxicity tests typically involve 24 to 96 hour exposures and chronic tests may last days, weeks or months, depending on the response being measured and the life history of the test organism. These tests were originally developed to regulate specific chemicals and the discharge of industrial effluents and may not represent exposure conditions at actual oil spills. NRC (2005) criticized 48 to 96 hour tests because they would be overly conservative, predicting greater toxicity than would be observed in an oil spill where the acutely lethal LMW components would volatilize or be biodegraded in less than 24 hours. However, this critique was written before the DWH oil spill for which there was a continuous discharge of oil for four months, broadening spill scenarios to include longer exposure times.

Nevertheless, *most oil spills are of short duration and information is needed on the long-term effects of short-term exposures, i.e., delayed or lingering toxicity*. Studies of delayed effects are few in number, although recent studies demonstrated that brief exposures (1 to 2.4 hours) of Atlantic herring embryos to realistic concentrations of CEWAF of crude oil following egg fertilization caused equivalent effects on embryo deformities and survival as continuous exposures throughout embryo development (Section 4.2.3). Exposures of fish embryos to low concentrations of oil impaired swimming capacity when the fish had developed as juveniles, well after the exposure had ceased and despite a lack of obvious toxicity during the embryo exposure (Section 4.1.4.5). Longer-term delayed effects on pink salmon migration were also evident years after embryos survived exposure to WAF of ANS crude (Section 4.1.1.4).

If exposures of fish embryos for less than 48 hours are sufficient to impair recruitment, growth, survival and reproduction of juveniles, the impacts of brief oil exposures may be far greater than anticipated.

Recommendation: Research is needed to develop brief and simplified toxicity testing protocols calibrated to realistic exposure scenarios and that assess delayed effects on fish embryos of acute exposures to oil.

4.3.3 Measurements of oil concentrations in toxicity tests

Varying proportions and concentrations of hydrocarbons in test solutions during toxicity tests generate considerable uncertainty in the estimated toxicity of oil. Uncertainty is even greater if hydrocarbon concentrations in test solutions are not analyzed. Toxicity expressed in terms of oil loadings greatly underestimates actual toxicity. Without a detailed chemical analysis of test solutions, the effects of chemical dispersion on oil toxicity can also be misinterpreted (Section 4.2.3).

Bias in estimates of toxicity of mechanically- and chemically-dispersed oil can be reduced by frequent analyses of test solutions to define the actual gradient of exposure concentrations, to assess whether exposures are constant throughout the test, and to establish means and variances for calculating endpoints (e.g., EC50s). Frequent analyses of test solutions by GC-MS provide a detailed understanding of test concentrations of oil and of the hydrocarbons associated with toxicity. Unfortunately, they can also be very costly, which may explain why many papers do not include measured concentrations of oil. Alternatives include fluorescence spectroscopy that can be calibrated against analyses of TPHs and TPAHs (Adams et al. 2014b; Martin et al. 2014). Fluorimetry is well-established as a survey tool in field studies of oil spills (e.g., Kim et al. 2010; Lee et al. 2012). At the concentrations of oil typical of chronic toxicity, there is a linear correlation between measures of TPAHs by GC-MS and concentrations of TPHs determined by fluorescence, enabling the expression of endpoints in terms of TPAHs (Martin et al. 2014), provided that quality assurance and quality control methods are followed.

As a result of the widespread use of dispersant during the DWH spill, there is also a need for inexpensive methods to characterize the concentrations of the ingredients of dispersants, in toxicity test solutions and treated surface waters (Place et al. 2010). Dispersant analyses would clarify the relative contributions of dispersant and oil to the observed toxicity of dispersed oil when dispersants are not completely sequestered by oil droplets. The active ingredient of Corexit® 9500 (dioctyl sodium sulfosuccinate) has been measured successfully by liquid chromatography-mass spectrometry (Kujawinski et al. 2011), but the cost precludes its frequent application for most toxicology research.

<u>Recommendation:</u> Inexpensive analytical methods should be developed for petroleum hydrocarbons and for chemical dispersants that can detect the toxic components at concentrations at or below the threshold of toxicity for most species (Section 4.3).

4.3.4 Confounding of risk assessments by oil droplets

The presence of microscopic oil droplets (<100 μm) in test solutions introduces another major source of uncertainty in estimates of oil toxicity. Uncertainties are due to significant differences among laboratories in protocols for preparing solutions of oil for toxicity tests, in design of exposure systems and in the analytical characterization of test solutions (Redman and Parkerton 2015). Chemical analyses of test solutions typically combine both particulate and dissolved oil because water samples are extracted with solvent. Each measurement represents the sum of hydrocarbons in droplet and dissolved phases, but results are often interpreted as if all hydrocarbons were freely dissolved and bioavailable. This bias applies equally to analyses of water sampled during oil spills. Thus, risk assessments comparing measured toxicity to measured concentrations of hydrocarbons in surface waters will be confounded by significant overestimates of oil concentrations in water and underestimates of oil toxicity. The clear implication for risk and impact assessments is that reliance on published toxicity data, without consideration of the inherent biases in toxicity publications, creates a high risk of predicting false positives (effects when none would occur) or false negatives (no effects when they would occur). These biases reduce the extent to which data can be compared or combined across studies and limit the database for assessments to a very small number of studies.

For many fish species, embryo toxicity appears to be caused by the dissolved components of oil, not particulate or droplet oil (e.g., Carls et al. 2008; Olsvik et al. 2011). If true, *the role of droplets is simply to transfer free-phase oil to the subsurface where partitioning from droplets to water contributes dissolved hydrocarbons (Redman 2015). However, droplets may also be a direct route of oil exposure for some species but not others*. Oil droplets have been observed to adhere to the gills of juvenile trout exposed to chemically-dispersed oil in fresh water (Ramachandran et al. 2004b) and to the eggs of Atlantic haddock in salt water, but not to eggs of Atlantic cod (Sørhus et al. 2015). Oil was more embryotoxic to haddock than to cod (Nordtug et al. 2011b; Sørhus et al. 2015), suggesting little contribution of droplets to toxicity. These results were consistent with experiments in which filtered (no droplets) and unfiltered (droplets) of mechanically-dispersed oil caused little difference in the level of gene expression of cod larvae (Olsvik et al. 2011). Relative to WAF, CEWAF of North Sea oil enhanced the accumulation and toxicity of oil droplets to filter-feeding invertebrates (*Calanus finnmarchicus*) (Nordtug et al. 2015). Other filter feeders (e.g., mussels) accumulate both dissolved and particulate oil but the relative contribution of each phase is not well-defined and may vary among species.

<u>Recommendation:</u> Research is needed to determine the extent to which oil droplets contribute to oil exposure, why droplets interact directly with some species but not others, and the mechanisms and environmental factors that promote droplet interactions with biological membranes.

There are no commonly-accepted methods for separating droplets from dissolved oil in samples collected, although centrifugation and filtration have been tried. Centrifugation is a challenge due to the small differences in specific gravity between water and oil. Contact of unpreserved samples with centrifuge tubes also risks the loss of dissolved hydrocarbons by absorption to the tube. Similarly, concentrations of dissolved hydrocarbons in water samples may be increased or decreased during filtration because droplets that accumulate on filters create an increasing volume of liquid phase oil for oil-water partitioning. To avoid these problems, hydrocarbons in water samples could be extracted and concentrated with passive samplers instead of solvents (Redman 2015). With solid phase micro extraction, dissolved hydrocarbons are absorbed onto a solid matrix followed by GC-MS analysis of the solid phase (Parkerton et al. 2000; de Perre et al. 2014). Solid phase micro extraction reduces the cost, time and potential error of oil analyses, but assumes that the sorbents accumulate hydrocarbons only from the dissolved fraction in water and not from droplet oil.

Droplet bias can be detected by measuring HMW markers of oil, such as phytane, which relatively water insoluble and should be non-detectable if solutions contain only dissolved hydrocarbons. The extent of droplet contamination can be estimated from the ratios of TPAH to HMW alkane concentrations in whole oil and in oil solutions, or by comparing measured concentrations of PAH to their solubility limits calculated from K_{ow} (Redman et al. 2012, 2014). At the moment, few clear strategies exist in fluorescence spectrometry for discriminating dissolved from particulate oil in field samples, although measurements of fluorescence quenching have been used to estimate the interferences by dissolved organic matter in laboratory-prepared mixtures (de Perre et al. 2014).

Recommendation: Research is needed to optimize the use of solid phase micro extractions for measuring dissolved hydrocarbons, to separate dissolved from particulate oil in fluorescence analyses, and to harmonize sampling and analytical methods between field and laboratory studies.

Landrum et al. (2012) reviewed the challenges of testing the toxicity of complex mixtures of organic chemicals and arrived at similar conclusions, with several useful recommendations to improve the utility of experimental data in ERAs (Text box). While it may not be practical to apply all of these recommendations to oil toxicity tests, they should be considered when interpreting and reporting results of toxicity tests.

Guidance for evaluating the aquatic toxicity of complex mixtures of organic chemicals (Landrum et al. 2012)

Establishing a dose-response relationship:

- Separate all dose-response analyses by endpoint;
- Differentiate constant exposures from pulsed or intermittent exposures;
- Identify potential biotransformation products that may be ultimately responsible for the observed effect(s);
- Measure both external concentration and internal (body residue) dose for mixture components, including biotransformation products, to determine those at which different toxicity endpoints are observed and to help identify potential biotransformation products that may be responsible for the observed effect(s);
- If possible, measure body residues for all chemicals in the mixture suspected of contributing to mixture toxicity; this provides more certainty than measures of external concentrations for actual target site concentrations, particularly when there are multiple exposure routes;
- If all mixture components are not or cannot be analyzed, transparently document the associated uncertainties so that surety of cause is not assumed;
- Ensure that measurement endpoints are appropriate to the mechanisms of toxic action of the mixture and its components so that comparisons are not 'apples to oranges'. Consider and account for toxicity modifying factors that can confound apparent conclusions, including environmental conditions of the test, life stages and behaviour of the test organisms, possible external or internal biotransformation of mixture components, and temporal dilution or variation in concentration of mixture components in the exposure medium (water, diet) or in tissues of test organisms;
- Do not assume that correlation proves causation - it does not;
- Consider all data and do not ignore inconsistencies that may well provide critical information to assist in determining causation;
- Determine causation relative not just to the mixture but to its constituent components, including biotransformation products - such products can sometimes be more toxic than the parent compounds;
- Conduct confirmation studies, such as bio-effect directed fractionation, or tests with individual or surrogate mixtures of mixture components, and/or perform modeling based on known mechanisms, such as molar or TU addition; and
- Discuss any and all uncertainties explicitly and transparently - do not overstate the cause of the toxicity when only inference has been established by focusing on a portion and/or portions of a mixture.

4.3.5 Realism in toxicity tests

The concern expressed in this review for maintaining constant concentrations of oil during toxicity tests runs counter to concerns that tests reflect the 'reality' of oil spills, when concentrations of oil vary enormously, both spatially and temporally. The 'spiked' CROSERF protocol for preparing and testing solutions of WAF and CEWAF models the rapid loss of hydrocarbons from the water column at actual spills by standardizing one decay rate of oil concentrations in test solutions (Singer et al. 2000). The method was described as more realistic than tests in which concentrations remain relatively constant. However, given the site- and spill-specific fate and behaviour of oil, standardizing tests to one time-varying scenario creates the same lack of realism as a constant exposure scenario. Interpreting exposure concentrations that vary temporally is difficult and presents significant problems for predictive models of toxicity used in risk assessments that assume constant exposure concentrations (Sections 4.1.4; 4.3.1). Predictive models treat toxicity as a fixed reference point that can be modified by known environmental conditions to estimate effects under natural conditions.

Given that results of toxicity tests are strongly influenced by protocols chosen for preparing and testing oil solutions (Redman and Parkerton 2015), laboratory tests can never be realistic. However, methods can be standardized to provide data comparable among labs, species and oils. Thus, NRC (2005) suggested that the CROSERF method be refined to:

- Standardize mixing energies for WAF and CEWAF;
- Prepare gradients of test concentrations by diluting stock solutions instead of preparing unique stock solutions for each concentration;
- Prolong the exposure to measurable concentrations of hydrocarbons;
- Replace nominal exposure concentrations with measured concentrations of TPHs and/or TPAHs, and report the time during the exposure when concentrations are measured;
- Include treatments to test the potential for photo-enhanced toxicity; and
- Substitute open test chambers for sealed test chambers to allow volatiles to evaporate during the test.

Many of these recommendations have been followed in recent studies. *For ERAs, effects under realistic conditions could be estimated by applying toxicity data to the unique site-specific circumstances of each potential or actual oil spill.*

<u>Recommendation:</u> Research is needed to determine the relationship between toxicity and exposure time, and the nature of delayed toxicity following acute exposures (Section 4.3.2).

4.4 Research Needs and Recommendations

The following is a synthesis of research needs identified in previous sections. Many involve the development and standardization of protocols for lab toxicity testing, post-spill field assessments and monitoring of impacts.

4.4.1 Research Needs

Research is needed:

- At ‘spills of opportunity’ and experimental oil spills to identify effects on aquatic species at the level of populations, communities and ecosystems due to the acute and long-term toxicity of spilled oil;
- On how the behaviour and fate of fresh and weathered oil in different ecosystems interacts with the habitat selection and unique life history traits of aquatic species to control species-specific oil exposure and toxicity. These interactions are particularly important for diluted bitumen (dilbit) relative to conventional oils, and northern and Arctic ecosystems relative to temperate ecosystems;
- To understand how different oil types (e.g., dilbit) and spill-control agents (e.g., chemical dispersants) affect aquatic species under different environmental conditions, including interactions with contaminants from municipal, industrial and agricultural effluents;
- On mechanically- and chemically-dispersed oil to determine how oil droplets affect the exposure and toxicity of oil to different species and life stages of aquatic organisms. These studies include a need to develop analytical methods to reliably discriminate droplet oil from dissolved oil. Studies on the distribution and effects of dispersed oil under exposure conditions similar to those that may be encountered during response operations (including subsurface injection of dispersants) are of particular importance;
- On strategies and protocols to recover spilled oil that avoid or minimize habitat damage, methods to restore damaged aquatic and riparian habitats and models to define the balance between the environmental costs of natural remediation and oil spill cleanup; and
- On methods for finding and measuring spilled oil in different compartments of freshwater and marine ecosystems, for measuring exposure and toxicity of oil to aquatic species *in situ*, and for assessing the structure and function of ecosystems that reflect the extent and time to recovery following oil spills;
- On the contamination of ground water due to soil contamination and the entrainment of oil droplets into bed sediments of rivers by surface water-ground water exchanges;

- To develop standardized oil toxicity test methods for all classes of aquatic organisms to enable reliable comparisons of toxicity among oils, species and different environmental conditions (e.g., salinity, temperature), including rapid changes in oil concentrations in water; and
- To refine models that predict acute and chronic toxicity to aquatic species, particularly to assess the uncertainty caused by violating the assumptions underlying these models and to reduce the variance of model predictions.

4.4.2 Operational/preparedness Needs

Baseline monitoring is needed in areas where oil is shipped or produced to resolve uncertainties about 'cause and effect' should a spill occur. Baseline monitoring should include:

- The physical and chemical characteristics of aquatic ecosystems; and
- The ecology, population dynamics, productivity, population demographics, abundance and seasonal and spatial use of habitat by locally-resident and transient aquatic species.

CHAPTER 5: MODELING OIL SPILLS IN WATER

Abstract

Oil contains thousands of compounds and its properties can change drastically as natural weathering processes proceed immediately following a spill. For this reason, earlier modeling of oil behaviour and transport was phenomenological with a heavy reliance on experimental observations. Since the early 1980s, advances in oil spill modeling have been largely focused on oil dispersion (formation of oil droplets), formation of oil particle aggregates (especially after the *Exxon Valdez* oil spill in 1989), emulsification, evaporation and general transport in open waters, as well as other types of ecosystems. As a consequence of the Deepwater Horizon spill and emerging concerns over the environmental risks associated with offshore oil and gas activities in frontier regions, more advanced numerical models have recently emerged to better predict various processes, especially in situations where no direct measurements could be made, such as in deep water or in the Arctic. Major modeling advances have emerged in the areas of dispersion, biodegradation, dissolution and oil-in-ice behaviour. To improve our understanding on the influence of environmental factors on the fate and behaviour of spilled oil, modeling efforts continue to be needed in the area of oil-in-ice, the prediction of oil dispersion by waves, oil droplet formation from blowouts, formation of oil particle aggregates and the biodegradation of oil droplets under various environmental conditions, including temperature, salinity, nutrients and light (to elicit the significance of photooxidation processes).

Introduction

In modeling, it is often said that a large spill of oil is actually multiple spills. This is because the oil properties change with time and distance from the source and the tools adopted near the source could be ineffective 20 km from the source. Also the tools used on day one could become obsolete on day 10 because of oil weathering or transport to a different type of environment (e.g., from open water to beaches). In addition, oil spills could cover large areas and it is cost prohibitive to model all processes occurring at the smallest scales. Yet, the impact is localized, dependent on the concentration at a particular receptor. Earlier modeling efforts of oil spills relied on using simple formulations for oil weathering that are calibrated to experimental studies. The resulting formulations have been used in subsequent oil spill models. However, no rigorous field validations were available or forthcoming due to lack of experimental replication or accurate characterization of the environmental conditions (such as wave energy, etc.). Improvements on these formulations have taken place in recent years in various categories, including emulsion, dispersion and biodegradation of oil. However, more work is needed, including the formation of oil particle aggregates (OPAs), a fraction that was previously not accounted for in mass balance calculations, which also influences the transport (e.g., sedimentation rates), fate (e.g., oil biodegradation rates) and effects (e.g., bioavailability) of the residual oil.

The change of oil properties with time is known as ‘weathering’ and it affects the subsequent transport and behaviour of oil. Chapter 2 discusses these effects in detail. For this reason, this chapter addresses first the modeling of the fate of oil due to weathering and then the modeling of the transport of oil in various compartments of the environment: lakes, rivers, shorelines, wetlands, etc. To facilitate understanding of the information in this chapter, most modeling equations discussed were not included in the write-up; rather, the equations were explained by discussing the terms in simple English.

5.1 Modeling of Oil Weathering

When oil is spilled into the environment, its physical and chemical properties change over time in a process known as weathering, which includes the following processes: spreading, evaporation, dissolution, dispersion, photooxidation, emulsification, OPAs and biodegradation (**Figure 5.1**). All of these are discussed in detail in Chapters 2 and 3. Analyzing and quantifying the degree of oil weathering (i.e., oil fate) is a necessary step to determining oil transport and persistence in the environment. For this reason, this chapter starts by addressing oil weathering.

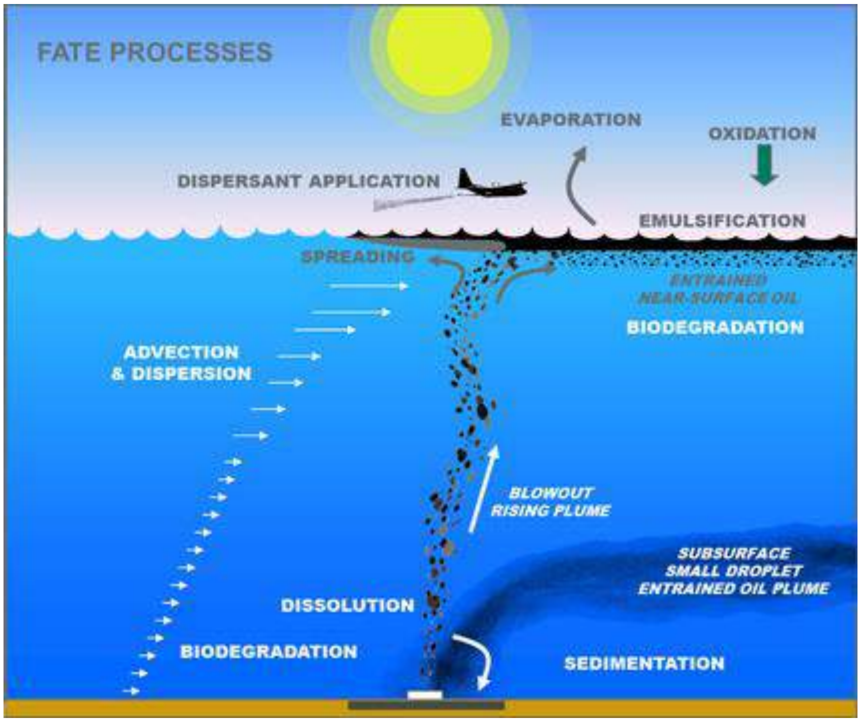


Figure 5.1 Illustration of the fate process of oil spills in water. *Image from Water Resources and Modeling Group of ERM Inc. (http://gemss.com/cosim.html).*

5.1.1 Oil evaporation

The modeling of oil evaporation is based on equations originally developed for water evaporation (Sutton 1934, Brustaert 1982), where the exchange of water between the waterbody and the atmosphere was modeled using a mass transfer formulation in which the exchange depends on the water vapour pressure in the atmosphere and on a mass-transfer coefficient that represents the hydrodynamics at the water-atmosphere interface (Brustaert 1982). Sutton (1934) developed a mathematical expression for water evaporation having the terms mass transfer coefficient, concentration of the evaporating liquid, wind speed, size of the water body and a ratio of kinematic viscosity (defined in Chapter 6) of the air to the molecular diffusivity in air. Sutton's formula shows that as the wind speed increases, water evaporation increases, which confirmed empirical observations.

Most of the modeling of oil evaporation relies on using the vapour pressure of various oil components based on distillation data and average boiling points. Blokker (1964) presented one of the earlier models under this category. Yang and Wang (1977) developed a model that accounted for the role of the slick area in affecting evaporation. However, one of the most widely used models for oil evaporation was developed by Stiver and Mackay (1984). That model included terms for the volume fraction evaporated, absolute temperature, a ratio called the 'evaporative exposure', and constants obtained based on experimental data. Similar models include those developed by Tkalin (1986) and Hamoda et al. (1989). The latter correlated the mass transfer coefficient to the API gravity of oil and the salinity of the water and found that oil evaporation increased slowly proportional to salinity. Bobra (1992) compared the Stiver and Mackay (1984) model to extensive experimental data of oil evaporation and reported that the model performed well for the first eight hours, but overestimated long-term evaporation in most cases.

In a series of later studies, Fingas (2011; 2013) challenged basing oil evaporation models on water evaporation, arguing that the evaporation of oil is not limited by the air boundary layer, but by the diffusion of oil components to the interface between the oil and the atmosphere. The author also noted that the vapour pressure of water is much lower than most of the hydrocarbon compounds of interest for evaporation. Thus, the author concluded that the limiting factor for oil evaporation was in the liquid oil and not in the air above it. The studies included evaporation experiments of diesel, ASMB (Alberta Sweet Mixed Blend) oil and water in wind tunnels at different wind speeds and observed that the wind speed increased the evaporation of water. However, the increase of oil evaporation with wind speed occurred only when comparing to the no-wind condition. All non-zero wind speeds gave essentially the same oil evaporation rate. Based on these results, Fingas (2013) developed two different empirical equations that predict evaporation of oil based on the properties of the oil, one for diesel and one for heavier oils. Both equations indicate that evaporation decreases with time under given environmental conditions.

A study by King et al. (2013) in a flume tank exposed to the atmosphere found that the density of the Access Western Blend increased to more than that of fresh water while the density of the Cold Lake Blend remained lower than that of fresh water. They used a hyperbolic law for estimating the increase in mass density with time of the two products.

5.1.2 Oil dissolution

In general, dissolution is not a major mechanism for oil spilled onto the water surface, as most of the components that dissolve have high vapour pressures and thus evaporate quickly. Thus, evaporation and dissolution for surface oil are competitive processes with evaporation the dominant one (French-McCay 2004). However, dissolution could become important for oil away from the atmosphere, such as from underwater releases, namely the Deepwater Horizon (DWH) spill (Camilli et al. 2012) or in the subsurface, such as in the aquifer of Bemidji oil spill site (Essaid et al. 1995; Cozzarelli et al. 2010; Ng et al. 2014). The compounds that dissolve rapidly and result in measurable concentrations in the water column are the monoaromatics, also known as BTEX (benzene, toluene, ethylbenzene and xylenes). Naphthalene, a PAH, also has a high solubility in water, and so are short chain alkanes, such as methane, ethane, propane and butane (Ryerson et al. 2012).

> Oil evaporation dominants the mass transfer rates for surface oils, while for underwater releases and in the aquifer, oil dissolution becomes important. For underwater releases, droplet size distribution is the most important parameter affecting the oil dissolution rate.

Mackay and Leinonen (1977) and Mackay et al. (1980) conducted theoretical investigations of mass transfer at the oil-water interface and concluded that the dominant mechanism of transfer of soluble hydrocarbons into the water column during an oil spill is by dispersed oil droplets rather than surface slicks. Thus, droplet size distribution is the dominant factor in determination of the oil dissolution rate in subsurface oil release. Small droplets (e.g. ~ 100 µm in diameter) ascend slowly through water and could remain in the water column for days or months. This buoyancy contributes significantly to oil dissolution. Large droplets (e.g., greater than a few hundred µm in diameter) rise to the water surface rapidly, so dissolution from those droplets is relatively inconsequential (French-McCay 2004). Mackay et al. (1980) showed that dissolution from surface oil is negligible.

The dissolution of oil differs from that of a pure compound due to the competition of high solubility compounds reaching the oil-water interface and subsequently the water column. In addition, polar compounds in the oil, such as the resins and asphaltenes, tend to migrate to the oil-water interface. However, they tend to remain at the interface due to their low solubility in water. Therefore, these compounds tend to lower the dissolution rate of the remaining oil components in the droplet into the water column.

5.1.3 Photooxidation

Photooxidation results from exposure of spilled oil to sunlight, which causes some components in the oil to oxidize, potentially facilitating their chemical and biological degradation. Yang et al. (2015) studied the photochemical behaviour of crude oil in a simulated freshwater environment and found that lower molecular weight alkanes were photooxidized more rapidly than the higher molecular weight compounds. They also found that PAHs can be photooxidized more readily than alkanes, which is consistent with prior studies (Garrett et al. 1998; Maki et al. 2001; Prince et al. 2003; Radović et al. 2014; D'auria et al. 2009). Prince et al. (2003) also report that the majority of aromatic fractions were converted to resins and asphaltenes. However, a more recent study (Aeppli et al. 2012) indicated that photooxidation produces oxygenated hydrocarbons that might persist in the environment and can produce carbonyl compounds (compounds with a C=O group such as carboxylic acids, aldehydes, amides, etc.) and alcohols, which are soluble in water and thus can be carried by water flow (Chapelle 2001).

5.1.4 Oil emulsification

When oil persists on the water surface for hours and days, it tends to incorporate water droplets within it, forming water-in-oil emulsions. This process is the opposite of oil dispersion where oil droplets are incorporated into the water column. The water-in-oil mixtures are grouped into four classes: stable, meso-stable, unstable and entrained water (Fingas and Fieldhouse 2004). The characterization is based on the persistence of the water-in-oil mixture and also visual observation. Stable emulsions, called mousse (Chapter 3), tend to be semi-solid material with a reddish-brown (even orange) color and can persist for weeks. Meso-stable emulsions tend to be liquid and brownish to black in colour and tend to persist for several days to a week under laboratory conditions. However, they can persist much longer in the environment. The remaining two classes are black in colour, and the water content of these water-in-oil emulsions varies. Stable emulsions contain around 80% water. Meso-stable emulsions initially contain around 70% water, and the amount of water decreases to around 30% after a week. The unstable and entrained-water classes contain usually around 10% water by volume (Fingas and Fieldhouse 2004), and are common in low viscosity oils (viscosity less than 20 cp[1]) or high viscosity oils (viscosity higher than 1,000 cp, such as weathered diluted bitumen).

Emulsification appears to increase as the resins and asphaltenes in the oil increase. These latter compounds act as surfactants and thus situate at the oil-water interface (Bobra 1992). Both asphaltenes and resins comprise polar compounds. Observations (Fingas et al. 1996, 2000, 2002) revealed that the weight fraction of asphaltenes was typically higher than 7% in a stable emulsion, and that the weight fraction of asphaltenes and resins was higher than 3% in a meso-stable emulsion. The presence of waxes (high molecular weight alkanes) was found to also promote emulsification but to a lesser extent than asphaltenes and resins. Thus, the stability of water-in-oil emulsions seems to depend primarily on the asphaltene content. However, it is thought that resin molecules, which are smaller than asphaltene molecules, tend to initially locate at the oil-water interface, causing the formation of the emulsion, but that asphaltenes subsequently migrate toward the interface and render the emulsion stable. In that sense, asphaltenes seem to be a stronger surfactant than the resins. Also, in fairly general terms, emulsification is promoted by the viscosity of the oil (i.e., oils that have moderate to high viscosity tend to emulsify more than lighter oils). Thus, emulsion formation increases with weathering of the oil, especially due to evaporation and dissolution. Both processes cause the viscosity of the oil to increase. Therefore, emulsification models depend on the outcome of the evaporation and dissolution models.

Traditional modeling of emulsification relied on predicting three parameters, the water content in the emulsion, the class of emulsion (discussed above) and the resulting viscosity of the emulsion (Fingas and Fieldhouse 2004; Xie et al. 2007). The water content is important because in a stable emulsion, it is 80%

[1] *Centipoise (cp) is a measurement unit of dynamic viscosity in the cgs (cm-g-sec) system of units.*

by weight, which means that an emulsion contains approximately five times the initial volume of the oil. This poses major challenges for removing and treating the emulsion in the environment. Mackay et al. (1980) developed an equation to estimate the water content of a water-in-oil emulsion containing two rate constants for water incorporation and a third rate constant that depends on the coalescing tendency of the emulsion. Mackay and Zagorski (1982) suggested a stability index, which is calculated from the asphaltene and wax content in the oil, other oil components and temperature. Thus, for a content of asphaltene > 7% the stability index is > 1.22, and for the content of asphaltenes and resins > 3% the stability index declines to 0.67. Values of the stability index between 0.67 and 1.22 represent a meso-stable emulsion, while values less than 0.67 represent an unstable emulsion. Zeidan et al. (1997) proposed a chemical composition index to determine the class of emulsion. The model contains terms for weight fractions of asphaltenes, resins and waxes. The dynamic viscosity of the emulsion can be estimated by the method of Mooney (1951). Xie et al. (2007) also considered the demulsification of the emulsion and represented it using an exponential decay curve for meso-stable and unstable emulsions. They noted that a minimum amount of energy was commonly needed to initiate the emulsion, and they also developed estimation methods based on the sea state.

In a departure from the literature on emulsification modeling, Fingas and Fieldhouse (2004) argued that the constituent oil fractions are not sufficient to fully predict the emulsification class. For example, diluted bitumen contains more than 20% by weight of either asphaltenes or resins, yet it does not form an emulsion because of its high dynamic viscosity (more than 10,000 cp). They considered an extensive database of emulsions and developed empirical relations to predict the classes of emulsions, and the corresponding water content and viscosity.

Emulsification was found to reduce oil evaporation and dissolution. Experiments by Ross and Buist (1995) revealed that the intensity degree of oil evaporation decreases with increasing water content and slick thickness, both due to emulsification. Xie et al. (2007) investigated these findings and developed an empirical model for oil evaporation from an emulsion. The model contained terms for the weight fraction of water, the oil evaporation from pure oil and the evaporation from the emulsion.

5.1.5 Oil dispersion

For surface oil spills, wave action breaks the oil slick into droplets (i.e., oil dispersion) propelling them into the water column. An empirical formula was developed by Delvigne and Sweeney (1988) and Delvigne (1994) for dispersion. The important terms in the formula were the particle size, the particle size interval, the entrainment rate per unit surface area of oil particles with particle sizes in a specific interval around the particle size term, an empirical constant dependent on the oil type and weathering state, the energy dissipated during breaking waves per unit surface, the fraction of surface area covered by oil, and the fraction of sea surface hit by breaking waves per unit time. The energy dissipated term and the sea surface fraction of breaking waves per unit time were further modeled using two additional semi-empirical formulas containing terms for root-mean of wave heights, wind speed and threshold wind speed for generation of breaking waves.

In another model, Mackay and Leinonen (1977) assumed that the dispersion of oil from the slick was the sum of two rates: a breaking wave rate and a non-breaking wave rate. This model included terms for the volume fractions of oil droplets permanently dispersed by non-breaking and breaking waves, the slick thickness and the fraction per second of slick area forced into the water column by the breaking waves.

Probably the most appealing aspect of the Delvigne and Sweeney (1988) model is that it estimates the amount of oil entrained based on the wave energy. Another appealing aspect of this model is the ease-of-use and low computational cost. However, no validation of the model has been made in field situations due to the large scale of natural systems and variability in the sea.

Zhao et al. (2014a,b) developed the model VDROP, a comprehensive model that estimates the droplet size distribution (DSD) based on the properties of the oil and the hydrodynamics of the system. While most models of its type consider the interfacial tension to be the only force resisting breakup, the VDROP model allows for situations where the viscosity of the oil resists the breakup of the droplets, which occurs when the oil is highly viscous and/or when dispersants are used, causing the interfacial tension to decline. Zhao et al. (2014a) considered that, after each breaking wave event (assumed every two minutes), droplets smaller than 100 µm were driven into the water column away from the surface. The energy dissipation rate in the model can be roughly estimated based on the sea state (i.e., amount of breaking waves).

5.1.6 Oil particle aggregation

As oil approaches coastal regions it tends to interact with the higher load of suspended particles in the water column to form OPAs, which move differently from oil droplets or particles alone (**Figure 5.2**). The suspended particles include mixtures of silt, clay, detrital organic matter and algae or plankton, whose concentrations near shorelines are much higher than encountered by oil offshore, especially if the oil came from a surface spill. There are two major types of OPA: 1) oil droplets coated by small particles resulting in the so-called Pickering emulsion (Le Floch et al. 2002; Frelichowska et al. 2010); and 2) large particles adsorbing oil onto them and trapping oil between them (Stoffyn-Egli and Lee 2003). The first type is the most common and results in a larger volume of trapped oil, and sometimes can consist of many oil droplets binding together forming a large OPA (Le Floch et al. 2002; Omotoso et al. 2002). In this type, the oil droplets of interest are typically larger than 50 µm, whereas the particles are typically smaller than a few µm.

> Alternative terms to OPA have been used, such as OMA (oil mineral aggregates) and OSA (oil suspended particulate matter aggregates). The term OPA was coined by the Boufadel group while addressing the diluted bitumen spill in the Kalamazoo River in Michigan 2010. The group argues that existing terms are restrictive as the particulates do not have to be minerals, and the suspension state is not an intrinsic property, rather depends on the hydrodynamics.

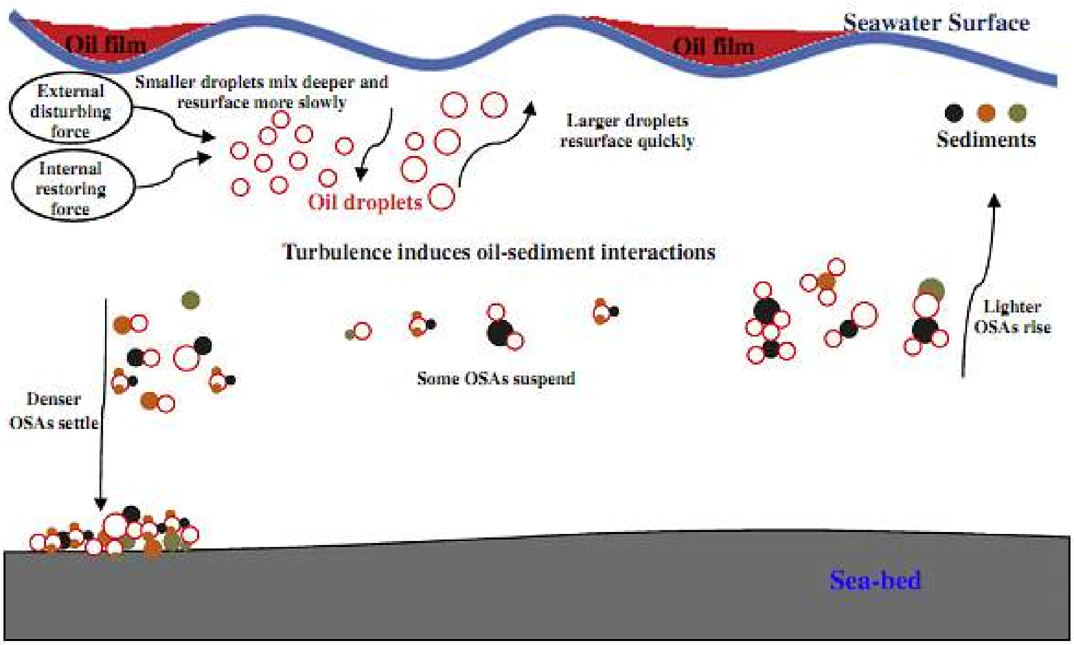


Figure 5.2 Formation and movement of various types of OPAs in marine systems. *The term OSA implies (oil suspended aggregates). The term OPA comprises OSA and OMA (as developed by the Kenneth Lee group). This image is reprinted from Gong, Y., Zhao, X., Cai, Z., O'Reilly, S.E., Hao, X. and D. Zhao. 2014. A review of oil, dispersed oil and sediment interactions in the aquatic environment: Influence on the fate, transport and remediation of oil spills. Marine Pollution Bulletin 79: 16-33. Copyright Elsevier (2014).*

Of interest in modeling the OPAs is the critical particle concentration, which is the concentration that results in complete coverage of the oil droplet, observed to be around 30 to 50% of the oil concentration expressed in the same units (Ajijolaiya et al. 2006). For example, if the oil concentration in the water column is approximately 100 mg/L, then a sediment concentration of 30 to 50 mg/L would ensure complete coverage of the oil droplets.

The formation of aggregates depends on the viscosity and adhesive properties of the oil droplets, the surface area and chemical and physical properties of the particles, and the salinity of the water and other factors such as the presence of dispersants (Lee 2002; Khelifa et al. 2005). High viscosity oils (dynamic viscosity >500 cp) or those with high adhesion (>50 g/m^2) (Jokuty et al. 1995) tend to bind to sediments rapidly. The efficiency of trapping increases with the hydrophobicity of sediments until it reaches a maximum and then decreases (Sun et al. 2010). This is because as the particles become more hydrophobic, they tend to attach more closely to oil. However, if they become too hydrophobic, they tend to clump together and thus their chance of adhering to oil decreases. In addition, the increase in salinity enhances OPA formation, and enhancement is high when the salinity increases to >1,000 mg/kg (Sun et al. 2010).

Common modeling approaches for the OPAs rely on estimating the trapping efficiency by empirical expression fitted to experimental data. This is unlike the approach that has been used for modeling oil dispersion in chemical engineering (Tsouris and Tavlarides 1994) or in oil spill mitigation (Zhao et al. 2014). A justification for the simplification in modeling OPAs is probably due to the fact that, unlike oil droplet models where only oil droplets interact with each other, an OPA model would require the interaction of droplets, particles and OPAs, resulting in an excessive number of equations to capture all interactions. Nevertheless, existing OPA models cannot predict based on the fundamental properties of the oil or particles, and they constitute a challenge when predicting the behaviour of oil in systems with high sediment (or particle) content, such as streams (Fitzpatrick et al. 2015) and shorelines (Owens and Lee 2003).

5.1.7 Oil biodegradation in open water

Since the biodegradation of oil depends on the oil-water interfacial area (Atlas and Hazen 2011), the biodegradation of slicks is considered negligible in comparison to that of oil droplets. Therefore, for oil spills on the water surface, dispersion is a key factor affecting biodegradation. The approach adopted in NOAA's *Automated Data Inquiry for Oil Spills* (ADIOS2) model consists of treating the oil as various classes (C_4-C_{12} alkanes; 2-3 ring aromatics) to allow for the reduction of the size of oil droplets following biodegradation (Viveros et al. 2015). This is a simple approach as the ADIOS2 model is intended for short-term prediction, mainly during the response to an oil spill. A recent work by Yassine et al. (2013) modeled oil biodegradation using Monod kinetics and a quasi-steady state approximation for the dissolution of low solubility hydrocarbons in the water column. They reported good agreement with data. Vilcáez et al. (2013) assumed that the microorganisms covered oil droplets completely. The simulation results revealed that small oil droplets biodegraded faster due to their larger surface area per unit mass. Their model suggested that oil droplets biodegraded faster than dissolved oil components due to their assumption of complete microbial coverage of oil droplets. However, they provided no data to confirm their assumption.

5.1.8 Oil biodegradation within beaches

When oil reaches the shoreline, it percolates into the subsurface when the tide falls, and after a few days a residual amount of oil remains entrapped within the sediments by capillary forces, regardless of the action of the subsequent tides and waves.

Numerical models have been used to predict biodegradation of petroleum hydrocarbons since 1980. However, most of them aimed at modeling the biodegradation of dissolved hydrocarbons (Borden and Bedient 1986; Essaid et al. 1995; Clement 1997). In the model of Borden and Bedient (1986), the biodegradation of dissolved hydrocarbons was assumed to be limited by the availability of oxygen. One- and two- dimensional models were used to investigate the effect of microbial kinetics and oxygen transfer on hydrocarbon biodegradation. Essaid et al. (2003) used the U.S Geological Survey (USGS) solute transport and biodegradation code BIOMOC coupled with the USGS universal inverse modeling code UCODE to quantify the BTEX dissolution and biodegradation at an aquifer site located in Bemidji, MN. Essaid et al. (1995) used a two-dimensional model to simulate the sequential aerobic and anaerobic biodegradation of volatile and non-volatile fractions of dissolved organic carbon. Clement (1997) developed a modular computer code called RT3D to describe reactive multispecies transport in three-dimensional groundwater systems with consideration of multiple electron acceptors for hydrocarbon biodegradation. These studies also accounted for the hydrocarbons in an immobile oil phase by adding oil sorption under equilibrium (Borden and Bedient 1986; Essaid et al. 1995) or non-equilibrium conditions (Clement 1997) into their models. The model SEAM3D (Widdowson et al. 2002) was developed to account for sequential electron acceptors in aquifers contaminated with dissolved hydrocarbons. In this model, the hydrocarbons used molecular oxygen as an electron acceptor, followed by nitrate, manganese, iron, sulfate (sulfate reducing), and finally carbon dioxide (methanogenic). SEAM3D was used to evaluate the potential biodegradation of oil trapped in the sediments of a beach in Grand Isle, LA (OSAT 2011), and it was found that the dissolution of oil was a limiting factor for the migration of oil off site. However, all of the aforementioned models applied to dissolved hydrocarbon or relied on physical dissolution from the immobile/oil phase into the mobile phase for biodegradation to occur. Thus, the biodegradation of the low solubility hydrocarbons, which occurs by microorganisms colonizing the oil-water interface, cannot be effectively accounted for.

Nicol et al. (1994) presented a framework for one-dimensional modeling of biodegradation of residual low solubility petroleum hydrocarbons in fully saturated porous media. The biodegradation of residual oil was limited by electron acceptor (dissolved oxygen) and nutrients (nitrogen and phosphorus), which were transported through the porous medium by advection and dispersion. El-Kadi (2001) developed a model for hydrocarbon biodegradation in tidal aquifers considering the impact of the water content and temperature on microbial activities. Both dissolved and trapped hydrocarbons were considered. The model assumed that trapped hydrocarbons were immobile in the porous medium and were subject to the same biodegradation mechanisms as dissolved hydrocarbons. For modeling trapped/residual hydrocarbon biodegradation, both studies (Nicol et al. 1994; El-Kadi 2001) assumed that the hydrocarbons dissolved in the aqueous phase by biosurfactants produced by the oil degrading bacteria are directly metabolized by the bacteria.

The model BIOB (Geng et al. 2013,2014; Torlapati and Boufadel 2014) was developed to simulate the biodegradation of low solubility hydrocarbons in porous media. In the model, the rate of hydrocarbon biodegradation was considered proportional to biomass growth (Rittmann and McCarty 2001; Tchobanoglous et al. 2002). In order to consider the washout of hydrocarbons in a beach environment, a hopane-normalized term was added to the equation of hydrocarbon removal following the work of Venosa et al. (1996). The biomass growth rate is assumed to be limited by the availability of hydrocarbons and nitrogen, expressed as a dual-Monod formulation (e.g., Molz et al. 1986). In field environments, the size of the microbial population in a porous medium is constrained by factors, such as pore space, production of inhibitory metabolites and sloughing of microbial biomass (Weise and Rheinheimer 1977; Kazunga and Aitken 2000; Rønn et al. 2002). To avoid unreasonably high microbial populations, Geng et al. (2014) used the formulation of Kindred and Celia (1989) and Schirmer et al. (2000) introduced a term to the model to account for the decrease in biomass accumulation when the microbial concentration approaches its maximum value. The BIOB model was calibrated to laboratory column data reported in Boufadel et al. (1999) and Venosa et al. (2010) and to field data reported in Venosa et al. (1996). The model was able to reproduce the experimental data of oil, oxygen consumption, carbon dioxide production and biomass as represented by the Most Probable Number. The BIOB model was also capable of capturing the impact of nutrient concentration of microbial growth and hydrocarbon biodegradation.

5.2 Oil Transport

In this section, the transport of oil is addressed in systems of increasing complexity. First the spreading of oil on the water surface is considered. This is followed by a discussion of the transport of oil on lakes, where wind and waves are the major conveyance mechanisms. Then, the transport of oil in streams and rivers is examined, which adds the complexity of the interaction of the main channel with stagnant zones and with the hyporheic zone (the subsurface surrounding the stream). Finally, the transport of oil in estuaries is reviewed where vertical salinity gradients could confine the dispersed and dissolved oil to the upper portion of an estuary.

5.2.1 Spreading

Fay (1971) and Hoult (1972) developed physical arguments for the spreading of oil spilled on a calm sea. They explained that initially the oil spreads due to gravity because oil rests higher than the water surface, and afterwards it spreads due to the interfacial tension between oil and water. The water inertia resists the spreading of the oil in the initial phase of the spill, and the water viscosity becomes the main resisting force after the initial phase. However, when wind and/or waves are present, the modeling of surface spreading would need to account for the elongation of the oil along the wind direction (Lehr et al. 1984). Thus, instead of a circular spill based on the Fay's analysis, one would obtain an ellipse with the long axis aligned with the wind direction.

5.2.2 *Transport in lakes and sea*

The movement of oil on lakes is driven to a large extent by the action of winds because the current velocity is small. Wind affects the movement of oil on water in three ways:

- Wind can transport oil floating on the water surface without affecting the water beneath it. The speed of oil movement carried by the wind could be up to 6% of the wind speed and is typically assumed to be 3 to 4% in some models (ASCE 1996; Barker 2011; Boufadel et al. 2014);
- Wind over a fetch of say 5 km can generate waves, which can alter the trajectories of oil. As the wave propagates, the water velocity beneath it changes: the water velocity is forward (in the direction of wave propagation) under the wave crest and backward under the trough. Thus, floating objects, such as an oil slick on the water surface or oil droplets dispersed in the water column, move forward when the crest passes and they move backward when the trough passes. However, the forward movement is greater than the backward movement resulting in a net forward transport known as the Stokes drift (Dean and Dalrymple 1984). The maximum value of the Stokes drift is at the water surface, and in general it decreases exponentially with depth. Waves also break up the oil slick into oil droplets, causing dispersion, and propels them into the water column. The subsequent transport of oil droplets would depend on the size of oil droplets, as noted by Elliot et al. (1986) and later by Boufadel et al. (2006, 2007). These studies explained the comet shape of oil spills, wherein a large mass of oil propagates ahead of a tail. The large oil droplets (which typically hold most of the oil mass) have a higher buoyancy and thus remain near the water surface, and get advected further forward by the Stokes drift than smaller oil droplets that tend to be deeper due to diffusion and wave motion; and
- Wind can generate Langmuir cells (Langmuir 1938; Leibovich and Ulrich 1972), which are circulation cells within the water column perpendicular to the wind propagation direction. They would transport the oil along windrows and cause it to down-well into the water column. A salient example of this was the 1993 *Braer* oil spill off the coast of Shetland, Scotland, where the oil disappeared off the water surface to reappear hours later, and the movement was attributed to Langmuir cells (Farmer and Li 1994).

5.2.3 *Transport in streams and rivers*

The transport of the bulk of spilled oil in a stream or river can be easily predicted based on the stream discharge and stream morphology, which provide the hydrodynamic properties needed by the model, such as stream velocity and the turbulent diffusion coefficients (Fischer et al. 1979; Rutherford 1994). However, a small but non-negligible amount of oil remains entrapped in dead or stagnant zones near the banks of the river and in the hyporheic zone, which is the subsurface surrounding the stream (Jones and Mulholland 1999). These zones behave as transient storage zones retaining water and oil from the main channel and releasing them at a slow rate, thus extending the residence time of an oil spill in the stream. The transport of oil in rivers could also be affected by the regional groundwater table, and whether the reach is gaining or losing water (Jones and Mulholland 1999). Field studies revealed that groundwater in rivers gaining groundwater could confine plumes into the main channel, which would increase their downstream transport due to the larger velocities near the thalweg[2] of streams (Ryan and Boufadel 2006).

Hyporheic flows (i.e., the flow between the main channel and the hyporheic zone[3]) are very important ecologically, as the hyporheic zone provides a spawning ground for fish. Fish embryos may be adversely affected by hydrocarbons, as hyporheic outflows from oil-contaminated rivers may carry dissolved and particulate oil into the hyporheic zone. Hyporheic flows also carry oxygen into sediments and remove metabolic waste products, such as ammonia, due to the metabolism of communities of bacteria, fungi and

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[2] The thalweg is a line along the stream length connecting the lowest points of the streambed.
[3] The hyporheic zone is a region beneath and alongside a stream bed, where mixing occurs between the shallow groundwater and surface water.

invertebrates that inhabit the hyporheic zone. If down-welling in shallow water transports oil into the hyporheic zone, particulates may be trapped as free-phase oil in the interstitial spaces between sediment particles and act as a source of dissolved hydrocarbons from oil-water partitioning (Hodson et al. 2011). In a field study of a tidal stream abutting Prince William Sound, Carls et al. (2003) reported hyporheic flows that would carry dissolved hydrocarbons to pink salmon (*Oncorhynchus gorbuscha*) spawning in the stream.

Hyporheic flows are generated by two non-exclusive mechanisms: 1) the irregular bed form generates a pressure gradient along the hyporheic zone, causing stream water to enter the subsurface upstream of a dune and to exit it at the lee side (Elliott and Brooks 1997; Tonina and Buffington 2007, 2009; Buffington and Tonina 2009); and 2) the subsurface heterogeneity in a streambed (Ryan and Boufadel 2006, 2007a,b) can engender hyporheic flows even though the bathymetry is flat (Ryan and Boufadel 2007a,b). Hyporheic flows are also affected by the groundwater table (Harvey and Fuller 1998) as they increase under baseflow conditions (i.e., low water table) and decrease under high flood conditions (i.e., high water table). Thus, an oil spill during baseflow would introduce oil more into the subsurface than an oil spill during high flows.

In many situations, a better understanding of sediment transport in rivers is needed to understand the transport of oil and OPAs. Sediment transport in rivers occurs through three complementary mechanisms:

- Wash load consists of very fine particles that are not present in abundant concentrations on the bed. Examples include suspended organic matter. Therefore, knowledge of bed material composition does not allow one to predict wash load transport very well;
- Suspended load is the load that is suspended in the water column but still interacts with the bed. The interaction usually occurs at ripples causing the shear stress to increase and sediments to be suspended from the lee side of the ripples; and
- Bed load has continuous contact with the bed and has a direct relation to the bottom stress in rivers. Both suspended and bed loads are commonly predicted using sediment transport models. Thus, to predict the formation of OPAs, sediment transport models might not provide a complete description of the transport, as they focus on the suspended load and bed load, while the formation of OPAs depends also on the wash load.

The types of OPAs greatly affect their transport. It is worth noting that the transport of OPAs is different from the transport of sediments for two key reasons:

- The OPAs do not in general have the same shape as oil droplets, and their density could vary from that of oil to a density much greater than that of water (due to sediments). Thus, they move differently from both the oil droplets and the sediment particles; and
- OPAs can form based on interaction with the wash load of rivers and not with the suspended and bed loads. Therefore, traditional sediment transport, which predicts only suspended and bed loads, might not be able to capture the dynamics of OPA transport when the OPA is generated based on interaction of oil with the wash loads.

5.2.4 Transport in estuaries

Flow in estuaries is characterized by reversals in flow direction due to tides and by the presence of a freshwater-saltwater interface. Large estuaries could have waves and could be strongly affected by wind and by the Coriolis force, which would tend to push the water to one of the banks of the estuary (Fischer et al. 1979). Estuaries tend to have a salt water toe overlain by fresh water exiting to sea. Therefore, for oil spilled inland in the estuary, dispersed or dissolved oil moving seaward would upwell to the water surface when encountering the saltwater toe (Short 2015). Thus, previously dispersed oil could re-coalesce again. The interaction of fresh and saline waters in estuaries is important not only for physical transport of spilled oil, but also because mixing of these waters often results in the combination and settling of clay particles due to the suppression of the double layer when fresh water approaches high salinity waters (Clark 1996).

5.2.5 Transport of oil within beaches

Transport of oil within beaches is not commonly modeled, as the free-phase oil washes out fast, and one ends up with residual amounts of oil trapped by capillarity and by organic content in sediments (Brost et al. 2000). However, sand beaches contain little organic material. Neglecting the organic content in sediments, Etkin et al. (2008) developed a holding capacity of beaches based on the beach sediment type and the tide range using the subsurface flow model MARUN (Boufadel et al. 1999).

The persistence of oil in a beach depends on the type of beach sediments and the beach groundwater table. While addressing the *Exxon Valdez* oil spill (EVOS), Li and Boufadel (2010) found that oil persisted at locations where the groundwater table drops into a lower sediment layer of low permeability, causing the entrapment of oil. Beach hydraulics was also found to affect the oxygen concentration in the oiled regions of the beach resulting in low oxygen concentrations (Boufadel et al. 2010) suspected to cause the persistence of the *Exxon Valdez* oil spilled in Prince William Sound. The mechanism is illustrated in **Figure 5.3**. The beach receives dissolved oxygen from the inland groundwater table and from the seawater during the high tide. As the tide ebbs, the oxygen propagates into the beach and gets consumed by abiotic and biotic reactions. For the EVOS, it was found that the oxygen concentration at the oiled region is around 1.0 mg/L resulting in anoxic conditions, which prevented aerobic oil biodegradation.

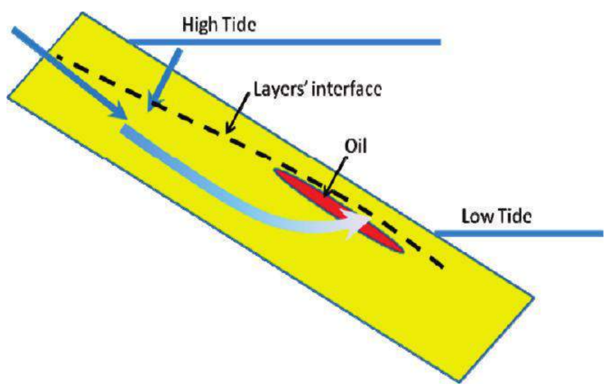

Figure 5.3 Beach showing the propagation of oxygen *(blue arrows) through the beaches of Prince William Sound , AK. Reprinted with permission from Boufadel, M.C., Sharifi, Y., Van Aken, B., Wrenn, B.A. and K. Lee. 2010. Nutrient and oxygen concentrations within the sediments of an Alaskan beach polluted with the Exxon Valdez oil spill. Environmental Science & Technology 44: 7418-7424. Copyright (2010) American Chemical Society.*

The role of nutrients in oil biodegradation has been noted since the 1970s (Atlas and Bartha 1972). But it gained a large visibility following the EVOS (Prince 1993; Bragg et al. 1994), where more than 50 tons of neat (i.e., solid) nutrients were dissolved and applied onto the beach surfaces. Wrenn et al. (1997) conducted tracer studies on a Delaware beach and found that the bulk of the nutrient plume persists in the beach for about 24 hours and thus re-application would be needed. This is understandable noting the hydraulics within the beach, as illustrated by **Figure 5.3**.

Tracer studies in Prince William Sound beaches were conducted by applying tracers on the beach surface at low tide (Li and Boufadel 2011) and by releasing them deep into the beach (Boufadel and Bobo 2011; Boufadel et al. 2011). In all cases, it was found that the applied solution moves slightly downward and landward during rising tides, and seaward during falling tides, confirming the numerical studies on these beaches (Guo et al. 2010, Xia et al. 2010).

More recently, Geng et al. (2015) noted that sand beaches in the Gulf of Mexico could have different limiting factors depending on the location within the beach: nutrients could be limiting in the shallow zone of the upper intertidal zone, while oxygen could be limiting in the deep area of the mid-intertidal zone.

Bioremediation has been considered one of the major non-intrusive technique for mitigating the impact of oil on shoreline ecology (Pritchard et al. 1992). The addition of nutrients is known as biostimulation (discussed in greater detail in Chapter 6), while the addition of microorganisms is known as bioaugmentation (Zhu et al. 2001). Prince et al. (1994) reported high degrees of success when nutrients were added to oil polluted beaches to remediate the EVOS. Venosa et al. (1996) conducted a bioremediation study on an experimental Delaware beach intentionally treated with oil in quintuplicate plots, and found that addition of nutrients to concentrations larger than 2.0 mg/L in the interstitial pore water enhanced oil biodegradation several-fold. However, they noted that the addition of a microbial culture grown on site in drums exerted no further enhancement beyond simple nutrient addition. Later, Li et al. (2007) developed a nutrient delivery technique that applies to most beaches, which consists of applying the nutrient solution onto the beach surface following the falling high tide and to rely on the beach water table to carry the applied solution to the oil-contaminated zone.

5.2.6 Floodplains

An oil spill that occurs during a flood would result in oil deposition onto the floodplain, whose hydraulics is more or less disconnected from that of the river under normal conditions. This causes the oil to deposit in patches that are disconnected, especially if the spill occurred during high vegetation seasons. Therefore, the fate of oil in the floodplain could be greatly affected by photooxidation, some of whose products are soluble in water. The biodegradation of oil in the floodplain could also occur, provided the sediments are sufficiently coarse to allow for oxygen replenishment from the atmosphere and also that the nutrient concentrations are not limiting.

5.2.7 Wetlands

In general, oil does not penetrate much into wetlands due to the fine texture of wetland sediment. However, channels and macropores due to bioturbation would constitute pathways to deeper penetration of oil. In addition, oil tends to adsorb to plants and plant roots. But in general the bulk of the oil gets trapped at the edge of the wetlands through adsorption to vegetation.

5.2.8 Underwater release

The release of oil under water due to a pipe rupture or well blowout causes the formation of a jet where the spewing oil moves in the water column due to the momentum. Eventually, the buoyancy of the oil starts to play a role, and the oil released at and beyond that location forms a plume. This is what happened in the DWH. However, for practical purposes one could refer to the oil release as a jet/plume. Upon rising through the water column, the vertical plume tends to get bent due to horizontal currents commonly present in waterbodies. Models that simulate such releases include the CDOG model (Zheng et al. 2003) and the Deepblow (Johansen 2000).

Jets/plumes generate a wide range of droplets whose transport and fate depends on the size. Small droplets tend to remain within the plume even when it is bent by horizontal currents. However, large droplets rise rapidly and could separate from the plume bent by horizontal currents (**Figures 5.1 and 5.2**). Indeed, that was observed in the DWH spill, where the transport time of large droplets (size of millimeters) to the surface was on the order of hours, while that of small droplets (<70 µm) was on the order of months (Kujawinski et al. 2011). For this reason, the DSD from a pipe rupture is of great interest in terms of predicting where the droplets and plume will move. Unfortunately, the models CDOG and

DEEPBLOW do not generate the DSD; rather, they require it as input. Johansen et al. (2013) developed a formula for predicting the D_{50} (median diameter) from an underwater blowout based on the orifice diameter and the properties of the oil. Their model was calibrated to experimental data from vertical jets whose orifice was 1 to 5 mm (Brandvik et al. 2013), and one case where the orifice diameter was 12 cm (Johansen et al. 2001). Using their model to obtain the D_{50}, the DSD would be obtained in the aftermath by assuming either a Rosin Ramler distribution or a lognormal distribution. The VDROP model combined with jet correlations resulted in the model VDROP-J, which provides the droplet size distribution from jets/plumes (**Figure 5.4a**). The model was used to predict the DSD from the DWH in Zhao et al. (2015) (**Figure 5.4b**). Zhao et al. (2014b) argued that there is no theoretical reason for the existence of a unimodal DSD (Droplet Size Distribution), as required when using the Rosin Ramler or the lognormal distribution.

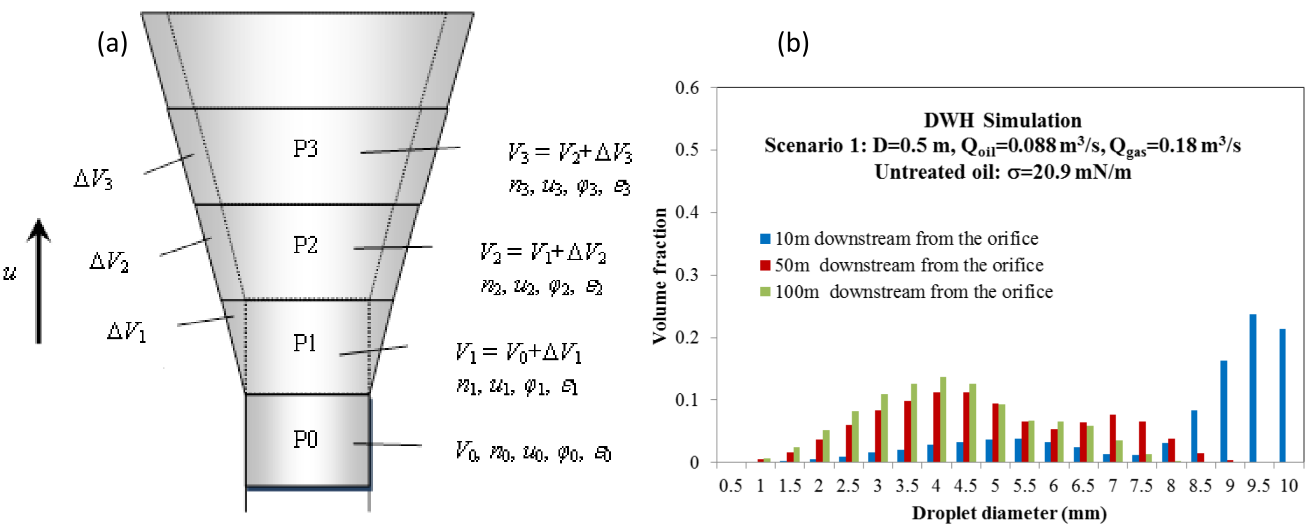

Figure 5.4 VDROP-J model*: a) illustration of the fluid parcel moving along the jet trajectory, where VDROP model is running for each fluid parcel location to obtain DSD along the plume. Of interest are the following quantities: The number of droplets per unit volume "n", the stream velocity "u", the holdup φ (ratio of oil mass to total mass), and the energy dissipation rate ε, which vary as the oil moves away from the orifice; b) simulation results for DWH blowout*[4].

5.2.9 Ice

Lee et al. (2011) provided a thorough review of the behaviour of oil in ice-infested waters in the Arctic. The findings of that report are summarized herein.

An obvious effect ice has on oil is to decrease the oil temperature causing the viscosity of the oil to increase. However, weathering processes (addressed above) could still occur. In particular, for oil pooled between blocks of ice, evaporation becomes the dominant weathering mechanism. Also high viscosity causes the oil to spread less on water and to become less amenable to physical or chemical dispersion (Fingas and Hollebone 2003). Oil spilled directly on ice would tend to spread less than on water as the ice roughness would resist the spreading more than water (ITG 1983).

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[4] *Images reprinted from:*

a) Zhao, L., Torlapati, J., Boufadel, M.C., King, T., Robinson, B. and K. Lee. 2014b. VDROP: A comprehensive model for droplet formation of oils and gases in liquids-Incorporation of the interfacial tension and droplet viscosity. Chemical Engineering Journal 253: 93-106. Copyright Elsevier (2014).

b) Zhao, L., Boufadel, M. C., Adams, E.E., Socolofsky, S., King, T. and K. Lee. 2015. Simulation of scenarios of oil droplet formation from the Deepwater Horizon blowout. Marine Pollution Bulletin. Accepted. Copyright Elsevier (2015).

Oil spilled on ice can become encapsulated within the ice structure in winter conditions when new ice is being formed. In some cases, this process can happen rapidly (within 18 to 72 hours). In salt water, the formation of ice is accompanied by the release of salt, resulting in 'brine channels' and 'brine pools' (see Figure 2.10), which contain highly concentrated solutions of sea salt. The channels provide pathways for oil migration into the water beneath the ice, and the pools provide mini-reservoirs for oil accumulation between the ice blocks (Bobra and Fingas 1986).

In terms of transport, studies have shown that as long as the ice coverage is less than 30% of the water surface, the oil behaves more or less independently from ice. However, as the ice coverage exceeds 30%, the oil is found to drift with ice (Ross and Dickins 1987; Venkatesh et al. 1990). In that case, one would need to use ice models to track the movement of oil. Recently, major efforts have been placed on remote sensing, namely using satellites to detect the presence and thickness of oil under the ice (Dickins et al. 2008; Dickins et al. 2011).

5.3 Research Recommendations in Priority Order

- Better models need to be developed, using basic properties of waves, for the prediction of oil dispersion by waves, especially for high viscosity oils.
- Models for blowouts need to generate the oil droplet size distribution (DSD) and not only the underwater trajectory of oil. These would need to account for the effect of gas on the release. Currently, the only model that can generate the DSD is the model VDROP-J (Zhao et al. 2014b), which covers only the near-field.
- Predictive models are needed for the formation and fate of OPAs in freshwater and saltwater environments. Existing models are phenomenological; they reduce the data but cannot make predictions.
- Models for the biodegradation of oil droplets need to be validated by comparison with data obtained from controlled experiments, especially when dispersants are used (Venosa and Holder 2007).

CHAPTER 6: REVIEW OF SPILL RESPONSE OPTIONS

Abstract

Chapter 6 discusses the evolving nature of oil spill response. The implementation and effectiveness of the various oil spill response options available are influenced by a variety of factors, such as oil types and properties (presented in Chapter 2), environmental and ecological conditions in the vicinity of the spill site (e.g., weather, wave, wind, daylight, ice conditions, visibility and sensitivity and distribution of species) (introduced in Chapter 3), technical, logistical and financial factors (such as responders' knowledge and skills, availability of personnel and equipment, time constraints, regulatory approvals, health and safety criteria, cost and economic impacts), and other constraints (e.g., community engagement). Some of those conditions and factors are temporally dynamic and interactive and should be comprehensively considered in oil spill contingency planning and response decision-making.

This chapter is divided into four main topical areas, namely: 1) natural processes; 2) physical response methods; 3) biological and chemical methods; and 4) factors affecting spill response and cleanup effectiveness. Under each main section, up to eight subsections present in detail the strengths and weaknesses of each response strategy to provide the reader with a clear understanding of how to implement each method based on influencing factors, such as how each method is affected by the environment and the type of oil being removed, and how each method is advocated or opposed for use based on its known effectiveness in different environments or ecosystems (depending on factors such as oil types, weather, wave impingement, ice conditions, daylight and visibility, ecological considerations and technical and economic conditions). Section 6.1 describes natural processes, such as natural attenuation, evaporation and photooxidation. Section 6.2 presents descriptions of physical cleanup processes, including containment and recovery, sorption, shoreline types, vegetation cutting, removal of oiled sediment, oiled sediment reworking, physical dispersion (influence of mineral fines) and in situ burning. Section 6.3 is concerned with biological and chemical strategies, such as bioremediation, phytoremediation, chemical dispersion, surface washing agents, solidifiers, herding agents and debris and detritus removal. Section 6.4 presents a discussion of the factors that affect spill response and cleanup effectiveness, such as oil types and properties, environmental and ecological factors (weather, wave height, ice conditions, daylight and ecological factors, including fish, invertebrate and wildlife mortality), and technical and economic factors impacting effectiveness.

Research recommendations for spill response needs and knowledge gaps are identified in priority order in Section 6.5. The underlying theme of the recommendations is the need to conduct controlled field studies to advance spill response strategies, especially for subsurface blowouts, Arctic oil spills, and freshwater shorelines. Most of what we know about oil spill response technologies has been developed from laboratory studies, mesocosm test systems and case studies (with limited controls and treatment replication). The stage for these studies should be primarily the Arctic, which has already been put forth in the needs from Chapter 3, because that is where our spill response knowledge is most lacking. We need to develop sufficient knowledge in understanding the fate, behaviour and impacts of different types of oils (in varying weathered and treatment states) in snow or ice conditions. Controlled field studies will help close this gap without significant negative impact on the environment if done properly. Furthermore, there is a need to improve our understanding of what to do about anaerobic biodegradation in sediments and to advance emerging technologies like bioventing, air sparging and/or dissolved air flotation to incorporate oxygen temporarily into the anaerobic zone of sediments and stimulate aerobic biodegradation of contaminating hydrocarbons. The results of such studies may aid in the cleanup of benthic environments contaminated by sunken oil from accidental spills or deep sea blowouts. Finally, regarding dispersant use, although some researchers have concluded that deep sea dispersant applications were successful during the Deepwater Horizon spill, it remains unclear to what extent the oil was dispersed physically due to the high velocity of oil emerging from the well into the water or chemically due to mixing with applied dispersant. This question needs to be answered by controlled experiments to reduce the uncertainty of this

treatment strategy. Questions about the persistence of dispersed oil in both the deep sea and on the sea surface need to be addressed with controlled empirical experiments.

Introduction

Oil spill response can be laborious, expensive and fraught with conflicting priorities. The implementation and effectiveness of the various oil spill response options available are influenced by a variety of factors, such as oil types and properties, environmental and ecological conditions in the vicinity of the spill site (e.g., weather, wave, wind, daylight, ice conditions, visibility and sensitivity and distribution of species), technical, logistical and financial factors (such as responders' knowledge and skills, availability of personnel and equipment, time constraints, regulatory approvals, health and safety criteria, cost and economic impacts), and other constraints (e.g., community engagement). Some of those conditions and factors are temporally dynamic and interactive and should be comprehensively considered in oil spill contingency planning and response decision-making.

> Spill response strategies are varied and greatly affected by a variety of factors, such as the type of oil (crude, refined, dilbit, etc.), the characteristics and remoteness of the spill site (water or ice, terrestrial, marine or freshwater shoreline, riparian zone, arctic, permafrost, etc.) and even political considerations.

Many of the approaches and technologies that have been used for treating oil spills were developed for marine shorelines, on-water-spills, and freshwater environments. These processes have been reviewed and described extensively in a number of technical documents, such as: Doerffer (1992), NOAA (1992), NOAA and API (1994), U.S. EPA (1999), NRC (2014), Canadian Coast Guard (2005), IMO (2005), Fingas (2011) and numerous ASTM manuals, monographs and data series (http://www.astm.org/DIGITAL_LIBRARY/MNL/mnltocall.htm). The most commonly used spill response cleanup options (**Table 6.1**) are briefly described in the following text. The rest of this chapter summarizes these technologies in more detail.

Table 6.1. Spill response cleanup options with chapter section designations that discuss each

Category of Response Options	Example Technology (Section)
Natural processes	Monitored natural attenuation (MNA) (6.1.1) Evaporation (6.1.2) Photooxidation (6.1.3)
Physical processes	Containment and recovery (6.2.1) Sorbents (6.2.2) Removal from shorelines (6.2.3) Vegetation cutting (6.2.4) Removal of oiled sediment (6.2.5) Oiled Sediment reworking (6.2.6) Physical dispersion (6.2.7) *In situ* burning (6.2.8)
Chemical and biological processes	Bioremediation (6.3.1) Phytoremediation (6.3.2) Chemical dispersion (6.3.3) Surface washing/flushing (6.3.4) Solidifiers (6.3.5) Herding (6.3.6) Debris removal (6.3.7)

6.1 Natural Processes

6.1.1 Monitored Natural Attenuation (MNA)

In this section, monitored natural attenuation (MNA) is discussed in the context of circumstances that would indicate it to be the method of choice for a given spill response. Examples of such cases include spills at remote or inaccessible locations when natural removal rates are expected to be rapid, or spills in sensitive wetland sites where cleanup actions by human intervention (e.g., trampling) may cause more harm than good. Since some natural weathering processes are slow (Figure 2.4), the monitoring component of MNA is essential to verify the loss of residual hydrocarbons and the recovery of impacted plant, animal and other species essential for an ecologically healthy habitat.

> MNA or natural recovery is an option that should always be considered when determining which response option should be implemented. It may be the best alternative especially in certain situations where human intervention could result in more harm than good. MNA is essentially a no direct response option that depends on nature to degrade the oil. For some spills, such as those that have contaminated highly sensitive wetland and salt marsh environments that serve as habitats for endangered species occupying several trophic levels, it is probably more cost-effective and ecologically sound to let the site recover naturally than attempt to intervene.

A primary mechanism of MNA is biodegradation. This natural process is particularly important in removing the non- and semi-volatile components of oil from the environment. The ultimate fate of spilled hydrocarbons in the environment is dependent on the role indigenous microbial communities play in the fate of the majority of hydrocarbons entering the biosphere (Leahy and Colwell 1990; Prince et al. 2010; Atlas and Hazen 2011). This is a relatively slow process and may require weeks, months or even years for microorganisms to degrade a significant fraction of oil, particularly if other factors (discussed in Chapter 3) are limiting. In recent years, with the advent of genomics and metagenomics research activities, a shift has occurred in our understanding of the ecological significance of microbial adaptation in response to oil spills that identify the change in structure and function of whole microbial communities in previously unknown ways (Macnaughton et al. 1999). Pre-genomics ecological studies relied on the use of microbial isolates to guide our understanding. In contrast to the results of studies of isolates that represented only a small percentage of the community structure developing in or near the spill site, recent advances in genomic studies have shown that microbial activity in low temperature and deep sea conditions may be quite robust (Atlas and Hazen 2011; Valentine et al. 2015).

6.1.2 Evaporation

Evaporation is an important natural cleansing process during the early stages of an oil spill, as the lighter weight, higher vapour pressure components in oil are removed rapidly when exposed to the atmosphere (Chapter 2). Depending on the composition and mass of the oil spilled, up to 50% of the more toxic, lighter weight components of oil may evaporate within the first 12 to 24 hours following a spill (U.S. EPA 1999).

6.1.3 Photooxidation

Photooxidation occurs when oxygen under sunlight reacts oxidatively with aromatic oil components (see Chapter 2; NRC 2003). Maki et al. (2001) reported that when Arabian light crude oil was first biodegraded and then exposed to sunlight, a substantial decline in the aromatics fraction with a concomitant increase in the resins and asphaltene fractions was observed. The oxygen content in the oil and thus the polarity increased as the irradiation was prolonged, and the bioavailability of the biodegraded

Photooxidation aids in the removal of dissolved hydrocarbons in water. Aliphatic and aromatic hydrocarbons are oxidized photochemically to oxygenated, more polar compounds that are more soluble than the parent compounds. Photooxidation may also result in higher molecular weight products through condensation reactions, ultimately leading to tar and gum residues.

oil increased by the photooxidation. *Photooxidation changes the physico-chemical properties of oil and its related components with the oxygenated forms being more polar, increasing the toxicity of the oil (Wang and Fingas 2003). The photooxidation products, while toxic, would not likely occur at toxic concentrations in water. However, evidence has shown that photooxidation within the tissues of transparent aquatic species causes rapid mortality (Chapter 4).* Thus, photooxidation may either produce potentially higher biodegradation rates due to increased hydrocarbon bioavailability or potentially lower rates due to toxic byproducts, depending on the oil composition and species sensitivity.

6.2 Physical Response Methods

6.2.1 Containment and recovery

Booms and skimmers are usually the first response method to an oil spill on water. It has met with varying degrees of success, mostly limited, depending on weather and sea state conditions.

According to Etkin and Tebeau (2003), a functional effectiveness of 10-30% can often be realized using mechanical recovery, with levels of 50% and greater being achieved on occasion (78% in the *Julie N* spill, up to 95% in others, such as the 2007 Burnaby syncrude spill in British Columbia [Crosby et al., 2013]). During a spill response, the threat to sensitive near-shore/coastal habitats by a spreading oil slick can be mitigated by deploying booms to trap and concentrate the advancing slick so that the oil can be physically recovered from the surface of the water by specially equipped boats or other devices (skimmers). Booms are floating, physical barriers made of plastic (usually marine grade PVC or urethane with a molded polyethylene shell), metal (for *in situ* burning [ISB]), sorbent fabrics or other materials having a cylindrical float at the top with a weighted bottom skirt under the water, which slow and trap or contain the spread of oil (NOAA 2015). Typical photos of boom deployment are shown in **Figures 6.1** and **6.2**.

Booms are commonly placed across a narrow entrance to a larger mass of water so that oil is prevented from passing through into marshland or other sensitive habitats. Deflection booms are used to deflect oil away from sensitive locations, such as shellfish beds or beaches used by birds as nesting habitats. Fire booms, discussed in more detail in Section 6.2.10, are used to collect oil from a slick and concentrate it into a thickness suitable for burning. Booms for ISB are typically fabricated with floating metal cylinders at the top that support a boom and skirt constructed with fire-resistant materials.

Although booms can be used in calm water (e.g. for streams, canals, ponds, lakes), open water (for harbours and open ocean conditions) and some fast water environments (for rivers, streams, estuaries and moving water lakes), their effective operational range is limited by rough weather and winds that induce strong currents and breaking waves.


Figure 6.1 Oil containment boom deployed in a saltwater application. *Source: NOAA*


Figure 6.2 Boom surrounding a set of floating pens at a salmon hatchery in Prince William Sound, AK, to protect the pens from oil spilled from the Exxon Valdez tanker. *Source: NOAA*

Sorbent booms, also known as ‘spaghetti’ or ‘sausage’ booms, are used for collecting thick oil in flowing waters. They are composed of absorbent strips in the interior of the boom contained by open-cell netting. This type of boom allows oil to penetrate more deeply into the interior, which increases absorbency and helps prevent spreading from the spill site. Importantly, the Oil Budget Calculator study during the Deepwater Horizon (DWH) response (Federal Interagency Solutions Group (FISG) 2010) showed that despite almost ideal weather conditions and substantial logistical support, physical recovery accounted for only about 4% of the cleanup due to the large oil encounter rate from the continuous oil release to an open water environment over a period of several months. This estimate was later modified to 4-10% (Fingas 2013c) due to a calculation error by the FISG.

Skimmers are boats and other devices (e.g. weirs) designed to recover oil from the sea surface (e.g., **Figure 6.3 and 6.4**). Each type of skimmer has its own characteristics and limitations in dealing with factors such as viscosity, sea state and debris. Typically, two boats will tow a collection boom to concentrate the oil to facilitate its recovery. High waves may compromise the ability of boom containment and skimmers to remain in contact with the oil. Devices that have a small mass, allowing them to follow wave movements, should be part of the spill response inventory.

***Figure 6.3 A ship skims oil spilled after the Deepwater Horizon/BP well blowout in the Gulf of Mexico in April, 2010**. Source: NOAA*

***Figure 6.4 Skimming the Delaware River in Philadelphia following the M/T Athos I spill on November 26, 2004.** Source: NOAA.*

Weir skimmers use a different oil collection method from those described previously. The skimmers float closer to the surface slick where the weir collects the oil while still allowing water to flow through. Some weir skimmers use a flotation system featuring four evenly spaced floats that help the weir adapt to changing water levels. This type of skimmer may be connected to a pump or vacuum system for rapid separation and removal of the floating oil. Vortex skimmers use an induced eddy to separate the oil from the water based on their differences in density.

> Skimmer systems such as weir skimmers may be more effective for high-viscosity oils, such as diluted bitumen, whereas skimmers with oil-attracting coatings may be more appropriate for conventional crude oil spills. Weir skimmers entrain large quantities of water, which enables them to cope with higher viscosity oils.

According to Wadsworth (1995), oil viscosity affects the efficiency of virtually all recovery devices. Recovery is affected by the tendency of many oils to form water-in-oil emulsions, whereby, in addition to making the oil considerably more viscous, the volume of material is increased by three- to four-fold. The kinematic viscosity[1] may increase to as much as 100,000 cSt as a result of emulsion formation. The injection of demulsifying agents[2] can be used to mitigate this problem and minimize the storage volume required for recovered oil. Conventional weir, vortex, oleophilic rope and disc devices are usually limited to use with oils having a maximum viscosity of 10,000 cSt, whereas screw, belt and air conveyor devices will often perform well with oil of viscosities up to 100,000 cSt.

Physical recovery is limited by high wave action, leading to the loss of oil from containment booms either through oil splashing over the booms or to poor wave-following characteristics of the booms, resulting in bridging between crests. Skimmers are also subject to limitations from wave action as failure to remain in contact with the oil often results in the uptake of large quantities of water. In addition, turbulence can lead to loss of oil under the skimmer. Thus, a recovery device should have a small mass to enable faithful following of wave movements.

For oils that do not flow readily, such as heavy crudes and refined products, and ambient temperature below the pour point, the oil will behave as if it were a solid and thus resist recovery. If conditions are right, oil tends to form oil-in-water emulsions, increasing viscosity and volume of the emulsified material. The recovery efficiency, defined as the relationship between the quantity of oil relative to water in the collected material, is an important determinant of a system's overall performance. Some oleophilic systems recover small quantities of water but are less effective at high oil viscosities. These systems are best used with smaller vessels that are more effective in restricted water depths. Non-selective systems, such as weir skimmers, entrain larger quantities of water, and this property often enables them to deal with higher viscosity oils, such as dilbit or refined fuel oil.

6.2.2 Sorbents

This subsection is adapted from Region 10 Regional Response Team and the Northwest Area Committee (2015). The purpose of using sorbents as a spill response tool is to aid in the cleanup and recovery of oil-contaminated shorelines, sensitive habitats such as wetlands and salt marshes, and small spills on water. The primary uses of sorbents include the following (adapted from Merlin and Le Guerroué 2009):

- Containment and recovery by rapid deployment in coastal areas, ports and harbours, estuaries and on rivers;
- Containment of slicks in association with a standard boom (to improve watertight seal);
- Protection of areas difficult to clean (riprap, reed beds, mangroves, etc.);
- Immobilization or recovery of floating pollutants on lakes or in stagnant waters;
- Rapid application on terrestrial spills or ground surfaces to prevent or at least reduce infiltration of the pollutant to the substrate;
- Sorption of leaks below a recovery worksite;
- Sorption of effluents from cleanup of rocks, structures and embankments;
- Sorption by filtration of pollutants suspended in the water column (water intakes, rivers);
- Cleanup or decontamination of personnel and equipment on cleanup sites; and
- Lining and protection of pathways.

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[1]Kinematic viscosity is the ratio of dynamic viscosity to density. The SI unit of dynamic or absolute viscosity is centipoise (cP) or mPa·s, and for water cP and cSt are equivalent. The kinematic viscosity of any fluid in cSt (centistokes) is the dynamic viscosity divided by the density of the fluid (in our case the oil). So, for oil, the kinematic viscosity will not be equivalent to the dynamic viscosity because of the division by oil density.
[2]Demulsifiers are a class of chemicals used to separate emulsions, e.g., water in oil, into oil and water phases.

An adsorbent takes up significantly less volume of liquid than an absorbent (Brinkman 1998). In Canada, sorbent pads and booms are frequently used in spill response. However, loose organic materials, such as peat, clay, straw, feathers, etc., are less prevalent because of the creation of more oily waste that must be burned or disposed to landfills. The preference is to collect bulk oil.

6.2.2.1 Selection of sorbents for floating oil spills on water

For fluid oil on open water with no current, bulk, pads and pillows should be used for containment. On open water with current and smooth-surfaced embankment, pads, pillows or sorbent booms with ballasted skirt should be used. On rough-surfaced embankments, either roll or sorbent booms with ballasted skirt should be used. For slow current (< 0.2 m/s) and small quantities of oil, sorbent rolls are used. For stronger current in a larger waterbody, standing floating booms or sorbent booms are used, but if these fail, sorbent rolls reinforced with rope are used instead.

For viscous oil, such as cold heavy fuel oil, dilbit or weathered emulsified crude oil, in open water with no current, standard floating booms or sorbent booms with ballasted skirt are used for containment or bulk and mops for recovery. In open water with current, rolls or sorbent booms with ballasted skirt or even mops are used if the current is slow. For deflection or recovery in faster current, sorbent booms with ballasted skirt or mops attached to a rope are used.

Recently, a natural plant-derived sorbent (sugarcane bagasse) was investigated in laboratory microcosms as a remediation strategy for low energy intertidal wetlands contaminated by crude oil (Chung et al. 2010). The results indicated that the use of this type of sorbent was beneficial not only in removing oil but also in preventing further contamination. This technique has potential to stimulate biodegradation by wicking oil out of contaminated anaerobic wetland subsurface to the aerobic zone on the surface where rapid biodegradation can take place. The bagasse, being biodegradable, would not need to be removed subsequent to treatment.

> The American Society of Testing and Materials (ASTM) developed performance standards for adsorbents (Method F726) and absorbents (Method F716). The combination of the liquid with the solid causes the absorbent to swell, thus absorbing many times its volume. The liquid is no longer available for release and the rate of vapour release is reduced by five to six times that of adsorbents.
>
> Three types of sorbents may be used in oil spill response: (1) products of mineral origin, such as expanded perlite or glass wool; (2) products of animal or vegetable origin, such as coarse sheep's wool, peat or cellulose peat or cellulose; and (3) synthetic products and organic polymers, such as polypropylene or polyurethane. Sorbents are selectively either hydrophobic, designed to recover non-polar pollutants (non-miscible with water), or hydrophilic, designed to recover polar products, such as water or materials soluble in water or non-polar products. Because these types of sorbents do not necessarily float on water but soak it up, they are used only on land.

<u>Recommendation</u>: Sorbents are widely used as a cleanup tool to combat oil spills in water and on shorelines. They have limitations, however. The need exists to determine if any advances have been or can be made to improve sorption as an effective response tool, especially in the use of biodegradable natural organic sorbents, such as bagasse that may possibly be left in place for biodegradation to take place. Significant amounts of debris and solid waste are generated when using sorbents for cleanup, so if natural sorbents can be developed that would sorb oil and then remain in place for ultimate cleanup by biodegradation, this would be a significant advancement in oil spill response.

6.2.3 Oil removal from shorelines

Various beach washing techniques at ambient and high temperatures under both high and low pressure settings have been used as part of containment and recovery operations to treat different types of substrate contaminated by oil.

6.2.3.1 Sand beaches

When oil first arrives on a beach, deposits of fresh product must first be removed before cleanup can take place by any means. One technique used for free product removal is scraping and either bagging or trenching (**Figure 6.5**). Large volumes of bulk oil are removed quickly, without generating excessive waste, by scraping the free product directly from the sand surface. Rubber squeegees are used to manually concentrate the oil, which is then pushed into trenches dug parallel to the waterline. For long stretches of contaminated sandy beach, the oil is collected by vehicles equipped with scraper blades and dumped into temporary storage pits above the high tide line. The oil is collected by vacuum trucks for later treatment.

Figure 6.5 Workers clean a sandy beach using traditional methods of hand labour and bagging the oil and debris. *Source: NOAA*

6.2.3.2 Pebble or shingle beaches

These types of beaches are "armoured" with pebbles or small- to medium-sized cobbles as opposed to fine sand. They are steeply sloped because waves are able to course through the highly porous surface, which decreases the effect of backwash erosion and increases sediment formation. In these low energy beaches, vehicle access is usually possible, and bulk oil is either collected into pools onto the beach surface or flushed into man-made trenches. The recovered oil is then collected in vacuum trucks and either transferred to temporary holding tanks or taken away for treatment. *However, pebble beaches are difficult to clean thoroughly because oil tends to penetrate into the subsurface, sometimes as far as the clay/mud base. Thus, flushing into trenches requires later stages of cleanup, usually by pebble washing. In such cases, a better cleanup method is to flush the oil off the beach at high tide into offshore booms, where the oil can be collected by skimmers.*

6.2.3.3 Cobble beaches

These types of beaches are characterized by higher energy wave action impinging on the surface. Thus, surf washing (also known as berm relocation or oiled sediment reworking) is often used for treating cobbles that have been exposed to beached oil (Lunel et al. 1996; Lee et al. 1997; Lee et al. 2003). Such cobbles are placed in the high energy surf zone where they are scoured naturally by the wave action. Where removal of large oiled cobbles has been difficult, large pits lined with plastic have been dug into the beach where the cobbles are washed with an oil-releasing agent and water. Oil is then skimmed and the clean cobbles are returned to the beach surface. However, this method usually leaves the cobbles oil-stained and is not used in sensitive environments, such as salmon spawning streams, shellfish beds, nursery areas, etc., because of the potential adverse effects on those sensitive habitats from the increased oil runoff, sheening or siltation.

Recommendation: Berm relocation, surf washing and sediment reworking have been used to accelerate shoreline cleanup in the past. A comprehensive review is needed to determine quantitatively how successful these technologies have been and where such techniques are best applicable or not recommended. Testing protocols need to be developed to determine the effectiveness and secondary ecological impacts of this response option.

6.2.3.4 Boulder beaches

Boulder beaches are usually found in high wave energy environments where clasts of these large dimensions are released directly by erosion of bedrock, or where material is delivered to the shore zone by slope movements, such as rockfall. Oil stranded in these areas can become mixed with sand, forming an oil/sand coating on the rock surfaces. This coating can be removed relatively easily by surface scrubbing, brushing or wiping **(Figure 6.6)**. However, re-oiling often occurs in these types of areas due to the constant movement of sand during tidal cycles, resulting in a protracted cleanup. Thus, wiping is a highly labour intensive treatment technique. *Other techniques, which may be more cost-effective than wiping include high pressure cleaning with or without the use of surface washing agents. If the impinging wave energy is high enough, natural recovery via physical abrasion from the waves is probably a better option.*

Figure 6.6 Workers clean oiled boulders by hand. *Source: NOAA.*

6.2.3.5 Bedrock shoreline with no beach

This shoreline type is frequently found along the coastal areas of Canada and common in many Canadian lakes, including portions of the Great Lakes (e.g., **Figure 6.7**). Rock surfaces on marine shorelines are often densely populated with kelp (and associated biofilm). They can have a thriving tide pool community and therefore should not be regarded as ‘barren’. Furthermore, wet kelp may reduce oil adhesion to rock surfaces. **Figure 6.8** shows workers cleaning oil spilled following a collision involving crude oil tanker *Eagle Otome* in Port Arthur, TX, on January 2010. Under inclement weather conditions following a spill, waves may deposit oil up on the rocks, which may have a lichen/moss coating or be inhabited by other vegetation, such as small willows or conifers that cling to the cracks in the rock.

Figure 6.7 North shore of Lake Superior. *Source: NOAA.*

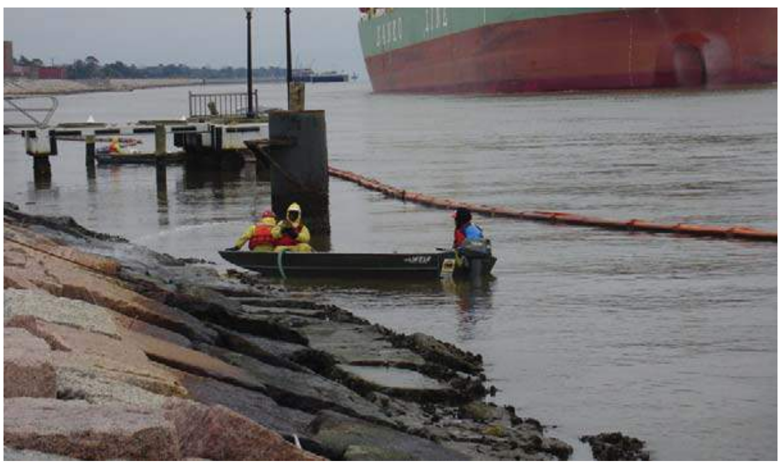

Figure 6.8 Workers cleaning oil spilled following a collision involving crude oil tanker Eagle Otome in Port Arthur, TX, on January 2010. *Source: NOAA.*

6.2.3.6 Low pressure washing or sediment flushing of a variety of beach types

Flooding a beach (**Figure 6.9**) with seawater can be used to flush fluid oils and oily debris from different shoreline types, particularly in sensitive areas (IMO 2005). This approach is less damaging to flora and fauna than most other methods. Booms are used to contain the flushed oil for skimming and removal.

Figure 6.9 Flushing out oil buried in a sand beach using low pressure water supplied through lances and perforated pipes. *Photo Credit: ITOPF; http://www.itopf.com/knowledge-resources/documents-guides/response-techniques/shoreline-clean-up-and-response/*

6.2.4 Vegetation cutting

Vegetation is cut to remove oil-contaminated vegetation from shorelines, wetlands or salt marshes **(Figure 6.10)** to prevent contamination of wildlife or remobilization of trapped oil. This strategy is based on the removal of oil from impacted environments by the pruning and collection of the upper parts of oiled plants for waste disposal. The cut vegetation is then collected and disposed. Any oil remaining near the roots or around the stems can be flushed out and recovered. Cutting can result in a temporary loss of habitat for small fish and invertebrates that dwell in those areas. Its feasibility depends strongly on the season in which the spill occurs. In general, winter cutting of dead standing vegetation has little effect on subsequent growth, but summer cutting could cause great damage to the regrowth of wetland plants and result in shoreline erosion. The use of cutting should also be avoided immediately prior to an anticipated rise in water levels because cutting followed by flooding could cut off necessary oxygen to plant roots (Pezeshki et al. 2000). The plants may or may not recover, depending on the type of oil spilled and differences in species and life stage sensitivity. This response method is generally used when large amounts of potentially mobile oil are trapped in the vegetation or when the risk of oiled vegetation contaminating wildlife is greater than the value of the vegetation that is to be cut. This response is conditionally recommended for sheltered, vegetated, low banks and marshes. See Chapter 4 for a discussion of the environmental impacts of vegetation cutting in the floodplain zone.

Vegetation cutting is also used for the removal of oil in the canopy of kelp beds, where thick layers of oil may adhere to kelp fronds or collect under the kelp canopy. This procedure is similar to shoreline vegetation cutting. The upper ~0.5 m of the kelp canopy are cut away by hand or with a mechanical kelp harvester and removed for disposal. Vegetation cutting is used when a large quantity of oil is trapped in the kelp canopy and the oil poses a risk to sensitive wildlife using the kelp habitat or when the remobilization of oil to other adjacent sensitive environments is likely to occur.

***Figure 6.10 Cleanup workers removing oiled vegetation during the Deepwater Horizon spill and using walk boards while cleaning to avoid causing further damage to the oiled marshes in Barataria Bay**. Source: NOAA.*

6.2.5 Removal of oiled sediment

This response technique is used to remove oiled surface sediments that cannot otherwise be cleaned *in situ*. Oiled sediment is removed by use of hand tools (**Figure 6.11)** or motorized equipment. Oiled sediment removal is restricted to the supratidal and upper intertidal areas to minimize disturbance of biological communities in the lower intertidal and subtidal zones. After removal, oiled sediments are transported for cleaning and/or disposal offsite. New sediments are not usually imported to replace those that were removed; however, a variation of this response that includes sediment replacement (described below) is used for beaches with low natural replenishment rates or high rates of erosion.

Physical removal of oiled sediment is frequently used on high amenity ‘tourist’ beaches (where pressure is high for rapid cleanup) and is most effective when a limited amount of oiled sediment must be removed. Close monitoring is required so that the quantity of sediment removed, siltation and the likelihood of erosion may be minimized in all cases. Such operations are generally restricted in fish spawning areas. Sensitive areas that are adjacent, and may be potentially affected by released oil sheens, must also be protected. During the DWH spill at the Grand Isle State Park in Louisiana, remediation operations included the excavation of the top few centimetres of contaminated sand for the removal of bulk oil by physical/chemical extraction at a temporary facility constructed near the spill site and its subsequent return to the beach **(Figure 6.12)** where the treated sediments were also surf washed for final polishing.

Figure 6.11 Cleanup workers manually remove oil following the M/V Westchester spill in the Mississippi River near Empire, LO, on November 2000. *Source: NOAA.*

Figure 6.12 Oiled sand removal in Grand Isle State Park following the DWH spill. *Source: K.Lee, DFO.*

6.2.6 Oiled sediment reworking

The objective of this variation of oiled sediment removal is to rework oiled sediments to break up oil deposits, increase surface area, facilitate physical oil dispersion and mix oxygen into deep subsurface oil layers. This activity exposes the oil to natural removal processes and enhances the rate of oil biodegradation. Under this protocol, oiled beach sediments are rototilled or otherwise mechanically mixed with the use of heavy equipment or relocated from the upper intertidal area of the beach to the surf zone. This latter procedure is also known as surf washing or berm relocation (Section 6.2.3). Generally, sediment reworking is used on sand or gravel beaches where high erosion rates or low natural sediment replenishment rates are issues. Sediment reworking may also be used where remoteness or other logistical limitations make sediment removal unfeasible. Sediment reworking is not used on beaches near shellfish harvest or fish spawning areas because of the potential for release of oil or oiled sediments into these sensitive habitats. *Sediment reworking is conditionally recommended for: (1) sand beach; and (2) cobble and gravel beach habitats* (Lunel et al. 1996; Region 10 Regional Response Team and the Northwest Area Committee 2015).

A new oil spill monitoring protocol called 'poling' was used in the Kalamazoo River spill in 2010 as a means of finding oil in the sediment. Poling involves disturbing the river sediment with a pole every 50 m or so to locate any remnants of oil residue remaining in the riverbed from the spill. Oil distribution in the sediments was estimated from the observation of oil sheens on the surface after disturbing the riverbed by poling. As a result of this survey method, identified areas with significant oil concentrations within the sediment were physically agitated by water jet washes as a means to facilitate residual oil release to the surface waters where it was physically recovered by skimming and the use of sorbent pads.

6.2.7 Physical dispersion (Oil mineral aggregates)

Suspended particulate matter within the water column, such as plankton and mineral fines, may form nuclei around which oil droplets may interact and adhere (Muschenheim and Lee 2003) to form oil-mineral aggregates (OMAs; Chapter 2). The subsequent ecological consequence of this process is dependent on the oil concentration and sedimentation rates. If the material is retained within the water column by physical oceanographic processes, oil toxicity may be reduced due to dilution of the residual oil by dispersion and enhanced oil biodegradation rates (as the process may enhance the surface area of the oil and nutrient availability; Figure 2.3). However, if the material rapidly sinks into the sediment and accumulates at elevated concentrations, biological impacts may result and the oil may degrade very slowly and thereby persist for long periods of time (see Chapter 3 for a discussion of anaerobic conditions) (especially if entrained within anaerobic sediments; Figure 2.3).

Several *in situ* remediation technologies, bioventing, air sparging and dissolved air flotation (DAF), developed over the last 20 years for the treatment of contaminated soils and groundwater have not been tried for remediating bottom sediments contaminated by sunken oil from spills. These technologies are characterized by injection of oxygen-rich air into the sediment to accelerate the aerobic biodegradation of oil in that anaerobic environment. Specifically, DAF achieves contaminant removal by dissolving air in the water or wastewater under pressure and then releasing the air at atmospheric pressure in a flotation tank or basin. The released air forms tiny bubbles that adhere to the suspended matter causing it to float to the surface of the water where it may then be removed by a skimming device.

<u>Recommendation</u>: Bioventing, sparging and DAF should be evaluated for their efficacy in treating and overcoming the adverse effects of sunken oil in the anaerobic zone of river or lake sediments. If successful, such techniques would greatly help in cleaning up benthic environments that have been contaminated by oil.

6.2.8 In Situ *burning*

ISB, a technique used to rapidly reduce the mass of oil spilled at a site, involves the controlled burning of oil that has spilled from a vessel or a facility at the location of the spill. ISB was successfully demonstrated by Environment Canada in a large-scale field experiment, the Newfoundland Offshore Burn Experiment (NOBE), on August 12, 1993. During each of two test burns, crude oil was poured into a towed U-shaped fireproof boom and ignited. The first test burn lasted for an hour and a half and the second for about an hour, with an average observed burning rate of 24 tonnes of oil per hour (Fingas et al. 1995a). ISB was conclusively validated as an operational physical oil spill response countermeasure following controlled burns near a swamp (**Figure 6.13**) and at sea (**Figure 6.14**) during the DWH incident.

Figure 6.13 A view of one of the controlled burns to remove oil spilled in a wooded swamp outside of Baton Rouge, LA, on January 19, 2013. *Source: USCG.*

Figure 6.14 After the Deepwater Horizon oil spill in the Gulf of Mexico in April 2010, ISB was one of the techniques used to remove oil from the water. *Source: NOAA.*

During at-sea ISB operations, oil on the sea surface is captured within a boom towed by two boats in a U-configuration and ignited using a hand-held igniter or an igniter suspended from a helicopter. Under favourable conditions ISB is a fast, efficient and relatively simple way of removing spilled oil from the water to minimize the adverse effect of the floating oil on the environment. Furthermore, it greatly reduces the need for storage and disposal of the collected oil and the waste it generates. The burn will continue only as long as the oil slick is thick enough—usually about 2-3 mm. Burning oil results in residues (approximately 1-5% of the starting oil) from incompletely combusted oil and gaseous emissions into the atmosphere that have raised environmental concerns. This is particularly true if the residue sinks.

Results of laboratory tests suggest the possibility that burn residues from ~40 to 60% of crude oils may sink. *However, whether results from laboratory tests can be extrapolated to large-scale spills is not known (NOAA 2015).*

To burn oil on the water, slicks must be thicker than 1-2 mm. During combustion the oil vapours ignite and burn, rather than the liquid itself. When the oil layer is thinner than ~1 mm, the heat is lost to the water, not enough vapours are released, and combustion ceases. Experiments have shown that ISB is best used under relatively calm conditions, as choppy seas may extinguish the fire altogether (ITOPF, http://www.itopf.com/knowledge-resources/documents-guides/response-techniques/in-situ-burning/).
When the current is stronger than about one knot, the boom cannot contain the oil, which splashes above the boom or escapes beneath it. This resulting entrainment typically occurs when booms are deployed perpendicular to the water flow (API 2015). Water-in-oil emulsions of over 50% will preclude ISB of even light crudes or refined products, while much less than that is required for heavier crudes (NOAA 2015).

Studies of the emissions from ISB have shown fairly consistent results. According to Ferek et al. (1997), about 85 to 95% of the burned oil is converted to carbon dioxide and water, 5 to 15% of the oil is not burned efficiently and is converted to particulates, mostly soot, and the rest, 1-3%, comprises nitrogen dioxide, sulfur dioxide, carbon monoxide, polycyclic aromatic hydrocarbons, ketones, aldehydes and other combustion by-products. The 5-15% estimated conversion to particulates differs from the 1-5% reported above, suggesting that a number of factors are in play when making estimates of ISB conversions. No ‘exotic’ chemicals are formed. Rather, the burning of oil on water seems to be similar to burning the oil in a furnace or a car’s internal combustion engine, with the exception that the burn is oxygen-starved and not very efficient, so that it generates ample amount of black soot particulates that absorb sunlight and create black smoke. ISB is not used if human populations are located near and downwind from the site. For oil spills occurring in ice-covered water or wetland or salt marsh environments, besides MNA, ISB may be the only spill response method available. ISB, however, should complement, not exclude, other means of spill response. ISB has been used successfully on numerous occasions when oil was trapped in ice or spilled into sensitive marshland.

Recommendation: ISB is fast gaining a foothold as a response technology for treating floating oil slicks. More research, including peer-reviewed literature, is needed to ascertain harmful emissions released to the environment during ISB, such as any incompletely combusted polyaromatic hydrocarbons (PAHs), toxic particulate matter, etc., and to determine the safety and effectiveness of ISB as an oil spill response tool.

6.3 Biological and Chemical Methods

6.3.1 Bioremediation

Many hydrocarbons (normal and cyclic alkanes, most monoaromatics and some PAHs; Table 2.1) are biodegradable under aerobic conditions, although many polar resins, most hopanes and asphaltenes are resistant to microbial attack. Thus, bioremediation is a viable response technique for cleaning up a shoreline contaminated by an oil spill, with the caution that light crude oils are much more easily

> Bioremediation is the exploitation of the ability of microorganisms to convert pollutants, such as petroleum hydrocarbons, into biomass, carbon dioxide, water and innocuous oxygenated end products. The oil serves as food for the microbes, providing energy and carbon for reproduction and growth. Biodegradation is the process microorganisms use to obtain that end. Thus, bioremediation is a human intervention, whereas biodegradation is a natural property of microorganisms.

biodegraded than diluted bitumen and heavy refined products, such as fuel oils. The passage of time has allowed the evolution of numerous diverse microbes to utilize hydrocarbons as a source of carbon and energy for growth (Atlas and Hazen 2011). It should also be noted that many of the oil deposits around the world, especially those near the surface, are actually residues of millions of years of bacterial degradation of organic, mostly plant-based material.

Two primary approaches are used in bioremediation: *bioaugmentation* and *biostimulation*. Bioaugmentation is the addition of an exogenous supply of oil-degrading microorganisms (grown offsite or in the laboratory) to the oil-impacted environment to supplement (augment) the existing microbial populations and accelerate biodegradation. Biostimulation describes the addition of nutrients or other growth-limiting chemicals, such as electron acceptors, to accelerate biodegradation by the indigenous microbial communities that are already present. Both these approaches have been extensively studied in the laboratory and the field.

The rationale for bioaugmentation is that indigenous microbial populations may not be capable of degrading the wide range of potential substrates present in petroleum (Leahy and Colwell 1990), and that addition of selected, competent microbes would permit efficient biodegradation. Other conditions under which bioaugmentation may be considered are when the indigenous hydrocarbon-degrading population is low, the speed of decontamination is the primary factor or when seeding may reduce the lag period to start the bioremediation process (Forsyth et al. 1995). However, bioaugmentation has never been demonstrated with statistical rigour to accelerate biodegradation to any appreciable extent in field studies. McGenity et al. (2012) pointed out that the reasons for past failures of bioaugmentation have been: 1) use of a pure culture rather than a community; 2) focus on biodegrading strains only, without partner microbes; 3) microbes not adapted to the environment and unable to compete for nutrients with indigenous microbes; 4) inadequate dispersion or access to the pollutant; 5) lack of protection from indigenous grazers or predators (e.g., amoebae); and 6) other factors limiting biodegradation (nitrogen and phosphorus).

Except for item 6, these factors were not in play in the statistically rigorous field research conducted by Venosa et al. (1996) on the Delaware shoreline involving MNA, biostimulation and bioaugmentation. In the bioaugmentation treatment, they applied both nutrients and indigenous microorganisms grown on site in 55-gallon drums containing the same seawater and crude oil and grown on the same shoreline under the same environmental conditions as the beach. The study design included quintuplicate plots of all three treatments, and bioaugmentation was unable to further accelerate biodegradation beyond simple nutrient addition, which did achieve statistically significant biodegradation rate enhancement. *While inoculation doesn't seem to be an issue, as reported by Jacques et al. (2008), the future development of good microbial consortia having complementary biodegradative pathways and bio-surfactant production capabilities to enhance the bioavailability of residual hydrocarbons may someday make bioaugmentation feasible on shorelines.*

Biostimulation has been successful in a number of laboratory, mesocosm and field studies, making it the strategy of choice in the open environment because of the ubiquity of oil-degrading bacteria (Venosa et al. 1996; Lee 2000; Zhu et al. 2001, 2004). Microbial population density is generally not the primary limiting factor over the time scales required for bioremediation. When high concentrations of oil are suddenly introduced into the environment, the microbial communities are faced with a huge increase in food (carbon) without a concomitant increase in the nutrients they need to grow at the maximal or near maximal rate (i.e., nitrogen and phosphorus; Chapter 3). Thus, the rates of biodegradation will be necessarily slow since growth of the microbes will be limited by the amount of nitrogen and phosphorus available for the transformations. Hence, biostimulation is used to supplement the limited available nutrients that indigenous microbes need to grow rapidly on the introduced carbon. This is true regardless of the environment in which the oil spill occurred (shoreline, open water, wetland, land, etc.). Two comprehensive guidance documents of oil spill bioremediation covering all aspects of microbial interactions with spilled oil, published in 2001 and 2004 (Zhu et al. 2001, 2004), are still relevant today.

The Redfield Ratio (defined and discussed in Chapter 3) is the stoichiometric relationship among carbon, nitrogen and phosphorus in plankton. To meet the theoretical demand for nitrogen and phosphorus during biostimulation, approximately 150 mg of nitrogen and 30 mg of phosphorus are consumed in the conversion of 1,000 mg of hydrocarbon to cell material (Rosenberg and Ron 1996). Therefore, a commonly used field strategy is to add nutrients at concentrations that approach a stoichiometric ratio of C:N:P of 100:10:1, which is similar to the Redfield Ratio of 106:16:1. However, the practical use of these ratio-based theories remains a challenge. Particularly in marine shorelines, maintaining a certain C:N:P ratio is impossible because of the dynamic washout of nutrients resulting from the action of tides and waves. A more practical approach is to maintain the concentrations of the limiting nitrogen and phosphorus within the pore water at a range optimal for rapid biodegradation (Bragg et al. 1994; Venosa et al. 1996). Commonly used nutrients include quick release water-soluble, solid slow-release and oleophilic fertilizers. Each type has its advantages and limitations. Zhu et al. (2001, 2004) and Venosa and Zhu (2005) provide guidance on how to maintain these concentrations in the field. *Importantly, the optimum C:N:P ratio for anaerobic hydrocarbon biodegradation in situ has not yet been defined.*

Recommendation: There is a need to quantify the persistence of oil of all kinds during and after biodegradation and oil that has been chemically-dispersed in the environment following high-impact spills to help stimulate innovations in bioremediation approaches. This is especially pertinent to cold temperature and anaerobic environments.

6.3.1.1 Wetlands

> Wetlands, salt marshes and mudflats are among the most sensitive and difficult ecosystems to clean.

Productivity in coastal marsh ecosystems is extremely rich, and such systems provide habitat and breeding grounds to many vital species. Use of heavy equipment and human trampling are not amenable to a viable response activity because these cleanup actions may cause more damage than the spill itself. If human presence is needed, wooden walkways (**Figure 6.10**) or boat-based activities should be used as much as possible. Effective response techniques for these sensitive environments may include less intrusive techniques, such as:

- Booms to contain and control the movement of floating oil at the edge of the wetland (Section 6.2.1);
- Sorbents for removal of the oil by adsorption onto oleophilic materials placed in the intertidal zone (Section 6.2.2);
- ISB (but on a stringently limited basis) (Section 6.2.8);
- Bioremediation (Section 6.3.1);
- Phytoremediation (Section 6.3.2); and
- Low pressure flushing with ambient seawater at pressures less than 200 kpa or 50 psi to the water edge followed by removal (Section 6.3.4).

Dispersants (Section 6.3.3) are unlikely to be appropriate for use near a coastal wetland or salt marsh due to the lack of mixing energy to aid in effective dispersion into the water column, limited water depth to effectively disperse the oil below toxicity threshold limits, and the unknown effect of either the dispersed oil or the dispersant itself on ecosystems in the area. *The use of dispersants in near-shore water could have short-term toxic effects on adjacent coastal habitats, such as subtidal animal communities. Direct spraying or contact of dispersants with wetland plants may also cause harmful effects on vegetation.*

6.3.2 Phytoremediation

> Phytoremediation has been defined as the use of green plants and their associated microorganisms in the soil to degrade, contain or render harmless environmental contaminants.

Phytoremediation (**Figure 6.15**), which takes advantage of the mutually beneficial interactions between plants and microbes for environmental cleanup (Cunningham et al. 1996)., is emerging as a potentially cost-effective option for cleanup of soils or sediments contaminated with petroleum hydrocarbons (Frick et al. 1999). As summarized by Macek et al. (2000), the main advantages of phytoremediation include less disruption to the environment, potential to treat a diverse range of contaminants and high probability of public acceptance. Major concerns regarding this technology include dissolution and migration of contaminants and relatively slow rates of remediation.

Degradation can be accomplished by both plants and associated microorganisms in the rhizosphere. *Plants can stimulate the growth and metabolism of rhizosphere microorganisms by providing root exudates of carbon, enzymes, nutrients and oxygen, which can result in more than 100-fold increase in microbial counts (Macek et al. 2000).*

A principal factor involved in the enhanced degradation of hydrocarbons in soil is the 'rhizosphere effect[3]', i.e., an increase in the numbers and activity of soil microorganisms in the plant-root zone. The plant-root zone has a high surface area, which contributes to growth of oil-degrading microorganisms (and other microbes) in response to high concentrations of hydrocarbons present in the rhizosphere following oil incursion. In addition to elevated microbial community numbers, the contribution of plant-root extracellular enzymes to the biodegradation of organic pollutants in the rhizosphere can be considerable. This has been demonstrated by the findings of Gramss et al. (1999), who showed that the roots of some plants release enough oxidoreductase enzymes to take part in the oxidative degradation of certain soil constituents. Active involvement of plant peroxidase enzymes in the phytoremediation process has also been suggested by several other authors (Kraus et al. 1999; Criquet et al. 2000; Chroma et al. 2002), including PAH degradation (Muratova et al. 2009).

[3] *The rhizosphere is the zone of soil or sediment surrounding plant roots and roothairs that is directly influenced by the living plant, e.g., exudates, moisture, nutrients, etc.*

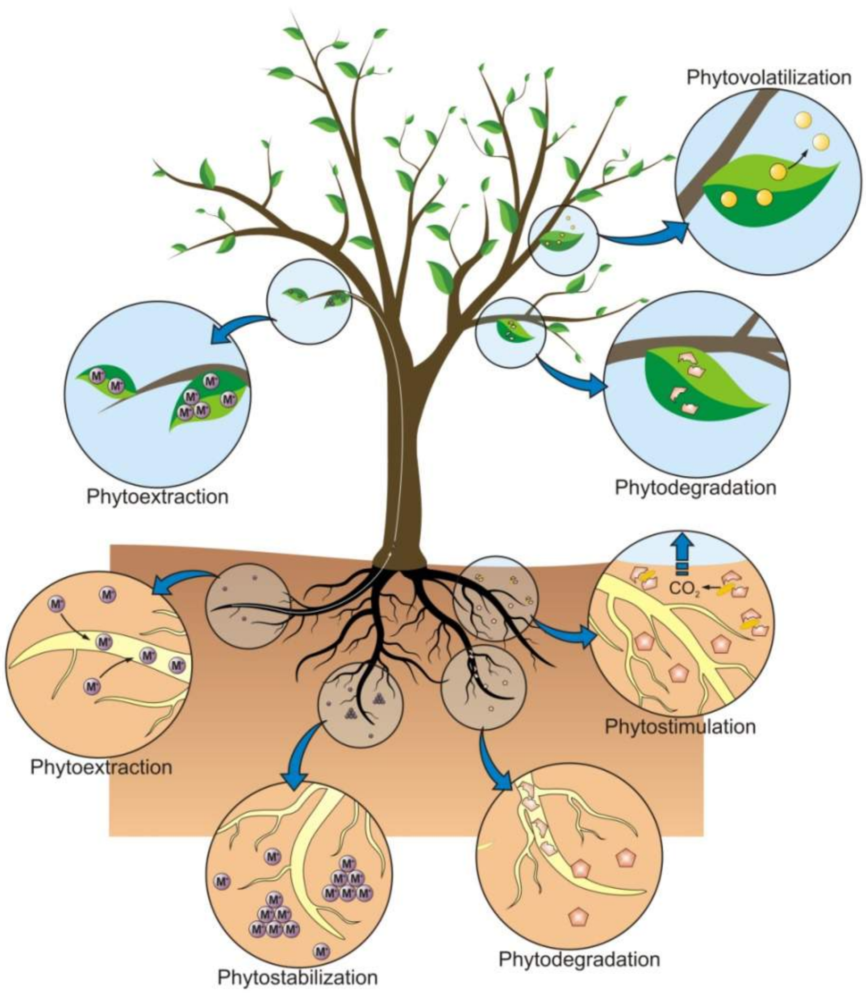

Figure 6.15 Schematic representation of phytoremediation activities. "M" indicates microbial cells. *Source: © 2014 Favas, P.J.C., Pratas, J., Varun, M., D'Souza, R., Paul, M.S. Published in Soriano, M.C. (ed.) Environmental Risk Assessment of Soil Contamination. InTech. Under CC BY 3.0 license. Available from: http://dx.doi.org/10.5772/57469*

Phytoremediation is mutually beneficial. The microbes can reduce the phytotoxicity of contaminants so that plants can grow in adverse soil conditions. Co-metabolism[4] may also play an important role in phytodegradation. Ferro et al. (1997) suggested that plant exudates might serve as co-metabolites in enhancing the biodegradation of the 4-ring PAH pyrene in the rhizosphere.

Other major mechanisms of phytoremediation include retention of petroleum hydrocarbons and their transfer from the soil to the atmosphere. Containment involves the accumulation of contaminants within the plants, adsorption of contaminants onto roots and binding of contaminants in the rhizosphere through enzymatic activities (Cunningham et al. 1996; Frick et al. 1999). Plants can also transport volatile petroleum hydrocarbons to the atmosphere through leaves and stems. However, these effects are less important than the rhizosphere effect during phytoremediation of petroleum hydrocarbons (Ferro et al. 1997).

[4] *Co-metabolism involves the partial oxidation of a chemical (e.g., hydrocarbon) by one organism (that receives no benefit from the metabolism), and the product is further metabolized by another organism that does receive benefit (e.g., can use the partially oxidized product for growth).*

Several full-scale studies in the 1990s and early 2000s highlight what is known about salt marsh remediation. Lee and Levy (1991) conducted one of the first field trials on oil bioremediation in a salt marsh environment. The study involved periodic addition of water-soluble fertilizer granules (ammonium nitrate and triple super phosphate, providing the nitrogen and phosphorus) to enhance biodegradation of waxy crude oil in a salt marsh in Nova Scotia dominated by *Spartina alterniflora* (saltmarsh cordgrass). Results showed that the effectiveness of nutrient addition was related to oil concentration, i.e., effectiveness was high at 0.3% oil contamination by mass, but not at 3% oil contamination. Lack of effectiveness at the higher oil concentration was attributed to the penetration of the oil into the reduced soil layers where anaerobic conditions precluded rapid degradation.

Field trials of bioremediation (Mills et al. 1997) were conducted on a coastal brackish wetland in Texas where two diesel pipelines, one gasoline pipeline and one crude oil pipeline ruptured, spilling ~4,700 tonnes into the tidal and coastal waters of the San Jacinto River. The effect of biostimulation was investigated by evaluating the application of diammonium phosphate alone and diammonium phosphate plus nitrate in replicated plots, providing nitrogen and phosphorus nutrients that otherwise would be limiting. Results showed that the diammonium phosphate treatment significantly enhanced the biodegradation rates of both total GC-MS-resolved saturates and total GC-MS resolved PAHs (Appendix A), and the addition of diammonium phosphate plus nitrate only enhanced the biodegradation of total resolved saturates.

Shin et al. (1999, 2000) investigated the effect of nutrient amendment on the biodegradation of a Louisiana 'sweet' crude oil and oxygen dynamics in a Louisiana salt marsh vegetated by *S. alterniflora*. Significant biodegradation of crude oil in the salt marshes occurred only when the tidal cycle exposed the surface of the marsh to air (Shin et al. 2000). This study again indicated that oxygen availability appeared to control the oil biodegradation process in salt marshes.

Phytoremediation was studied in a freshwater wetland on the St. Lawrence River, QC (Venosa et al. 2002) (**Figures 6.16 and 6.17**), and later on a salt marsh in Nova Scotia (Garcia-Blanco et al. 2007) (**Figure 6.18 and 6.19**). Both studies intentionally released crude oil onto replicated experimental plots. In the freshwater wetland study, the released oil was raked into the top two inches of sediment to simulate penetration of the oil into the anaerobic or anoxic zone. In the salt marsh study, the oil was not raked into the sediment but left on top of the aerobic sediment. Results indicated that addition of nutrients did not result in enhancement of biodegradation of crude oil contaminating the freshwater wetland plots because the oil was in the anaerobic zone where biodegradation is substantially slower. In such a wetland environment, oxygen became limiting at depths within a few millimeters below the surface. However, in the aerobic salt marsh study, the investigators found statistically significant depletion of the hydrocarbons in nutrient-amended plots compared to those not receiving nutrients. This was a clear example of the rhizosphere effect caused by the biostimulation from added nutrients.

Figure 6.16 Photograph of crude oil being applied to one of the plots in the St. Lawrence field study of freshwater phytoremediation. *Source: Venosa et al. (2002)*

Figure 6.17 Aerial photograph of the plot layout in the St. Lawrence River Field study of freshwater phytoremediation. *Source: Venosa et al. (2002)*

Figure 6.18 Photograph of a team taking samples from a plot in an experimental phytoremediation project conducted in 2001 in Dartmouth, Nova Scotia.

Figure 6.19 Aerial photograph of the experimental plot layout in the salt marsh phytoremediation project in the 2001 Dartmouth, Nova Scotia project.

Another field study on the performance of oil bioremediation in salt marsh ecosystems was carried out in a tropical marine wetland located at Gladstone, Australia (Burns et al. 2000; Duke et al. 2000; Ramsay et al. 2000). This study evaluated the influence of a bioremediation protocol on the degradation rate of a medium range crude oil and a Bunker C oil stranded in salt marshes dominated by *Tecticornia* (a succulent plant) and situated behind a mangrove forest. The bioremediation strategy used in this study involved nutrient addition alone for the salt marsh sites. The addition of the fertilizer to the salt marshes showed a stimulation of the degradation of the crude oil and resulted in about 20% more oil loss compared to the untreated plots. However, the nutrient amendment did not significantly impact the rate of loss of Bunker C oil in the salt marsh plots, likely because of its high proportion of recalcitrant components (Appendix C).

<u>Recommendation</u>: Most of what we know about oil spill response technologies has been developed through results from studies in the laboratory, mesocosm test systems and case studies (with limited controls and treatment replication). It is the consensus of the scientific community (and the Panel) that controlled field trials are needed to advance our spill response strategies, especially for subsurface blowouts, Arctic oil spills and freshwater shorelines.

6.3.3 Chemical dispersion

Dispersants are chemicals that reduce the oil-water interfacial tension (NRC 2005), thereby decreasing the energy needed for the slick to break up into small droplets and mix into the water column. They are typically applied by spraying from aircraft (**Figure 6.20**) and/or boats. The composition of most commercially available dispersants is proprietary, but in general they consist of one or more nonionic[5] surface active agents (surfactants) dissolved in a solvent carrier (NRC 1989). Some dispersants also include one or more anionic surfactants and other additives. Lower viscosity oils are more amenable to natural and chemical dispersion than higher viscosity oils, such as fuel oils and dilbit.

> The rationale for using dispersants as an oil spill cleanup tool is to reduce wind-driven transport of oil to highly productive coastal waters and sensitive shoreline habitats by breaking the surface oil slick into small droplets to facilitate the transport of the oil into the water column. This would also reduce its exposure to surface water biota (e.g., sea birds). Furthermore, oil in the water column may be diluted to concentrations below the toxicity threshold limits of resident biota. Because microbial attack of oil occurs at the oil-water interface, droplet formation also enhances the biodegradation rates of the residual oil.

Natural dispersion takes place when wave and wind action are sufficiently high (winds > 5 m/s, for example) to overcome the oil-water interfacial tension and break the slick into droplets of various sizes (Figure 2.6). A notable example of such occurred in 1993 when gale-force winds caused the grounding of the tanker *Braer* in Shetland, UK, spilling a low viscosity crude oil into the water. Dispersion occurred naturally, causing minimal shoreline impact. Under less energetic wave action, chemical dispersants enhance natural dispersion, facilitating the breakup of the oil into small droplets that are transported into the water column.

Another form of natural dispersion occurs when microorganisms, especially alkane degraders, produce their own biosurfactants (Bodour et al. 2003). These biosurfactants are similar to the synthetic surfactants in chemical dispersants in their mode of action, which is reducing the interfacial tension between oil and water, solubilizing hydrocarbons and thus facilitating their uptake across the membrane into the cell for metabolic purposes. Bodour et al. (2003) reported that biosurfactant-producing bacteria are widely distributed in both undisturbed and contaminated soils. The majority of hydrocarbon-degrading bacteria reported in the literature belong to the genus *Pseudomonas* (Widada et al. 2002; Bento et al. 2005). A wide variety of metabolic and physiological factors is required for the degradation of different compounds in oil (Frielo et al. 2001). All such properties are not found in one organism but rather in consortia. More research is needed to augment our understanding of the effectiveness of these biosurfactants in enhancing bioremediation of oil-contaminated environments.

Specially formulated products containing surfactants and solvents are sprayed (generally at concentrations of 2-5% by volume of the oil) from aircraft or boats onto the slick. Surfactants are the active (i.e.,

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[5]*Nonionic dispersants (e.g., some alcohols and ethers) do not have an overall electric charge; anionic dispersants are electronegative (e.g., have carboxyl, sulphate or phosphate groups) and cationic dispersants are electropositive (e.g., have amino or ammonium groups).*

interfacial tension-reducing) ingredients in dispersants. Surfactant compounds are amphiphilic[6] (i.e., have hydrophobic and hydrophilic components within the same molecule), which causes them to accumulate at oil:water interfaces (Porter 1991). Nonionic surfactants are most common in dispersants because they have much lower aqueous solubility than do anionic surfactants (Porter 1991), and they are generally less toxic and less affected by electrolyte concentration than are anionic and cationic surfactants (Porter 1991; Myers 2006).

Figure 6.20 An aircraft releases chemical dispersant over an oil slick in the Gulf of Mexico in 2010. *Source: NOAA /US Coast Guard*

Figure 6.21 is a schematic diagram showing the spraying of a dispersant onto a floating slick and the slick breaking apart into small droplets that get driven into the water column by wave action. The water-loving end of the surfactant is attracted to the water while the oil-loving end is attracted to the oil. The oil droplet is surrounded by the surfactant molecules, forming what is called a micelle or a surfactant-stabilized oil droplet. Eventually, as water mixes with the droplets, their concentration declines and the bacterial communities in the sea are able to break down the oil quickly, leaving no lasting residue that might exert toxicity to the seawater biota.

[6]*Amphiphilic is a term describing a chemical compound possessing both hydrophilic (water-loving, polar) and lipo-philic (fat-loving, non-polar) properties.*

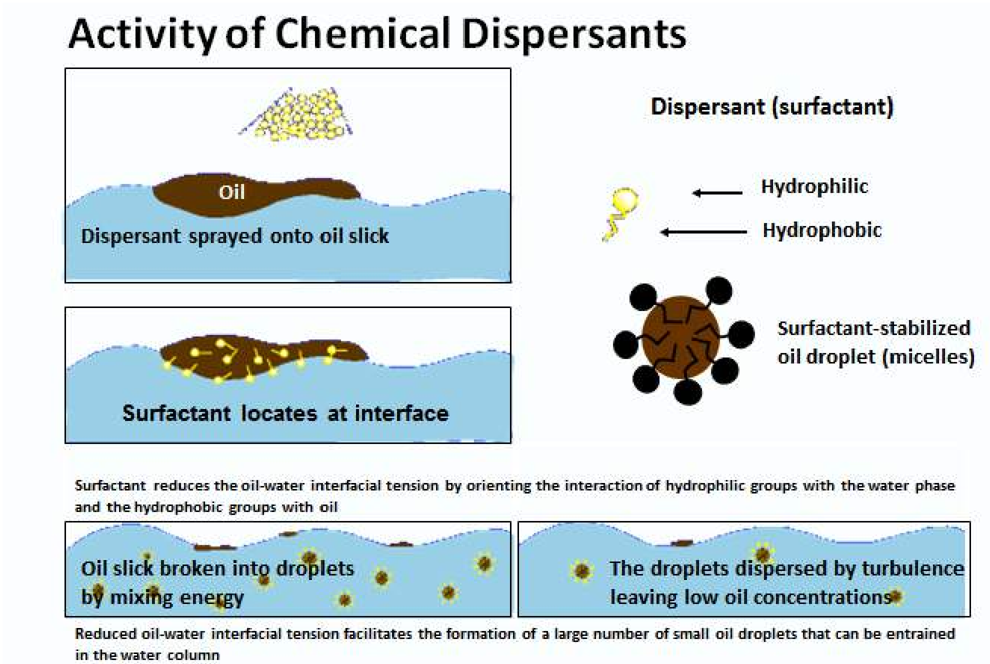

Figure 6.21 Schematic diagram of how oil is dispersed by dispersants.

A typical measure of the relative importance of the hydrophobic and hydrophilic characteristics of nonionic surfactants is the hydrophilic-lipophilic balance (HLB), which ranges from 0 for completely lipophilic or hydrophobic molecules to 20 for completely hydrophilic (charged) molecules. **Figure 6.22** shows the HLB scale ranging from highly oil-soluble to highly water-soluble. Surfactants with low HLB tend to stabilize water-in-oil emulsions, whereas those with high HLB stabilize the more desirable oil-in-water emulsions (NRC 1989; Clayton et al. 1993). Commercial dispersants tend to have overall HLBs in the range of 9 to 11, which is often achieved by combining surfactants having higher and lower HLB. Although the industry consensus suggests that combining surfactants with different HLB improves dispersant effectiveness (NRC 1989; Clayton et al. 1993), others have offered alternative findings (Fingas et al. 1990a).

To date, most chemical dispersants have been formulated for marine use, as the dissolved divalent cations in seawater (particularly calcium and magnesium) are integral to dispersant efficacy (Chapter 3). Development of freshwater-compatible or -specific dispersants has lagged mainly because of regulatory decisions against the use of dispersants near water intakes. A fundamental laboratory study was conducted in 2008 to determine if it is possible to produce a dispersant for use in fresh water (Wrenn et al. 2009). The authors found that dispersants can be designed from scratch (rather than modifying existing commercial dispersants) to drive an oil slick into the freshwater column with the same efficiency as in saltwater as long as the HLB is optimum for that environment.

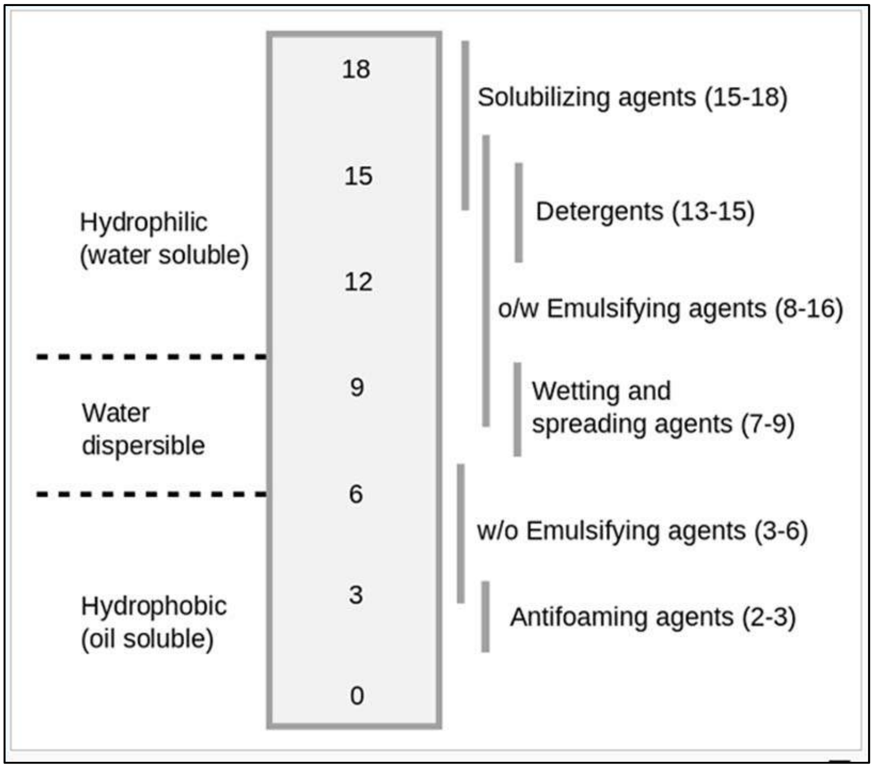

***Figure 6.22 Hydrophilic-Lipophilic Balance diagram showing the HLB scale**. (Source: MHK; https://en.wikipedia.org/wiki/Hydrophilic-lipophilic_balance. This figure is licensed under the [Creative Commons Attribution-Share Alike 3.0 Unported](#) license)*

> The effect of using dispersants on an oil slick is not simply to dilute the oil. Rather, creating the small oil droplets and driving them into the water column increases the surface-area-to-volume ratio, thereby inducing significantly faster biodegradation by oil-degrading microbial communities within the water.

The purpose of the solvent in a dispersant is to provide the surfactant mixture with an appropriate viscosity, which ensures that it can be pumped through spray nozzles at environmental temperatures. The solvent may be water-miscible[7] (e.g., 2-butoxyethanol) or immiscible (e.g., normal alkanes) (NRC 2005).

Mixing energy driven by wind and wave action is required to achieve effective dispersion. Depending on a site's energy level, tiny droplets of oil (ideally <70 µm in diameter) are mixed in the upper meter of the water column creating a subsurface plume. This plume of dispersed oil droplets rapidly mixes and expands in three dimensions (horizontal spreading and vertical mixing) down to as much as 10 meters below the surface. The rise speed[8] of these droplets is extremely slow and is overcome by the turbulence in the upper depth of the sea, essentially resulting in neutral buoyancy of the droplets. The ideal size of the droplets precludes re-coalescence and re-formation of a surface slick. As a result of this mixing, oil

[7] *Water-miscible solvents mix completely with water to form a single phase, whereas immiscible solvents form two phases.*

[8] *Rise speed is the rate at which submerged droplets will resurface (similar to the concept of terminal velocity for objects falling through air), which depends on droplet size and coalescence; large droplets may take several hours or days to resurface, whereas small droplets may remain submerged for a long time regardless of their nominal density and buoyancy.*

concentrations decrease rapidly from the initial peak concentrations, e.g., from 10 or 100 ppm down to 1 ppm or less, within hours (Lee et al. 2013).

Microorganisms act on the small dispersed droplets at the oil-water interface (Figure 2.3), so increasing this surface area by reducing the droplet size increases the area for biodegradation to occur. Thus, the ultimate fate of oil is its destruction. The transient effect might be negative to fish and other waterborne animals (Chapter 4), but such an effect may be short-lived due to rapid dilution of the oil to concentrations below toxicity threshold limits, enhanced oil degradation and resilience of the living populations. Dispersants and dispersant applications are rarely 100% effective, however, so some oil will likely remain floating on the water surface.

In some cases, dispersing oil changes the trajectory of the oil plume from onshore to alongshore, as the transport of dispersed oil is less affected by the wind. Therefore, oil dispersion may help protect sensitive shoreline environments, as wind usually is the dominant environmental factor that carries floating oil to strand ashore.

Dispersant effectiveness is limited by certain physical and chemical variables, such as sea state and oil properties. Sea state has already been discussed briefly above. When wave energy is sufficiently high, re-coalescence of the small dispersed oil droplets is minimized. Salinity is also an important variable. Dispersants in use today have been optimized for use in seawater (salinity of ~35 g/kg). Lower salinities substantially lessen dispersion effectiveness of commercial products unless the dispersant has been manufactured to work in brackish or fresh waters. This is accomplished by manipulating the HLB as discussed previously.

The discussion above would not be complete without mentioning the 2010 DWH blowout in the Gulf of Mexico. In that spill, at least 430,000 to 500,000 tonnes of light oil gushed out of a deepwater well for almost three months before the well was finally repaired and the blowout contained (McNutt et al. 2012; Fingas 2013). Approximately 3,000 tonnes of two chemically similar anionic dispersants (initially Corexit 9527, followed by Corexit 9500, which lacks the miscible solvent 2-butoxyethanol) were injected into the subsurface oil plume as it escaped the well's riser tube and a further 4,000 tonnes were applied to oil at the sea surface (Gray et al. 2011). Significant amounts of data on fluorescence, droplet size distribution, dissolved oxygen, total petroleum hydrocarbons (TPH) and volatile organics analysis (VOA) measurements were collected by the U.S. Coast Guard, NOAA, U.S. EPA, BP, DFO and other organizations deployed in the area and were published daily. Data were obtained from vessels deployed on the surface of the water lowering instruments and samplers to the vicinity of the well and dispersed oil plume, plus autonomous vehicles taking real-time data. These data were important to understanding the hydrodynamic behaviour of the water and the direction of the currents carrying the plume of dispersed oil. Initial findings suggested that the deep subsurface dispersed oil did not experience significant buoyant rise or sinking after release and instead behaved as neutrally buoyant particles or as dissolved materials in the water. All of the measurements indicated that the majority of the deep subsurface dispersed oil was carried predominately to the southwest away from the wellhead by the prevailing currents at depths of 900–1,300 m. Analysis of TPH, VOA and coloured dissolved organic material (CDOM) fluorescence data (Appendix A) indicated the presence of deep subsurface dispersed oil up to 100 km northeast of the well.

Measurements of the dispersed oil plume in the deep sea during the DWH spill at 1,100 to 1,300 m below the surface **(Figure 6.23)** showed that most of the plume consisted of particle sizes ranging from 2.5 to 60 µm in diameter. In the same area, a dissolved oxygen anomaly was observed signifying biodegradation activity. Furthermore, light scattering measurements in the LISST particle size analyzer of water samples collected from that plume displayed the characteristic bimodal distribution typical of chemically- as opposed to physically-dispersed oil (Li et al. 2008, 2009). This suggests, but does not scientifically prove, that the oil in the deep zone was likely chemically dispersed at least part of the time due to the injection of dispersant into the oil exiting from the riser tube (injection of dispersant was not always active). Although it is plausible that the extreme turbulence of the oil as it gushed from the well may have caused extensive physical dispersion without the need for chemical dispersant use, review of reported data and information in the literature suggested that it was less likely and that the application of dispersants in the deep sea was successful in dispersing the oil at the source (Venosa et al. 2012). Later, however, Valentine et al. (2014) reported finding oil contamination in the sediment downstream from the well at 1,500 m water depths. The amount of contamination is still being investigated. For a detailed discussion of toxicological issues associated with the use of dispersants in oil spill response, please refer to Chapter 4.

In addition to the dispersant injected at depth into the oil spewing from the wellhead, significant quantities of dispersants were used on the Gulf's surface during the DWH response. Some of the oil that made it to the surface migrated to coastal habitats. The use of dispersants likely increased the bioavailability of the oil (its ability to be taken up or acted upon by organisms) and enhanced the opportunities for biodegradation. However, dispersants also may have increased the potential exposure of sensitive organisms. The fate of the released oil and its many components remains poorly understood. This is an active area of research among oceanographers, engineers and marine chemists. Certainly, the use of dispersants at the sea surface reduced the exposure of the coastline to oil and application of dispersants at the wellhead reduced the amount of oil reaching the surface, but effectiveness of both the surface and the deep sea dispersion was not quantified.

Dispersants have been used successfully as an effective oil spill response technique. For the first time ever, dispersants were used during the DWH blowout to disperse oil as it exited from a deep sea well in the Gulf of Mexico. Although many have concluded that dispersants were successful during the DWH spill, it is still unknown for certain to what extent the oil was dispersed physically due to the high velocity of oil emerging from the well into the water or chemically in response to mixing with applied dispersant.

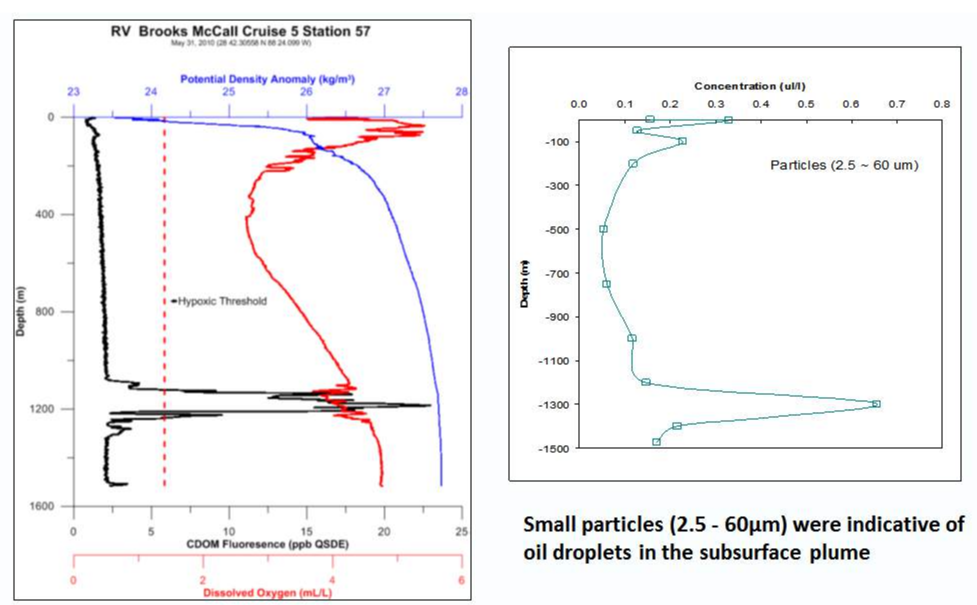

Figure 6.23 Data collected during the Deepwater Horizon blowout showed clearly that at approximately 1200 m below the surface, the dissolved oxygen spiked downward (red curve) suggesting biodegradation while the fluorescence spiked upward signifying the presence of the oil droplets in that same area. *Source: K. Lee, DFO*

<u>Recommendation</u>: The relative importance of turbulence and chemical dispersion needs to be measured in controlled experiments to reduce the uncertainty of the chemical dispersion treatment strategy. Controlled empirical experiments, preferably in the field, need to determine the persistence of dispersed oil in the deep sea and at the sea surface. The ecological and toxicological consequences of dispersants and dispersed oil in wetland, salt marsh, mudflat and deep sea

environments need to be evaluated at cold and warm temperatures, in part by using mesocosms and wave tanks. Analytical chemical techniques for monitoring dispersed oil or dispersants in the water column at extremely low concentrations need to be improved, especially in fresh water. Research is needed to develop, if practical, effective and non-toxic biosurfactants as alternatives to traditional chemical dispersants currently on the market.

6.3.4 Surface washing by chemical washing agents

Surface washing removes free product stranded on the shoreline without removing sediment. Collected oil is placed in containers and carried off the shoreline. This process is most effective on sand and gravel beaches and riprap[9], but can also be used on other types of terrain except soft mud substrates and mud flats, where the oil would be pushed downward into the sediment causing a worse condition than before. Surface washing is most useful for light to moderate oiling by medium to heavy oils. Removal of surface oil is typically used only along the edges of low, sheltered or vegetated riverbanks and marshes and must be closely monitored.

6.3.5 Solidifiers

Solidifiers are chemical agents applied as powders, granular mixes or gels that react with oil with minimal volume increase to form a cohesive, solidified mass that floats on water (Ghalambor 1997). Use of solidifiers for oil spills on water has been investigated since the early 1970s (Dahl et al. 1997). In some cases, polymeric solidifiers are modified with other inorganic or organic additives, which serve as chemical bonding agents. Due to the need for recovery and disposal of the immobilized oil, solidifiers are generally impractical for wide-scale application to large spills and have been only used on small oil spills on land or restricted waterways (Schulze and Hoffman 1993).

Solidifier booms have also been shown effective in removing sheen from wastewater holding ponds. The U.S. EPA Region 4 authorized solidifiers to be used as an alternative to sorbents or mechanical recovery when removing small or thin sheens from water or small amounts of oil from land (Michel et al. 2008). As reviewed by Fingas (2013a), a solidifying agent manufactured by BP was tested by the Canadian Coast Guard for treating oil-under-ice in the Beaufort Sea and oil in open sea conditions off Newfoundland, with the conclusion that the product’s usefulness was equivocal in the first case and not practical in the second case because of the large mass ratio of solidifier:oil required. Hand-spraying the product onto an experimentally oiled Arctic marine shoreline on Baffin Island similarly yielded little benefit (Fingas 2013a). Various other solidifiers have been laboratory-tested by Environment Canada.

Use of solidifiers for oil spill response has some drawbacks and thus has received little attention. For example, their effectiveness depends on the type and composition of the crude oil tested (Fingas et al. 1990b; Dahl et al. 1997). Another disadvantage has been the large amount of material that needs to be applied and recovered. It has been reported that 16 to over 200% by weight (solidifier-to-oil mass ratio) is required to solidify crude oil (Fingas et al. 1995b). Moreover, practical application methods and appropriate tests under various conditions and environments have been lacking (Delaune et al. 1999). In recent reviews of oil spill solidifiers, Fingas (2008, 2013) noted a lack of rigorous scientific assessment of their effectiveness at spill sites. Temperature may play an important role in the solidification of oil mainly because of the variations in viscosity and API gravity of the petroleum product. At low temperatures solidifiers have been found to be less effective (Fingas 2008, 2013a). In contrast, Pelletier and Siron (1999) tested a silicone-based solidifier on a light crude oil and reported that temperature did not appear to have a major impact on effectiveness, although more testing would be required to confirm this finding.

[9] *Riprap is rock, concrete or other material used to armor shorelines, streambeds, bridge abutments, pilings and other shoreline structures against scour and water or ice erosion.*

The effectiveness of a solidifier product is dependent upon a number of incident-specific variables, including oil type, oil amount and weather conditions, such as the sea state, sea temperature and wind conditions.

In their review of environmental considerations for non-dispersant chemical countermeasures, Walker et al. (1999) reported that the effectiveness of solidifiers probably decreases for emulsified, weathered, thick and heavy oils because of the difficulty of mixing the product with viscous liquids. They also reported that salinity does not affect the ability of solidifiers to solidify oil on water.

The density and viscosity of the oil reflect the chemical and physical variations of crude oils. Changes in viscosity depend on environmental conditions, particularly temperature. Viscous oils tend to clog the outer layer of the solidifier, thus decreasing further sorption of oil. Fieldhouse and Fingas (2009) reported that product performance was similar at 0 and +15 °C, but at -15 °C longer contact times were required for the samples to reach a state sufficiently solidified to prevent release of oil from the solidified material. The study also reported that low temperature was a limiting factor for generating a solidified product, while at room temperature, the treated material became a cohesive mass. Low temperature was also found to result in longer solidification times or reduced effectiveness due to increased oil viscosity.

Sundaravadivelu et al. (2015) recently conducted an intensive, statistically rigorous laboratory study of oil solidifier performance using a variety of products and oil types at 5 and 22 °C. The removal efficiency and final consistency of the product depended on oil type, temperature, bulk density of the product and application ratio. *Products with lower bulk powder density had high specific surface areas, which resulted in increased oil removal efficiency. For these products, the efficiency was significantly higher at 22 °C than at 5 °C (by 10 to 20%). However, variability was lower as a function of temperature for products with higher bulk density and less removal effectiveness (only 4% increase at the higher temperature). Overall, the best predictor of solidifier effectiveness was found to be its bulk density.*

Recommendation: A laboratory protocol is needed to compare and test effectiveness of commercial solidifier products. Research is needed to determine whether solidifiers are effective or feasible to use on larger oil spills, and whether the product and oil can be recovered after such use.

6.3.6 Herding agents

Herding agents gather thin oil slicks together or move them (at the surface) towards a desired location for collection or ISB, particularly in partial ice cover (Fingas 2013b). Buist et al. (2008) sprayed a herding agent onto the seawater surface surrounding an experimental oil slick, which resulted in the formation of a monolayer of surfactants on the water surface, a process first reported by Garrett and Barger (1972). When the surfactant monolayer reaches the edge of a thin oil slick, it changes the balance of interfacial forces acting on the slick edge and causes the oil to contract into thicker layers. *Since herders do not require a boundary to 'push against', they work even in open water.*

A herding agent is a chemical containing a surfactant and a solvent, similar to a dispersant but in different proportions with different functions.

Surfactants considerably reduce the surface tension of the water surrounding an oil slick (from about 70 mN/m to 20 to 30 mN/m[10]). Although commercialized in the 1970s mostly to concentrate the oil for skimming and recovery, herders were not used offshore because they worked only in very calm

[10] *mN/m (millinewtons per metre) is a unit used to measure surface tension at an interface.*

conditions. When wind speeds were 2 m/s or greater, booms were needed to contain the slicks, and breaking waves were observed to disrupt the herder layer. *A recent strategy in loose pack ice is to herd freely-drifting oil slicks to a burnable thickness (i.e., greater than about 3 mm). Once a sufficient thickness is attained, the oil may be ignited for ISB. The drift ice acts as an additional containment barrier to aid in reducing the time needed for the development of a slick thick enough to burn. Buist et al. (2008) succeeded in burning oil in drift ice using a non-proprietary hydrocarbon-based cold water herding agent (called USN).*

Based on earlier studies (Buist et al. 2008; 2010a,b), work has continued on herding agents for ISB in Arctic waters (Buist et al. 2011). Recent herding agents were capable of thickening a slick to > 4 mm, suitable for ISB (Buist et al. 2010b), and when tested on experimental oil spills, >90% of the oil was combusted. Based on the results of earlier work (Buist et al. 2008), the researchers concluded that *herding agents work best on relatively fresh crude oil and light distilled product slicks that are still of relatively low viscosity and remain ignitable. Slicks that have gelled or significantly emulsified and viscous residual fuel oil slicks would not be good candidates for herder use*. As with most oil spill response techniques, rapid response improves the chances of success when using herders for ISB.

<u>Recommendation</u>: The utility of herding agents, especially for use in the Arctic, needs to be quantified and properly tested to provide a scientific basis for their application to oil spills.

6.3.7 Debris and detritus removal

All spill incidents involve the production of huge quantities of recovered oil, wastewater, debris, detritus, heavy metals and other solid materials during the spill response that are usually disposed in landfills. Heavy metals are especially important because of their toxicity and persistence in the environment. These cleanup materials include sorbents, debris (seaweed, trash, logs, mooring lines, etc.) and clothing (**Figure 6.24**). Interim storage and permanent disposal options have to be defined. *It should be noted that disposal of contaminated materials in landfills simply moves the pollution from the shoreline to another site*. Accordingly, the work plan should include provisions for reducing the volume of material to be disposed in landfills and should address options, such as recycling, using waste oil in road asphalt and removing excess liquid from the waste oil to decrease volumes. Oiled debris removal is recommended for sand beaches, gravel beaches, sheltered rocky shores, man-made structures and sheltered rubble slopes. It is conditionally recommended for exposed rocky shores, tidal flats, sheltered vegetated low banks and marshes (Region 10 Regional Response Team and the Northwest Area Committee 2015).

In addition, incineration is one of the most efficient methods of disposal for recovered oil, used oil sorbents and debris in a relatively short time and involving not much labour force. The general disadvantage of incineration is high transportation cost of the disposed material to the incinerator facility and regulatory prohibitions in many Canadian jurisdictions. *A recent comprehensive review of all the methods used for treating oily sludge in the petroleum industry was published by Hu et al. (2013), including how to deal with heavy metals and hazardous liquid waste.*

<u>Recommendation:</u> The change of heavy metal concentrations during different oily sludge treatment processes is worthy of investigation in future research, and the integration of available heavy metal control technologies into oily sludge treatment is recommended.

Figure 6.24 Detritus removal during the Motiti Island oil spill off the coast of New Zealand, 2011. *Source: Maritime New Zealand*

6.4 Factors Affecting Spill Response and Cleanup Effectiveness

6.4.1 Oil types and properties

> The types and properties of spilled crude oil are among the most significant factors influencing the efficiency and effectiveness of oil spill response.

Very light oils (e.g., jet fuels and gasolines) are highly volatile (evaporate in one to two days) and have high concentrations of toxic soluble compounds. Ventilation and/or absorption are usually effective cleanup methods in conjunction with fire and inhalation prevention measures. Light oils (e.g., diesel, No.2 fuel oil, and light crudes, including Bakken crude) are relatively volatile and thus easier to treat effectively than heavier oils. Medium oils (e.g., most conventional crude oils) are generally less volatile than lighter oils, increasing the potential for impacts on waterfowl and wildlife. Heavy oils and diluted bitumen (e.g., Bunker C, weathered dilbit and railbit) are receiving increasing attention due to their resistance to evaporation and biodegradation and their potential long-term damage to the environment, waterfowl and fur-bearing animals. They have fewer components that dissolve in water (Kok 2011; Dejhosseini et al. 2013). Cleanup is extremely difficult for both marine and inland spills. For detailed information about crude oil types and properties, refer to Chapter 2 and Appendix B.

The main physical properties that can affect the behaviour of oil are density, viscosity and flash point (Fingas 2012; Yasin et al. 2013). Oils with high API gravity tend to be free flowing (low viscosity), have a high proportion of volatile compounds and low flash points and pour points, which facilitate their cleanup. However, the properties of oils with high wax or asphaltene content cannot be solely determined by API gravity. Viscosity increases as the oil weathers (Demirbas et al. 2015). Volatility refers to how quickly the oil evaporates into the air. High volatility usually can increase the amount of oil that evaporates into the atmosphere. Flash point is the lowest temperature at which sufficient vapour exists above the spilled oil to yield a flammable mixture (Gülüm and Bilgin 2015). Light crude and oil products have low flash points that are suitable for ISB.

The fate and behaviour of the spilled oil will influence response effectiveness. Abiotic processes at water surface and within the water column include spreading, evaporation, emulsification, oxidation, dispersion, dissolution and sedimentation (see details in Chapter 2 and 3). Biotic processes in the water column usually refer to biodegradation and uptake by living microorganisms. Emulsification (high viscosity) and sedimentation can impede the effectiveness of response techniques (Cai et al. 2014b). Weathering processes that influence changes in oil properties can be significantly influenced by ambient environmental conditions. *Thus, comprehensive consideration of the above oil types and properties and their weathering processes, along with environmental factors, are necessary for making sound response decisions and actions.*

6.4.2 Environmental and ecological factors

6.4.2.1 Weather

The feasibility and effectiveness of oil spill response are heavily dependent on the weather conditions prevalent at the oil spill site. Generally, a clear, sunny day without strong wind would be favoured by spill responders, especially in offshore spill sites (Fingas 2012; Doerffer 2013). Such weather conditions would encourage natural attenuation (e.g., evaporation), help the responders deploy equipment and enhance the efficiency of booming, skimming, ISB and dispersant application (Verma et al. 2013).

In hot or warm weather and water conditions, evaporation usually dominates as higher temperature tends to increase the volatility of spilled oil, especially for lighter products. The viscosity of water-oil emulsions decreases with increasing temperatures. Therefore, mechanical cleanup techniques, such as booming and skimming, are much easier to deploy and more effective in warm conditions. Temperate conditions also favor ISB due to the ease of igniting the oil slick. While indigenous microorganisms are adapted to their environment, their rates of activity are generally enhanced at higher temperatures in both the water column and the sediment. *Oil biodegradation rates and extent are generally higher in warm water environments. For example, an increase of 10 °C in temperature can double the metabolic rate of an animal, plant or microorganism (Tyagi et al. 2011; Hassanshahian et al. 2012). The bacterial metabolic rate has been reported to be on the order of 800% higher in the Gulf of Mexico than in Alaska (Mortazavi et al. 2013).*

In contrast, oil spill cleanup is usually complicated by cold and harsh climatic conditions such as those that prevail in northern Canada and the Arctic. Deploying response equipment and personnel is challenging not only because of these harsh conditions but also the lack of access and the long distances between the source of cleanup equipment and the spill. Physical constraints include the fact that during winter months, it is often too cold to work and daylight hours are limited (or non-existent). In addition, *cold weather may cause health and safety issues due to factors such as potential hypothermia among responders, brittle failure of metal components, freezing of sea spray causing vessel instability, etc.* The recovery of oil in extreme cold weather requires a different approach than in warm weather and the likelihood of injury to responders increases significantly (Daling et al. 2010; Buist et al. 2011). Different sets of skills and technologies are needed by responders to ensure effective spill response in harsh environments (Oskins and Bradley 2005).

Cold conditions may also compromise the effectiveness of mechanical containment and other cleaning efforts. For example, mechanical oil recovery, such as through the use of skimmers and pumps, may be compromised because the equipment may freeze up and the increase in oil viscosity reduces recovery efficiency. In the case of ISB, ignition may be difficult and burning may be slow and inefficient. In addition, considerable debate continues over the effectiveness of dispersants on crude oil degradation at low seawater temperatures (Daling et al. 2010). The main concern is that as the temperature decreases, chemical and biological processes slow down and oil viscosity increases, making dispersion of oil more difficult (EPPR 2015). In contrast, reduced oil spreading rates extend the ‘window of opportunity’ for dispersant use (Nuka Research 2010; Arctic Oil Spill Response Technology Joint Industry Programme

2013), followed by a reduction in the size of the chemically-dispersed oil droplets, thus enhancing the potential for effective biodegradation in a cold marine environment (Cai et al. 2014a; Greer et al. 2015).

In summary, the effects of weather conditions on oil spill response include:

Warm weather

- Evaporation dominates (higher temperature increases volatility and decreases oil viscosity), resulting in better use of mechanical and ISB responses; and
- Microbial communities grow and metabolize hydrocarbons faster at higher temperatures, speeding up biodegradation.

Cold weather

- Deployment of response equipment and personnel is challenging due to lack of access and long distances to the spill site;
- Daylight hours may be limited or plentiful depending on the latitude of the spill site and season;
- Injury potential to responders is heightened due to the harsh conditions;
- Different skill sets and equipment are needed (chain saws and ice augurs);
- Crude oil biodegradation rate is much lower at low temperatures;
- Oil viscosity increases, which reduces recovery efficiency;
- Cold temperatures may compromise the effectiveness of mechanical equipment;
- ISB ignition may be difficult and burning may be slow at cold temperatures;
- Reduced oil spreading rates extend the opportunity for dispersant use and reduce the size of oil droplets;
- Cold conditions may cause health and safety issues to responders; and
- Mechanical equipment may freeze up.

6.4.2.2 Wave height

Wave height is an important consideration for any recovery method that relies on containment before collection or removal. Waves can impact mechanical spill response by the following factors (Fingas 2012; Andrade et al. 2013):

- Causing boom and skimmer failure or reducing their effectiveness;
- Making vessels difficult to keep on station;
- Creating unsafe conditions for crew to work on deck;
- Making deployment or retrieval of equipment challenging or impossible;
- Causing oil to submerge so that it is no longer available for recovery; and
- Limiting the ability to track and encounter oil.

Oil is often entrained beneath or splashed over booms in short-period wind-waves exceeding 1–1.5 m, although booms can accommodate higher wave heights in a long-period ocean swell (Deng et al. 2013). The issue of boom limitations in high waves also affects the practicality of using ISB in rough sea conditions (Gong et al. 2014). *Steep, wind-driven waves typically impart a more significant detrimental effect on spill response operations than longer period swells. In addition to driving sea state conditions, wind can also impede on-water mechanical response through direct limits to both operating vessels and* *equipment (Wang et al. 2012; Li et al. 2014a).* These conditions can be problematic in harsh northern Canadian and Arctic regions, as well as large inland lakes, such as those in southern regions of Canada and the Great Lakes, which can have severe wave heights during rough weather. However, it should be noted that many Arctic areas experience less severe wind and sea conditions than most open seas and thus may not significantly experience these problems (Dickins 2011). This is because the regional presence of ice dampens wave action and often limits the fetch over which winds might otherwise create larger, fully developed waves.

In summary, extreme wave height and wind can produce unsafe conditions to operate boats, vessels and aircraft. They may also combine with low temperature to further cause wind chill (Gong et al. 2014). For mechanical recovery, these conditions can move booms and skimmers away from oil slicks or make them less or completely non-functional. In regards to ISB, they may impede oil containment and ignition and compound unsafe conditions. Dispersant spray application, use and monitoring are also hampered by these energetic conditions. However, high waves and wind do offer positive effects, such as potential oil movement away from sensitive areas (if in a right direction) and extra mixing energy, promoting natural dispersion and evaporation (Nuka Research 2010).

6.4.2.3 Ice conditions

In an environment with static ice and snow conditions, the first response timelines may be lengthened if oil remains contained, concentrated and trapped for extended periods of time. In dynamic ice conditions, the 'window of opportunity' for spill response operations can be extended if the oil can be tracked until it appears naturally on the surface or until vessels and crews can access it at some distance from the original spill site (EPPR 2015). Tracking oil in or under ice and snow remains a challenge for *in situ* and remote monitoring technologies. *Furthermore, the choice for spill response strategies is limited in harsh conditions, such as those encountered offshore in moving pack ice and rivers in late winter and early spring when they are high and often over-topping river banks and ice floes are moving rapidly or piling into ice jams that cause even more flooding.*

> Existing trajectory models are limited in their capability to model oil fate and behaviour in the presence of a range of sea ice conditions.

Conventional booms and skimmers for mechanical containment and recovery of spilled oil become increasingly ineffective as ice concentrations increase much beyond 10% or more (Lampela and Jolma 2011). For example, ice may tear or move containment booms or clog skimmers or reduce their efficiency and manoeuvrability. The length of boom that can be deployed and maintained under freezing conditions, even for a short period, depends on the severity of the ice conditions. Limited effectiveness is still possible in very open drift ice (10-30% ice cover) and in isolated polynyas[11] within closer pack ice (Wilkman et al. 2014). However, even the presence of small fractions of ice interferes with boom operation and quickly reduces flow to the skimmer head. Any limited containment of oil, which may be possible in open drift ice, requires rugged, high strength booms to withstand contact with the ice. In addition, ice may also create difficulties for deploying fire booms and reduce ISB effectiveness.

The fundamental limitations associated with maintaining and operating booms and skimmers in ice are further complicated in polar areas by the lack of coastal infrastructure and approved on-land storage sites (Pilipenko et al. 2013; Schmidt et al. 2014). The presence of ice may also preclude spill response vessels from getting close to the spill site or to track spilled oil. Due to downtime associated with the clogging of water intakes on vessels, additional ice scouts or ice management vessels may be needed during response operations (Wilkman et al. 2014).

[11]*A polynya is an area of open water within the sea ice pack.*

> To date, dedicated mechanical systems for operations in pack ice have not progressed beyond the prototype stage.

Although ice conditions preclude the effectiveness of booming and skimming, many field observations and experiments have shown that partial ice cover can also act as a barrier preventing oil from spreading as it forms a natural containment system. *With high ice concentrations and a fringe of fast ice, spilled oil may be rapidly encapsulated within the ice leading to thicker oil films and making burning, skimming and dispersant application more effective (Dickins 2011).* Conversely, ice cover can protect the oil from weathering processes, such as evaporation, dispersion and emulsification, and reduce the mixing energy that is needed for effective chemical dispersion (Nuka Research 2010). Although the deployment of fire booms to support ISB operations may be hampered by the presence of ice, it may not be necessary as the ice itself may also act as a boom.

NRC (2014) recently released a comprehensive review of the current state of the science regarding oil spill response and environmental assessment in the Arctic region north of the Bering Strait. A committee of industrial and governmental organizations tasked the NRC to review research activities and recommend strategies to advance research and address information gaps, to identify opportunities and constraints for advancing oil spill research, to describe promising new concepts and technologies, and to assess the types of baseline information needed to monitor the impacts of an oil spill and to develop plans for recovery and restoration. The report reviews oil spill countermeasures applicable to the Arctic, including bioremediation, dispersants, ISB, chemical herders, mechanical containment and recovery, detection and tracking and trajectory monitoring.

The report identified seven research and development needs for improved decision support, including those listed below:

- Improving methods for ISB, dispersant application and use of chemical herders;
- Understanding limitations of mechanical recovery in both open water and ice;
- Investing in under-ice oil detection and response strategies;
- Integrating remote sensing and observational techniques for detecting and tracking ice and oil;
- Determining and verifying biodegradation rates for hydrocarbons in offshore environments;
- Evaluating the toxicity of dispersants and chemically-dispersed oil on key Arctic marine species; and
- Summarizing relevant ongoing and planned research worldwide to achieve synergy and avoid unnecessary duplication.

<u>Recommendation:</u> Initiation of multi-disciplinary research programs is needed to address specific questions related to cold and harsh environments, such as developing sufficient knowledge on the fate, behaviour and impacts of different oil types (in various weathering/treatment states) in snow or ice conditions. Special training of personnel and development of equipment for harsh environments or extreme weather are needed. Better understanding of the ecological effects in cold environments of various oil spill cleanup measures would be beneficial to spill response.

6.4.2.4 Available daylight and visibility

Daylight duration and intensity directly affect oil weathering processes. A series of field spill experiments in the Russian Arctic showed that photooxidation of spilled oil was a more significant process in the 24-hour summer daylight than in more temperate climates (Serova 1992; Ivanov et al. 2005). *However, shorter daylight and lower solar energy in fall and winter, as well as the associated low temperatures, can reduce evaporation and biodegradation activity by microorganisms.*

Visibility is an important safety factor during mechanical response operations in the field. Low horizontal visibility can impede or prevent on-water mechanical recovery by making it difficult to see and track oil slicks and by making vessel or air support operations unsafe. Low vertical visibility (cloud ceiling) limits aerial observation from rotary or fixed-wing aircraft. Darkness precludes some aspects of mechanical recovery and makes it infeasible to conduct ISB or aerial dispersant spraying (Nuka Research 2010; Jacobs et al. 2015). Darkness also increases risk of accidents and makes it more difficult to deal with emergencies, such as a man overboard (Genwest 2012; Salt et al. 2012).

6.4.2.5 Ecological considerations

Ecological concerns tend to become a major driving force for spill contingency planning and risk management (U.S. Coast Guard 2001; Aurand and Coelho 2006a,b; Webler and Lord 2010). *A drive is underway to improve understanding of the ecological effects of various oil spill cleanup measures to improve operational spill response guidelines. This need is highlighted by recent studies that provided evidence of negative ecological impacts associated with the application of chemical dispersants in the DWH oil spill (Goodbody-Gringley et al. 2013; Kleindienst et al. 2015) and spill mitigation techniques used in the August 10, 2000 Pine River, BC, Pembina pipeline rupture.* The environmental impact in the latter spill included mortality to fish, insects and some wildlife. Moreover, the District of Chetwynd, BC, had to discontinue use of the river, as well as many groundwater wells near the river, as a source of potable water. See more discussion in Chapters 4 and 8.

It will take time to fully understand and quantify the impacts of dispersants in order to create best practice guidelines. *Nevertheless, some mitigation measures that should be considered include: using mathematical tools to optimize the dose and operational processes or developing more potentially eco-friendly dispersants based on biosurfactants*[12] (Zhong and You 2011; Cai et al. 2014b).

Conversely, significant research and practical efforts have been made in bioremediation and a considerable amount of new knowledge has been developed. For example, indigenous microbial species and nutrient levels are crucial factors that are often taken into account during design and application of *in situ* bioremediation due to their impacts on oil fate and behaviours (JRP 2013). Consideration of ecosystem vulnerability is discussed further in Chapters 7 and 8.

6.4.3 Technical and economic factors

A number of technical factors need to be taken into account when arranging and deploying response equipment (**Table 6.2**). The specific operational conditions for each device are usually suggested by manufacturers and/or determined by responders through drilling and field application, although some special or uncommon environmental conditions (e.g., Arctic and extreme weather conditions) are not well addressed mainly due to lack of sufficient knowledge or tests. However, the feasibility of adopting a specific response technique depends on the proximity of equipment needed at the spill site and the time required to transport it there (Li et al. 2014b). In addition, responders' knowledge, experience and skills should also be considered when choosing the technique or equipment (U.S. Coast Guard 2001). Proper training of the response personnel can greatly increase response efficiency and reduce the possibility of having health or safety issues.

[12] *Biosurfactants are surface-active chemicals produced by organisms. They may have more selective activities than manufactured (synthetic) dispersants and are often biodegradable.*

Table 6.2 Examples of oil spill response equipment and their affecting factors *Sources: Transport Canada (2013) and EPPR (2015)*

Equipment	Affecting Factors
Command equipment	Weather and sea conditions
Dispersant systems	Wave, ice and oil types/weathering degree
Air-inflatable booms	Wave, ice and wind
Skimmers	Wave, ice and oil types/weathering degree
Temporary storage equipment	Capacity
ISB devices	Weather and sea conditions, wind
Vessels	Capacity and compatibility with onboard devices
Pumps and generators	Efficiency and power
Subsea well intervention equipment	Water pressure and sea conditions

For persistent spills, especially caused by heavy oils and diluted bitumen, the cleanup cost may include long-term soil/shoreline remediation and groundwater restoration expenses. The lack of adequate support funds may result in inappropriate or untimely response (Fingas 2011).

It is usually required by law that employers provide a safe and healthy workplace free of recognized hazards, as well as health and safety plans for response crew. Employers must also provide training and required protective equipment to enable the application of different response techniques (Michaels and Howard 2012). Therefore, the conditions at the spill site and the logistic capacity (e.g., in remote locations or under harsh weather conditions) can affect decisions about the most appropriate set of techniques/devices.

A commonly encountered question, and often the most difficult issue to address, is "how clean is clean?", which for the most part is a site-specific question dependent largely on the species at risk. It also invokes question about the intended end use of the spill site after cleanup: whether the site will be restored, remediated, rehabilitated or reclaimed (decision categories more commonly applied to terrestrial or shoreline sites than to open water)[13]. Michel and Benggio (1999) reported how to select the cleanup endpoints to meet the spill-specific requirements. Generally, cleanup endpoints need to be determined in the early stage of response according to general information and knowledge of the spill site and oil type/properties (Sergy and Owens 2007). Ongoing monitoring is necessary to allow for the modification of endpoints or techniques used, if required. Cleanup should proceed as long as it can accelerate the recovery of the spill site and should be terminated if it would slow down the recovery or have no value (Sergy and Owens 2008). *The judgement of clean conditions depends on the availability and quality of baseline data that are sometimes missing or incomplete (refer to Chapter 7).*

6.4.4 Other factors

Response structure and communication may also influence the response effectiveness given that response personnel, such as onsite response crew, offsite decision makers, technical consultants and other stakeholders, need to communicate and follow up with guidelines and regulatory structure for

[13] *Restoration returns the site to the condition pre-dating the spill; remediation removes or reduces (hazardous) wastes from the site to minimize current or future adverse effects; rehabilitation returns the site to a meet a previously determined use plan; and reclamation converts a disturbed site to former uses or to a different, but productive state (Powter 2002).*

preparedness and response (Transport Canada 2013). The selection of best available response technique should consider local communities and especially aboriginal groups in Canada in case response measures affect traditional use of lands and waters in either the short- or long-term (e.g., fishing, tourism, agriculture and aquaculture) (Colten et al. 2012). The extent to which each response technique is used should be the subject of consultation with local communities. In addition to aboriginal groups, consultations should include user groups (e.g., fishermen), scientists, community members, business, media and non-government organizations and should include the potential for local people to be involved in the cleanup activities (subject to safety and training requirements) (Hoffman and Jennings 2011).

6.5 Research Needs and Recommendations

6.5.1 High Priority Research Needs

6.5.1.1 Cold, harsh environments and controlled field studies

Current technologies, equipment and response personnel are needed to be fully capable of effectively responding to major inland or offshore spills in Northern Canada and Arctic regions. Special skills and equipment are needed both now and to be developed for inland or offshore oil spill responses under cold and harsh conditions. Related to this, most of what we know about oil spill response technologies has been developed through studies in the laboratory, mesocosm test systems and case studies (with limited controls and treatment replication). It is the consensus of the scientific community and the Panel that controlled field trials are needed to advance our spill response strategies, especially for subsurface blowouts, Arctic oil spills and freshwater shorelines.

6.5.1.2 Sediments

Three *in situ* remediation technologies developed over the last 20 years for the treatment of contaminated soils and groundwater have not been tried for remediating bottom sediments contaminated by sunken oil from spills. These remediation strategies are bioventing, air sparging and dissolved air flotation (DAF), all of which can be used to oxygenate anaerobic sediments to stimulate aerobic biodegradation of oil that settled to the bottom. One or all of these techniques may be successful for treating and overcoming the adverse effects of sunken oil in the anaerobic zone of a river or lake sediment. If such advances can be made, it would be a huge help in cleaning up benthic environments that have been contaminated by oil from accidental spills.

6.5.1.3 Dispersants

Although some have concluded that dispersants were successful during the DWH spill, it remains uncertain to what extent the oil was dispersed physically due to the high velocity of oil emerging from the well into the water or chemically in response to mixing with applied dispersant. This question needs to be answered by controlled experiments to reduce the uncertainty of this treatment strategy. Also, questions about the persistence of dispersed oil in both the deep sea and on its surface need to be addressed with controlled empirical experiments. This can be partially ascertained through the use of mesocosms and wave tanks. A further need is to determine if effective and non-toxic microbial biosurfactants, discussed in Chapter 3, can be developed as alternative sources of dispersants.

6.5.2 Medium Priority Research Needs

6.5.2.1 Bioremediation, including phytoremediation and wetlands

Substantial new research on hydrocarbon biodegradation has been conducted in the Gulf of Mexico following the DWH spill in 2010. There is an ongoing need to quantify the persistence of oil of all kinds during and after biodegradation and oil that has been chemically dispersed in the environment following a high impact spill to help stimulate innovations in bioremediation approaches. This is especially pertinent to cold temperature and anaerobic environments.

6.5.2.2 Herding Agents and In Situ Burning (ISB)

Recent advances in the study of herding agents (Buist et al. 2008; Buist et al. 2010 a, b; Buist et al. 2011; Lee et al. 2013) have been made that suggest they might be useful in corralling an oil slick for ISB. This may be especially true in Arctic environments. The utility of herding agents for this purpose needs to be quantified and properly tested to confirm this response approach. Such advances could measurably improve the use of ISB in Arctic oil spills. ISB is fast gaining a foothold as an effective response technology for treating a floating oil slick. More quantitative date are needed to determine the emissions that are released to the environment from ISB that may affect downstream ecosystems adversely, such as any incompletely combusted PAHs, toxic particulate matter, etc. It is also important to determine the safety and effectiveness of ISB. More peer-reviewed articles published in the literature are needed in support of ISB as a safe and effective oil response tool.

6.5.3 Low Priority Research Needs

6.5.3.1 Berm Relocation, surf washing, sediment reworking

Berm relocation, surf washing and sediment reworking have been used successfully to accelerate shoreline cleanup in the past. Concerns about this process have been primarily linked to the potential fate and ecological effects of the oil released during sediment relocation. The results of preliminary studies to date suggest that the oil in near-shore waters is diluted to concentrations within regulatory guidelines for ocean disposal for dredged sediments (Lee et al. 2003b). More research is needed to advance the status of this cleanup methodology in terms of fate and effects or released oil.

6.5.3.2 Sorbents, surface washing agents (SWA), solidifiers

Sorbents are widely used as a cleanup tool to combat oil spills in water and on shorelines. They have their limitations, however. The need exists to determine if any advances have been or can be made to improve sorption as an effective response tool, especially in the use of biodegradable natural organic sorbents, such as bagasse, that may possibly not need to be removed for biodegradation to take place. Significant amounts of debris and solid waste are generated when using sorbents for cleanup, so if natural sorbents can be developed that would sorb oil and then remain in place for ultimate cleanup by biodegradation, this would be a significant advancement in oil spill response. There is additional need to determine if any adverse effects on the ecosystem accrue from the use of SWA chemicals in spill response. In regard to solidifiers, recently, new research has been advanced in the understanding of the mechanism of solidifiers in removing oil floating on water. It is unknown if these materials can be made effective on larger oil spills.

Chapter 7: Prevention and Response Decision Making

Abstract

This chapter emphasizes on the past and current development and practices from two important aspects: preparedness and prevention before an oil spill and response assessment and decision-making after a spill. The review leads to the identification of challenges and future research needs.

Section 7.1 focuses on the research status and current practices in oil spill preparedness and prevention. 1) Prevention - Concerns are growing due to spill risks in the Arctic, some major ongoing or proposed pipeline projects, and the recent spills caused by pipeline raptures and roadside accidents. Continued efforts are identified in understanding the associated impacts and improving prevention strategies. 2) Oil spill monitoring - Advances in remote sensing and airborne imaging have created a promising set of cost-efficient and practical tools in oil spill response. The widely employed shoreline cleanup assessment team (SCAT) approach needs further improvement to integrate with response modeling and decision making. 3) Oil and Sample Analysis - Environmental forensics analysis and biological monitoring have played an ever increasing role in oil spill investigation and response decision making, although future needs are identified such as for the Arctic and dilbit. 4) Baseline data - Challenges and gaps exist, particularly in data acquisition, integrity, sharing/coordination, and uncertainties. 5) Sensitivity and Vulnerability - Incorporation of sensitivity and vulnerability analysis into risk assessment has been increasingly adopted, but quantitative research are limited on integration with modeling and decision making and for the Arctic. 6) Preparedness and contingency planning - The challenge is how to determine what level of preparedness is appropriate for each area of response. There lacks a comprehensive national framework in place for training and exercises that involves all key stakeholders, as well as sufficient capability to manage potential risks to the coast line.

Section 7.2 reviews the research and practice in oil spill early warning, technology selection, mathematical modeling, risk and impact assessment, cleanup process simulation, decision making and information technologies. 1) Early warning - Most existing response systems lack, or are weak in, effective early warning function/ability to identify, diagnose and react promptly to minimize the oil discharge into the environment at an early but critical stage of the emergency. It is challenging to incorporate the selected indicators into early warning and real-time monitoring systems and into spill response decision-making processes. 2) Technology screening and evaluation – Approaches, such as best available technology standards, have been used for response technology selection but difficulties exit in reflecting technical limitations and working conditions varied with environmental and human factors. New/updated guidelines are needed to govern application based on improved knowledge. 3) Spill modeling – Substantial modeling efforts have been made in the past decades but one of the key challenges is how to use/refine modeling tools to more effectively and dynamically couple with response process simulation/control, risk assessment and uncertainty analysis to support response decision-making. 4) Net Environmental Benefit Analysis (NEBA) – With recognition of the value of NEBA, future considerations are identified especially for response actions such as socioeconomic, political and legal factors, operational and logistical constraints, influence of human judgment, ecosystem services, and interactive, collateral and long-term cumulative impacts. The chronic oil leakage from routine operations and discharge of hydrocarbons in wastewater effluent (e.g., produced, ballast, bilge and quench water) have not been given good research attention. 5) Performance evaluation and post-event management - It is critical to assess response performance during and after a spill event to learn lessons for future improvement. Adaptive management especially with integration of risk analysis has been limited in the field. 6) Risk assessment - There is a lack of assessment of future oil spill risks due to increased traffic associated with the opening of routes in the Arctic waters. Concerns are emerging on human health risks including psychosocial impacts of a major spill. 7) Cleanup process simulation and control – Efforts are very limited in simulating, predicting and optimizing cleanup processes (e.g., *in situ* burning, skimming, and dispersion) individually and collectively and their effects on response effectiveness. 8) Response

decision support systems (DSS) – Inadequate decision support is one of the major challenges that limit the efficiency of current response practices. Due to limited attention and investment, existing DSS are rare and lack dynamic and interactive support from other modeling tools (risk analysis, spill modeling, NEBA, process simulation, etc.) and field validation. Uncertainty is a major hindrance to improving efficiency and confidence of decision making. These are especially true for the Arctic waters where the window of opportunity is significantly short. 9) Information technologies - Artificial intelligence and geomatics tools have received increased interest and further coupling with modeling and visualization techniques is desired to better address complexity and dynamics of spills and response operations.

The review of oil spill prevention and decision making is summarized in Section 7.3 and then leads to the high-priority research recommendations described in Section 7.4. First, it is needed to develop modeling methods to simulate and optimize individual and collective cleanup processes (e.g., booming, in situ burning, skimming, dispersion and bioremediation) for supporting response decision making. Secondly, it is urgent to develop and apply oil spill response decision support systems, which can dynamically and interactively integrate monitoring and early warning, spill modeling, vulnerability/risk analysis, response process simulation/control, system optimization, and visualization. Thirdly, research investment is in high demand on trial tests and field validation of new prevention and decision making methods to demonstrate feasibility, increase confidence for implementation, and improve response capabilities. Fourth, research is needed to better quantify modeling uncertainties, evaluate their propagation, and mitigate their impacts on spill response decision making. Fifth, further research and development are desired on environmental forensics, remote sensing and in-situ measurement, early warning and diagnosis, and biological monitoring to improve spill prevention and decision making. Finally, special research efforts should be given to some emerging concerns (e.g., diluted bitumen, aging/subsea pipelines, and railcars) and the harsh and Arctic environments for improving effectiveness and confidence of prevention and response strategies and decisions.

7.1 Prevention and Preparedness

All pre-spill strategies emphasize prevention as a key emergency management activity. Prevention focuses on reducing the likelihood of a spill, thus reducing risk. The basic principle of spill prevention is that risk reduction through prevention is much more effective than risk reduction through management of consequences. Prevention is based on understanding the science and technologies associated with oil operations and potential oil spills, and applying that understanding to the specific environment in which any activity is taking place, with the goal of managing risk throughout an operation (US GAO 2012). With a high level of knowledge, many potentially high-risk activities can be anticipated and the risk of spills may be reduced. For example, when an oil well or tanker is properly designed for the range of anticipated risks, established procedures are followed, equipment is properly inspected and maintained and training is provided. Thus, spill incidences may decline as suggested by ExxonMobil (2013) and the tanker spill statistics shown in Chapter 1. Furthermore, if accidents occur, the causes and outcomes can be analyzed providing new information to be used to update and improve prevention policies and measures.

7.1.1 Prevention

7.1.1.1 Tanker safety and spill prevention

Possessing the world's longest coastline with a total length of more than 243,000 km, Canada ships 80 million tonnes of oil per year off its east and west coasts (Transport Canada 2015e). *As more shipping and oil exploration are considered for the Arctic, tanker traffic in the Arctic region may increase significantly from the current low levels of less than 15 tankers per year. Therefore, tanker safety and spill prevention are among the top priorities.*

Safety provisions for oil tankers include navigation safety focused on preventing tanker accidents, including collisions, groundings and explosions. Navigation safety regulations are set by international and national agencies and include measures such as:

The *Canada Shipping Act* was established in 2001 respecting shipping and navigation and to amend the *Shipping Conferences Exemption Act, 1987* and other Acts.

- Speed regulations;
- Passage plans that respect safe navigation and the environment;
- Mandatory pilotage zones;
- Appropriate navigation technology; and
- Reporting requirements regarding vessel routing measures (e.g. traffic separation, two-way routes, recommended tracks, precautionary areas, and areas to be avoided) (Transport Canada 2014).

In Canada, Northern Vessel Traffic Service Zones are established where ships carrying over 500 tonnes must check in with officers for inspections of safety and navigation equipment and for examination of potential pollutants. Compulsory pilotage and tug escort services for difficult waterways are provided by the four Pilotage Authorities in Canada (WSP 2014). Moreover, joint industry-government guidelines for the control of oil tankers and bulk chemical carriers in ice control zones of Eastern Canada were established in 2012 (Transport Canada 2015b). These guidelines address the special risks of ice damage in certain waters off the east coast during winter and spring and include provisions, such as: having an 'ice advisor' on board when transiting an active Ice Control Zone, travelling at moderate speeds commensurate with visibility and ice conditions, being equipped with searchlights for night time navigation, and obtaining current ice information and a recommended route to follow.

Since 2001, Canadian regulations under the *Canada Shipping Act* have required double hulls for oil tankers built after 1993. The Canadian phase-out date for single-hulled large crude oil tankers was 2010. The phase-in period for double-hulled smaller oil tankers was up to the end of 2014. The International Maritime Organization phase-in period for double-hulled tankers worldwide will be fully implemented in 2015.

The Northern Canada Vessel Traffic Services Zone is established under the *Canada Shipping Act, 2001*. It consists of: a) the shipping safety control zones prescribed by the *Shipping Safety Control Zones Order*; b) the waters of Ungava Bay, Hudson Bay and Kugmallit Bay that are not in a shipping safety control zone; c) the waters of James Bay; d) the waters of the Koksoak River from Ungava Bay to Kuujjuaq; e) the waters of Feuilles Bay from Ungava Bay to Tasiujaq; f) the waters of Chesterfield Inlet that are not within a shipping safety control zone, and the waters of Baker Lake; and g) the waters of the Moose River from James Bay to Moosonee (Government of Canada 2010).

The results of improved tanker safety are reflected in data on the frequency of oil spills due to tanker accidents. Globally, even with increased tanker traffic, there has been a consistent downward trend in large oil spills (**Figures 7.1**). In and around US waters, the average annual oil spillage (spills greater than 0.14 tonnes or one barrel) by oil tankers and tank barges has decreased by 91% and 67%, respectively, in the decade 1998-2007 compared to previous decades (**Figure 7.2**). In Canada, the most significant oil spill in eastern coastal waters occurred in 1970, when the tanker *Arrow* spilled over 10,000 tonnes of Bunker C fuel oil off Chedabucto Bay, NS (also refer to Chapters 1 and 8). Since then, no large spills greater than 700 tonnes have occurred in Canadian coastal waters. The most significant spill in the last 20 years off the British Columbia coast was in 2006 when the ferry the *Queen of the North* sank with 240 tonnes of oil on board, including 225,000 litres of diesel fuel, 15,000 litres of light oil, 3,200 litres of hydraulic fluid and 3,200 litres of stern tube oil (BC Ministry of Environment 2015). The annual

Canadian ship-source spill frequency for crude oil from 2003-2012, based upon the data from the Canadian Coast Guard Marine Pollution Incident Reporting System, was close to zero for all spill sizes (WSP 2014a,b). The recent WSP reports (2014a,b) quantified the risk of marine spills in Canadian waters and gave an optimistic estimate of future ship-source spills as shown in **Table 7.1**.

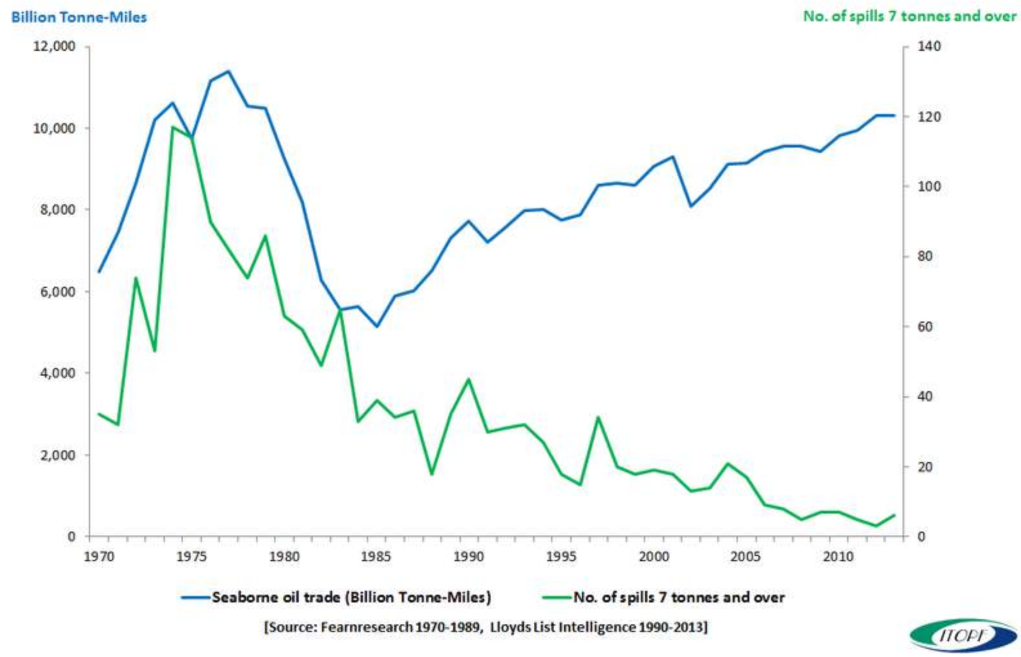

Figure 7.1 *Seaborne oil trade and number of tanker spills seven tonnes and over, 1970 to 2013 (Crude and Oil Product; vessels of 60,000 DWT and above; barges excluded. Image from ITOPF (2015))*

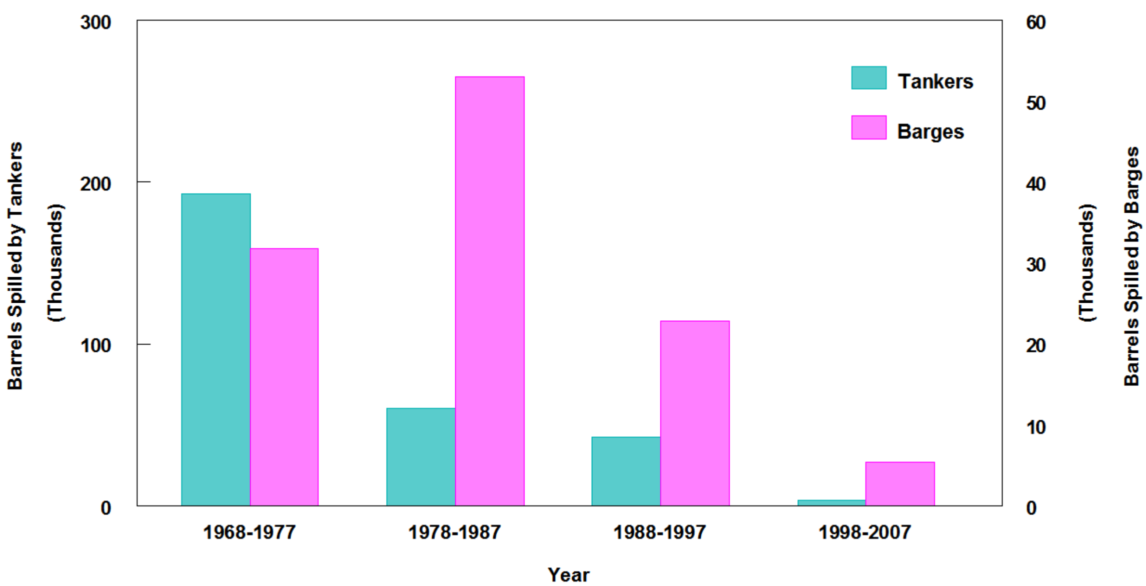

Figure 7.2 *Average annual large oil spills by oil tankers and barges in US Data from API (2009)*

Table 7.1 *Future Ship-source spills in Canada*[a]

Volume (m^3)	10-100	100-,1000	1,000-10,000	>10,000
Annual Frequency	0.022	0.014	0.019	0.004
Return Period (yrs)	46.4	69.2	51.6	242.3

[a]Data from WSP (2014a,b)

7.1.1.2 Pipeline safety and spill prevention

The major existing pipelines carrying crude oil in Canada are (**Figure 7.3**): the Trans Mountain from the Edmonton area to Vancouver and Anacortes, WA; the Keystone pipeline from the Edmonton area through southern Saskatchewan and Manitoba; the Enbridge pipeline from the Edmonton area through southern Saskatchewan and Manitoba before entering North Dakota and then to a network delivering oil to destinations, such as Chicago, Sarnia (via Michigan) and the Gulf of Mexico; the Express pipeline from Hardisty, AB, through southeastern Alberta to Montana and then east/southeast where it joins the network delivering oil to the Gulf of Mexico; and the Enbridge Line 9 running between Sarnia and Montreal. Other feeder pipelines include the Western (Pembina) between Kamloops and Edmonton, the Rainbow pipeline from Norman Wells and pipelines from the Fort McMurray, Cold Lake and Lloydminster oil sands and heavy oil producing areas. With the exception of Enbridge Line 9, all crude oil pipelines in Canada are in the four western provinces.

Due to the strong growth of oil and natural gas production in Canada and the US, pipeline capacity is expected to expand to provide access to new markets. A number of pipeline projects are being proposed to connect the growing supply with replacement markets in eastern Canada and beyond to growing global markets (CAPP 2015*). Although the statistics indicated no significant increase of numbers and volumes of pipeline incidents in Canada since 2008 (**Figure 7.4**), concerns are growing due to major ongoing or proposed projects and the recent frequent spills in North America such as Refugio Oil Spill in California on May 19, 2015 (Panzar et al. 2015), Yellowstone River oil spill in Montana on January 21, 2015 (Yan 2015), Mid-Valley Pipeline Spill in Louisiana on October 13, 2014 (Maykuth 2014), and Hiland Crude Pipeline Spills in North Dakota on March 21, 2014 (MacPherson 2014)*. The National Energy Board (NEB), which regulates pipelines in Canada, recently introduced new pipeline performance measures (NEB 2014b). These measures include training and competency assurance, 'integrity management' (pipeline conditions, equipment inspection, assessment of pipeline hazards, shutdowns for hazard control etc.), integrity inspections, environmental inspections, contractor awareness and damage prevention (e.g., unauthorized activities by other industries or municipalities). The conditions attached to the recent NEB approval of the reversal of Northgate Line 9B reflect these measures (e.g., analysis of threats to integrity of the pipeline, a remaining life analysis, repairs to all features in pipeline sections identified by engineering assessments and a hydrostatic testing program) (NEB 2014a).

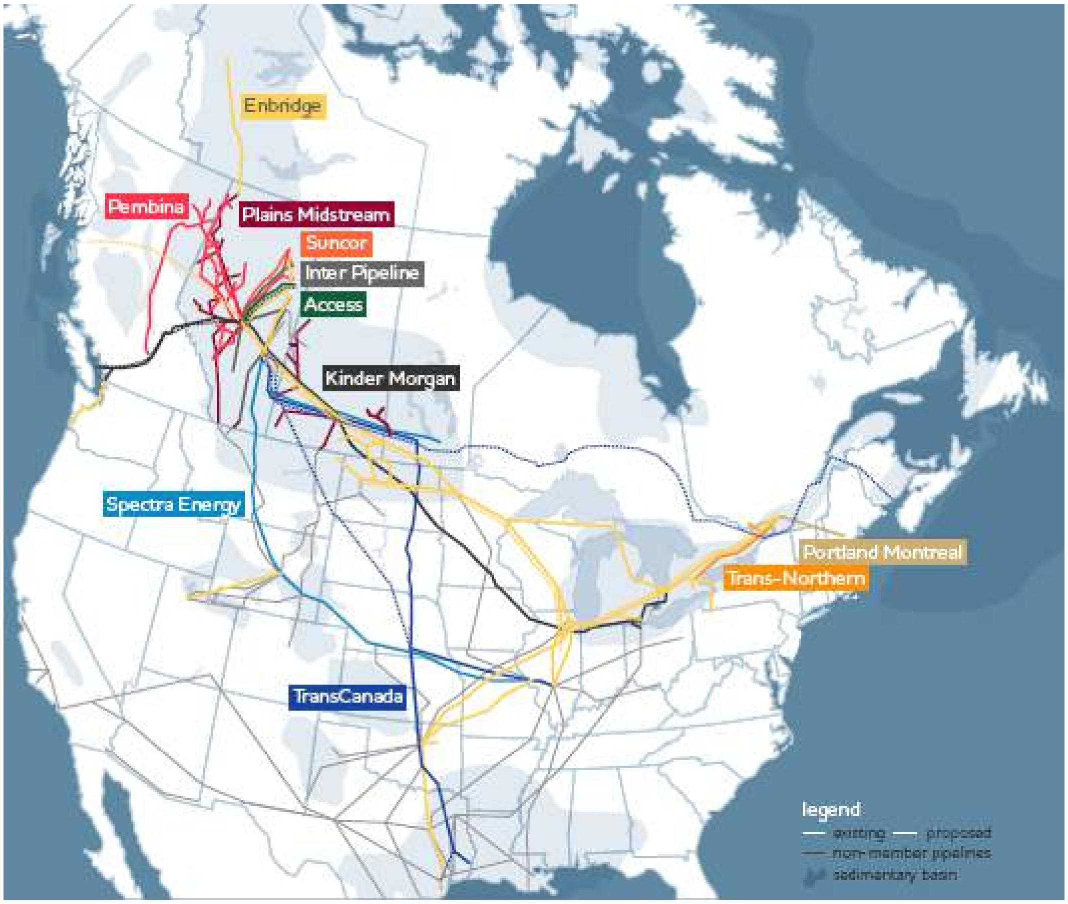

Figure 7.3 *Canadian Energy Pipeline Association (CEPA) liquids pipelines map. Image used with permission from CEPA.*

The NEB requires its regulated companies to promote a positive safety culture and expects safety culture programs to apply not only to worker health and safety but to process safety (NEB 2015a). Process safety focuses on preventing catastrophic incidents associated with the use of chemicals and petroleum products. Safety culture is a vital component of spill prevention and includes the empowerment of employees to take immediate action (e.g., closing of valves) without waiting for authorization up a chain-of-command.

In 2012, Enbridge filed an application with the NEB to reverse the flow on the segment of Line 9 between North Westover, ON, and Montreal (Line 9B) and that the entire Line 9 capacity from Sarnia, ON, to Montreal be increased with a revision to regulations to allow transportation of heavy crude (NEB 2015b). The NEB had previously approved flow reversal between Sarnia and North Westover in July of 2012. Line 9 originally flowed eastward after its construction in 1975. Flow was reversed in 1998 as oil from areas such as West Africa and the Middle East became more affordable. However, western Canadian crude is now priced lower than foreign oil, leading Enbridge to propose to reverse the flow of Line 9 once again to provide oil to two refineries in Quebec, which represent 20% of Canadian capacity. The NEB approved the reversal on March 6, 2014, subject to 30 conditions which are currently being addressed by Enbridge (NEB 2014a). However, concerns regarding the potential risks and regulatory requirements (e.g., environmental review) associated with using aged facilities have been raised.

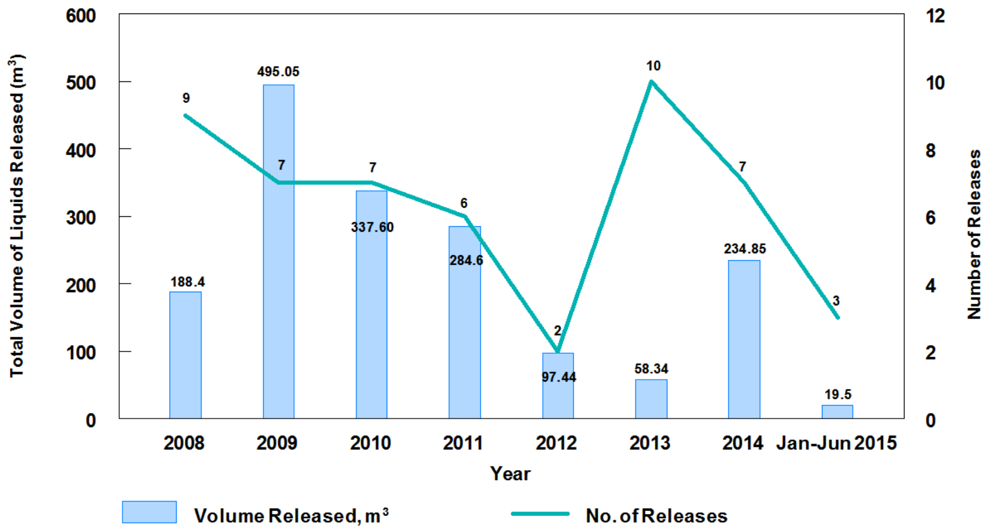

Figure 7.4 *Total volumes of liquids released vs. number of liquid releases in Canada between 2008 to 2015. Image adapted from NEB (2015c)*

Under the *NEB Onshore Pipeline Regulations* (OPR), companies must immediately notify the NEB of any incident that relates to the construction, operation or abandonment of a pipeline. *Generally, spills of crude oil from pipelines in Canada have been infrequent, small (< 1 to 30 m^3) and rarely enter water bodies, although there are variations in volumes and frequencies among provinces and companies (AER 2015). However, some larger incidents have revealed the need for an increased focus on prevention.* Regulatory examination of larger releases in the range of 1,000-5,000 m^3 in Alberta since 2011 indicated issues, such as: failings in the identification of risks related to corrosion and corrosion repair; and inadequate leak detection alarm and response processes and lack of training and supervisory oversight (ERCB 2013). For example, a large spill caused by a ruptured year-old pipeline was observed on July 15, 2015, at Nexen Energy's Long Lake oil sands site in Alberta. It released about five million litres of bitumen, sand and produced water and affected an area of about 16,000 m^2 along the pipeline's route (The Canadian Press 2015a). During the writing of this report, Alberta's energy regulator issued an order on August 21 to immediately suspend the company’s operations of 95 pipelines in northeastern Alberta due to non-compliance with the *Pipeline Act* surrounding pipeline maintenance and monitoring in its Long Lake oil sands project (The Canadian Press 2015b).

These recent events further raised the attention and importance of how to prevent and monitor spill incidents in transporting oil by pipelines. Research investment is inadequate to support the development of optimal response strategies and enhancement of response capacities in preventing and remedying spills from aging pipelines for crude oil transport.

Note that Canada-based Enbridge Partners will stop using its No. 5 pipeline under the Straits of Mackinac to transport heavy crude oil under an agreement reached September 3, 2015, with the state of Michigan (Dalbey 2015). This binding legal agreement places a permanent ban on use of the aging pipeline to transport heavy crude and formally implements the first recommendation of the Michigan Petroleum Pipeline Task Force Report released in July to “prevent the transportation of heavy crude oil through the Straits Pipelines” (Department of Attorney General 2015). The Report gave the recommendation based on the Coast Guard’s public acknowledgement that they lack capacity to effectively respond to spills of heavy crude oil in the Great Lakes (Matheny 2014). In addition, Governor Rick Snyder of the State of Michigan issued an executive order creating the Michigan Pipeline Safety Advisory Board on the same day of signing the agreement.

Information regarding the nature and extent of effects of both smaller or larger pipeline incidents, and the corresponding response actions, is presented in Chapter 6 and later in this chapter.

7.1.1.3 Oil transport by rail: safety and spill prevention

On August 3, 2005, 43 cars derailed just west of Edmonton spilling 700,000 litres of Bunker C fuel oil and 70,000 litres of a wood preservative into the waters of Wabamun Lake, a recreational mecca for many Edmontonians and home to the Paul Band First Nation (Benoit 2007). As admitted by Alberta Premier Ralph Klein at that time, his government was unprepared to deal with the oil spill into Lake Wabamun caused by a train derailment (CBC 2005). A Transportation Safety Board report into the derailment found that CN did have an emergency plan to respond to the spill, but pointed out that it would have been more efficient had there been closer coordination with other agencies (Benoit 2007). The Government of Alberta formed a Commission to investigate the incident and the most significant among the Commission's findings was the absence of a regulatory framework to govern emergency response to major spills of environmentally hazardous goods that fall outside the purview of the *Transportation of Dangerous Goods Act* (Benoit 2007).

Authorities have learned from recent spill events and are gradually improving response management. For example, in response to the derailment and explosion at Lac Mégantic, QC in July 2013, Transport Canada, which regulates the transport of crude oil by rail, took immediate action by establishing a two-person minimum for locomotive crews on trains carrying dangerous goods, and by imposing stricter rules for securing unattended trains (Transport Canada 2015a). Transport Canada has begun a process of enhanced inspections, documentation and follow-up for rail safety, including more frequent inspections at sites where petroleum products are transferred from one mode of transport to another (e.g., from truck to rail). The department has also proposed or introduced fines, mandatory certificates and new safety and transportation of dangerous good regulations and reporting requirements on railways and shippers. Through *Protective Direction 32*, railway operators must provide municipalities and first responders with information on the dangerous goods being transported through their communities. The department has also updated regulations to bring cross-border consistency to the way dangerous goods are identified, providing emergency personnel with a clear understanding of the risks posed by goods being transported.

> After the Lac Mégantic spill, further measures required by Transport Canada have included (Transport Canada 2015a):
> - Removal of the least crash-resistant DOT-111 tank cars from dangerous goods service;
> - New safety standards for DOT-111 tank cars, and requiring those that do not meet the new standards to be phased out by May 1, 2017;
> - Slower trains transporting dangerous goods and introducing other key operating procedures
> - Emergency response plans for even a single tank car carrying crude oil and refined products; and
> - Setting up a task force that meets regularly and brings municipalities, first responders, railways and shippers together to strengthen emergency response capacity across the county.

Railway companies are now expected to have safety management systems, which include safety goals, performance targets, risk assessments, responsibilities and authorities, rules and procedures, and monitoring and evaluation processes. The systems can help companies better comply with federal legislation. Transport Canada monitors compliance through formal safety management system audits and detailed inspections and takes enforcement action in case non-compliance is identified.

According to the Transportation Safety Board of Canada, there were 174 railroad accidents involving dangerous goods in 2014, up from 145 in 2013 and a previous five year average of 131 (TSB 2015). Only one accident in 2014 involved the release of petroleum crude oil. The number and type of rail incidents in **Figure 7.5** illustrates the range of causes, any of which could apply to crude.

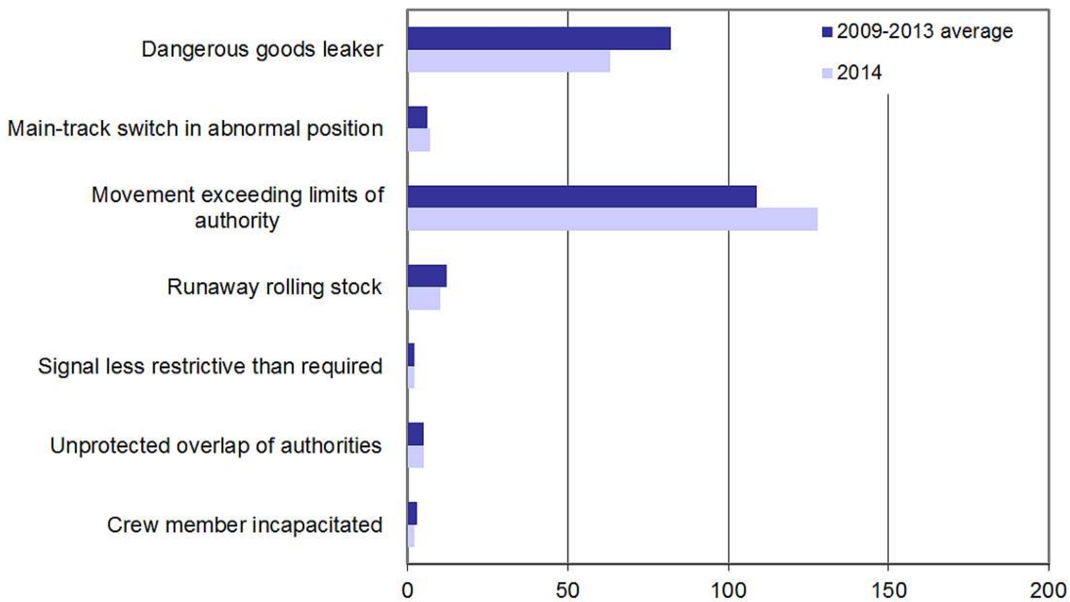

Figure 7.5 *Number of rail incidents by type in 2014. Image from TSB (2015).*

New prevention measures target these causes, as evidenced by Transport Canada's intention to expand mandatory requirements under the *Railway Safety Management System Regulations*. The proposed changes (Transport Canada 2015a) include processes to:

- Encourage employees to report accidents to senior management;
- Analyze data and trends to identify safety concerns;
- Manage organization knowledge so employees can perform their duties more safely;
- Improve work scheduling to prevent employee fatigue; and
- Create annual safety targets and develop tools to achieve them.

Recommendation: Continued efforts are needed to understand the associated impacts of, and improve response management for, spills caused by railroad accidents.

7.1.1.4 Oil transport by truck: safety and spill prevention

The Motor Carrier Division of Transport Canada is primarily responsible for facilitating the reduction of accidents involving large commercial trucks in Canada. Provincial and territorial regulations govern the operation of the commercial truck industry except for the rules and regulations set by the Division in support of the safe operation of extra-provincial motor carriers that carry goods across a provincial or international boundary (Transport Canada 2015c). However, provinces and territories are allowed to regulate extra-provincial truck carriers under the *Motor Vehicle Transport Act* on behalf of the federal government. In addition, the federal *Transport of Dangerous Goods Act* applies to crude transport by truck. However, the provinces are responsible for inspecting vehicles under the Act. Fifteen standards for motor carrier safety are included in the National Safety Code and are supported by provincial regulations. A Safety Management Systems approach is emphasized by the Motor Carrier Division, which is the same approach used to oversee other modes of transport (marine, rail) by Transport Canada. This approach expects the industry to develop a safety culture aimed at identifying and managing risks.

As outlined in Chapter 1, *while the total volume of crude oil transported by truck in Canada is very small relative to transport by pipeline, the number of incidents per volume of crude transported is an order of magnitude greater*. Experience with truck-related oil spills indicates that the largest threats are: contamination of nearby water bodies; effects on drinking water supply or water use for industrial or agricultural purposes; fire and explosion and economic impacts caused by property damage; disruption to traffic due to road closures; and disturbance to habitats (Christopherson and Dave 2014). *Therefore, how to decrease the number and severity of crude oil spills involving truck transport is an important issue. Suggested prevention measures could include: improved monitoring and maintenance of key infrastructure at delivery points and fuel loading terminals; identification of high-risk sections of common routes (dense population or highly sensitive environmental areas); and improved truck design and data collection/accessibility for risk management.*

7.1.2 Oil spill monitoring

7.1.2.1 Onsite monitoring

Canada conducts regular aerial surveillance of marine shipping under the National Aerial Surveillance Program. Transport Canada reported that in 2011-2012, surveillance crews observed more than 12,000 vessels and detected 135 pollution occurrences nationally, with an estimated total volume of 1,014 litres of oil (Transport Canada 2015e). There is also an obligation for owners of vessels and operators of oil handling facilities to report marine spills to the Canadian Coast Guard.

During and after spill cleanup operations, it is essential to continuously monitor the sea or site state and weather conditions, as well as the movement and behaviour of the oil. In marine environments, oil spills can be tracked using specially-designed buoys to follow oil movement. Fingas (2012) reviewed oil spill tracking buoys and devices from 1970 until the present and pointed out that the buoys were being beneficially used during exercises and on occasion to simulate oil spills to improve preparedness. Visual monitoring can be undertaken from vehicles, vessels and/or, ideally, from spotter planes or even unmanned aerial vehicles, which can also ensure that the heaviest concentrations of oil are being targeted (Ferraro et al. 2009; Pisano 2011). Lieske et al. (2011) performed a comparative and retrospective analysis of the spatial pattern of oil pollution for the Canadian east coast based on the data obtained from visually unaided aerial surveillance, side-looking airborne radar-assisted aerial surveillance, as well as remote sensing images. The results provided insights into Environment Canada's surveillance programs and offered a useful technique to combine information from different surveillance regimes. Observers should look out for a visible reduction in oil coverage, as well as a change in the appearance of the oil, often seen as a coffee-coloured plume within the water column in good viewing conditions (Chapman et al. 2007; Tan 2011). Submerged flow-through systems using ultraviolet fluorescence spectrometry (UVFS) have also been used to monitor oil concentrations and plumes in water to indicate the effectiveness of dispersion (Lambert 2003; Chatterjee 2015). Although UVFS cannot measure the exact amount of oil, it is able to qualitatively determine whether or not dispersed oil in the water column has increased significantly and therefore whether or not the application of chemical dispersants has been successful (Chapman et al. 2007). The laser fluoresensor is one of the most useful and reliable instruments to detect oil on various backgrounds, including water, soil, weeds, ice and snow. It is the only reliable sensor to date to detect oil in the presence of ice or snow (Brown and Fingas 2003). *However, detection and monitoring of oil spills are always challenging for a number of reasons, such as the substantial land and sea area to cover, low probability and high variability of discharge detection, and limited efficiency, high uncertainty and logistic difficulties due to harsh conditions (e.g., dense vegetation, snow and ice coverage, low visibility, rough waves and darkness).*

In recent years, autonomous underwater vehicles (AUVs) and remotely operated vehicle (ROVs) have been proven especially productive and efficient in spill monitoring. They have emerged as the platform of choice for many surveying tasks, such as bathymetric, near-bottom geophysical and optical surveys. Hundreds of shallow water AUVs (e.g., REMUS) and ROVs (Allen et al. 1997) are operated around the world. Fewer deepwater AUVs and ROVs exist; however, these larger, more expensive systems are routinely used for industrial, military and scientific applications. Notable examples of these systems include the Hugin (Marthiniussen et al. 2004) and Autosub (Griffiths et al. 1999). After the Deepwater

Horizon (DWH) oil spill, a new 4,500 m depth-rated AUV sentry was developed and applied in two separate cruises (WHOI 2010).

7.1.2.2 Remote sensing

Remote sensing technologies have been tested and applied in oil spill responses for decades with mixed results (Goodman 1994; Fingas 2011; Salt et al. 2012). Their incorporation into oil spill response requires confidence in the robustness and reliability of the information, based on capturing oil spatial patterns consistent with oil spill response processes. Beyond technical challenges, considerations of cost-effectiveness and difficulties in conducting field trials have limited actual field applications to data processing (Leifer et al. 2011).

Recent technological advances in remote sensing, multi-spectral airborne imaging and echo-sonic tools, along with increased efficiency and lower cost, have created a new set of potentially practical tools for application in oil spill monitoring, preparedness and responses. For example, Ying et al. (2011) discussed recent research and progress in monitoring sea surfaces covered by oil using microwave remote sensing technology and also proposed a simple and effective filtering technique based on synthetic aperture radar (SAR) for sea oil slick observation. Leifer et al. (2011) reported a new spectral library approach that uses near infrared imaging spectroscopy data from the airborne visual/infrared imaging spectrometer (AVIRIS) instrument on the NASA ER-2 stratospheric airplane. Extrapolation to the total slick used MODIS (moderate resolution imaging spectroradiometer satellite visual-spectrum) broadband data, which observes sunlight reflection from surface slicks. Ermakov (2013) summarized the results of field studies of the effect of damping of short wind waves due to surface films conducted using radar and optical methods. The results showed that film slicks can be characterized by their specific "spectral contrast sign" and can be discriminated from some look-alikes like wind depression areas. Some radar-based oil spill detection systems (e.g., Rutter's system) have been proven to be effective through extensive field tests and adopted on various platforms, such as floating production storage and offloading vessels, offshore workboats, patrol vessels and specialty cleanup vessels. Etkin et al. (2013) foretold that with more field testing and reductions in costs, some of these technologies will eventually become more 'tools in the toolbox' for spill response.

<u>Recommendation:</u> Develop improved *in situ* and remote oil leak detection systems to detect spills soon after an incident and post spill monitoring, including autonomous, remotely operated detection devices (e.g., AUVs and ROVs).

7.1.2.3 Shoreline monitoring

When shoreline impact occurs or is likely to occur after a spill, shoreline monitoring and assessment are critical components of the response program, and they provide essential information for setting goals and priorities and making decisions for an effective shoreline response (IPIECA 2015). The Shoreline Cleanup Assessment Team (SCAT) approach, which originated from the *Exxon Valdez* oil spill (EVOS) response in 1989, has been widely used in many spills and continuously developed to meet specific spill conditions (Owens and Sergy 2004; Owens and Reimer, 2013). A SCAT survey uses a set of specific and standard terminologies to define and assess shoreline oiling conditions, although the process itself is diversified and the assessment activities can be designed to match the individual spill conditions (Owens and Sergy 2000; IPEICA 2014). The surveys may be applied to spills in both marine coastal and freshwater environments and have become integral components of spill response in Canada, the US and several other countries. *An effective SCAT or shoreline assessment program should be integrated into a shoreline response program and provide critical information to support the contingency planning, response decision-making and implementation/closure processes.*

The scope and scale of a SCAT survey is governed by a range of parameters that include: the coastal character and configuration, the type and amount of spilled oil; the size of the affected area; and the needs of the response organization. The basic principles that govern a SCAT survey are (Owens and Sergy 2000):

- A systematic assessment of all shorelines in the affected area;
- A division of the coast into geographic units or 'segments';
- A set of standard terms and definitions for documentation; and
- A team of interagency personnel to represent the various interests of the responsible party, land ownership, land use, land management or governmental responsibility.

The first complete manual for SCAT surveys was developed by Environment Canada (1992), followed by production of a more simplified Field Guide (Owens and Sergy 1994). Other agencies have adopted the approach and produced similar field forms and manuals (e.g., US National Oceanographic and Atmospheric Administration and U.K. Maritime and Coastguard Agency) (US NOAA 1994, 2013; MCA 2007). Environment Canada has developed generic second generation SCAT protocols to standardize the documentation and description of oiled shorelines. The Second Edition of the SCAT manual was developed by Environment Canada in 2000 particularly with updated standard field forms, which are directly compatible in format and content with the ones used by the NOAA. In 2004, the Arctic Edition of SCAT Manual was published by Environment Canada. It is based on the Second Edition but provides new material on the unique shoreline types, characters of the various forms of snow and shore-zone or nearshore ice, cold climatic conditions, and behaviour of oil in arctic regions, as well as on the SCAT activities in these environments (Owens and Sergy 2004).

<u>Recommendation:</u> Future improvements may focus on how to more effectively and dynamically integrate SCAT into the entire response system covering offshore to shoreline operations, as well as the survey data, into the response modeling and decision-making processes.

7.1.3 Oil and sample analysis

7.1.3.1 Physical analysis

Efficient determination of oil properties can enable effective oil spill response and countermeasures. Some frequently used analytical methods for major oil properties (viscosity, density, specific gravity, flash point, pour point and interfacial tension) are summarized in Appendix B.

7.1.3.2 Chemical analysis

Crude oil generally contains hydrocarbons (e.g., paraffins, aromatics, naphthenes and asphaltenes) and heterocompounds (e.g., sulfur, oxygen, nitrogen and metal ions) (Yang 2013a). To be able to unambiguously characterize, identify, categorize and quantify all sources of hydrocarbons entering the environment is important and necessary for oil spill response. Analytical techniques have been applied extensively in the laboratory to measure and quantify oil constituents belonging to four primary categories: saturated hydrocarbons, aromatics, resins and asphaltenes (Wang et al. 2003) (In-depth discussion can be found in Chapter 2). A summary of the frequently used instrumental techniques is given in Appendix A.

Advances in environmental forensics analysis have played an ever increasing role in oil spill analysis (Wang and Stout 2006). Biological markers or biomarkers (see definition in Chapters 2 and 4) are among the most important hydrocarbon compounds in petroleum for chemical fingerprinting (Wang et al. 2002, 2003; Yim 2011; Radović et al. 2014). Biomarkers have also been proven useful in identification of petroleum-derived contaminants in marine and aquatic environments. Consequently, biomarker fingerprinting techniques have been gradually recognized and increasingly used in characterization, correlation, differentiation and source identification in oil spill investigations (Wang et al. 2012). Biomarkers can be detected in low quantities (µg/L and sub-µg/L levels) in the presence of a wide variety of other types of petroleum hydrocarbons by the use of the gas chromatography/mass spectrometry (GC/MS). For example, Wang et al. (2011) presented integrated forensic oil fingerprinting and data interpretation techniques to characterize the chemical compositions and determine the source of the 2009 Sarnia, ON, oil spill incident. Other examples in the literature confirm the advantages of forensic fingerprinting using these biomarkers (Yim et al. 2012; Yang et al. 2013a, b; Wang et al. 2013, 2014). Recently, efforts were also reported on identifying suitable biomarkers and applying them for dispersed oil fingerprinting (Song et al. 2014).

<u>Recommendation: Develop and refine</u> environmental forensics technologies for analysis of oil components of interest. Establish standard fingerprinting protocols including new biomarkers to track dispersed oil, diluted bitumens and other petroleum hydrocarbons of interest. Develop protocols to monitor oil in contaminated sediments (on river or sea beds), particularly in the presence of ice and harsh marine conditions.

7.1.3.3 Biological monitoring

Biological monitoring (or biomonitoring) is the use of a biological community to provide information on the quality or 'health' of an ecosystem (NYSDEC 2015). Basic parameters for biological monitoring include (Reilly and York 2001):

- Mortality of large animals and plants, which are easier to monitor (identification of mortality among smaller organisms and plants need special input);
- Sublethal effects, such as bioaccumulation, gene activation, CYP1A induction, behavioural changes or histopathological effects (e.g., presence of disease or injury Chapter 4), which need specialist input;
- Changes in community structure, such as changes in species diversity; and
- Tainting after fish ingest the oil and incorporated into its fatty tissues.

Existing response technologies cause various levels of impacts on the environments. For example, recently interest has increased in the impact of dispersants and dispersed oil particularly focusing on the DWH spill. Judson et al. (2010) discussed the potential for toxicity of the dispersants used in that spill and potential alternatives at the spill site, especially given the limited toxicity testing information that is available. Using a series of *in vitro* high-throughput assays, eight commercial dispersants were analyzed. White et al. (2012) examined deepwater coral communities three to four months after the well was capped to assess the potential impact on offshore ecosystems. The results showed the presence of recently damaged and deceased corals beneath the path of a previously documented plume emanating from the Macondo well providing evidence of impact on the deepwater ecosystems. Paul et al. (2013) presented data on general toxicity and mutagenicity of upper water column waters and, to a lesser degree, sediment pore water of the northeastern Gulf of Mexico and west Florida shelf at the time of the spill in 2010 and thereafter. See more discussions in Chapter 4.

Biological monitoring is a proven approach to help collect baseline data before a spill event and evaluate the effectiveness and impact of response and cleanup actions after the event. It can also provide assistance to development of more eco-friendly and cost-effective response technologies.

<u>Recommendation:</u> More research on monitoring parameters/protocols and technologies, as well as result interpretation and integration with decision-making processes, are desired.

7.1.4 Baseline data

Many environmental and ecological databases and archives hosted by governments have been used in oil spill responses in Canada. Continued efforts have been made to establish and maintain the sources of baseline information at the federal, provincial and local levels. Some examples are as follows:

- National and interagency programs, such as:
  - The GIS Services Group of Canadian Coast Guard maintains databases containing geographic locations of features (e.g., light stations, aids to navigation, pollution response sites) and events (e.g., search and rescue incidents). The databases are incorporated into a GIS (Dollhopf et al. 2014); and
  - The Canadian Aquatic Biomonitoring Network (CABIN) maintained by Environment Canada to support the standardized collection of biological monitoring information and assess the health of freshwater ecosystems in Canada (Environment Canada 2015a, b).
- Provincial government monitoring programs, such as:
  - GeoBC , which provides a one-stop shop for spatial information for the province, including base maps, specific datasets such as conservation status information for 7,400 plants and animals and fisheries sensitive watersheds, and digital imagery;
  - The BC Burrard Inlet Environmental Action Program, as an interagency partnership (now disbanded unfortunately), compiled baseline data on habitat types, intertidal vegetation, number of bird nests, outfalls, docks, impervious surfaces and numerous other coastal conditions in the inlet (Chang et al. 2014). These could be instrumental in ranking environmentally sensitive areas to inform a hierarchy of response efforts in the event of an oil spill;
  - The Alberta Environmental Monitoring, Evaluation and Reporting Agency, a science-based, comprehensive, arm's-length organization responsible for coordinating province-wide environmental monitoring and evaluation with emphasis on the oil sands region; and
  - The Canada-Newfoundland and Labrador Offshore Petroleum Board (CNLOPB), which has continuously produced and compiled the environmental assessment reports conducted by authorized consulting company and made them open for access by the public (Lin et al. 2009; Payne et al. 2012).
- Local conservation authorities, such as the Grand River Conservation Authority in Ontario, which manages water and other natural resources on behalf of 39 municipalities and close to one million residents and operates a network of automatic gauges throughout the watershed to measure river and stream flows, weather conditions and water quality (GRCA 2015).
- Provincial compliance monitoring data for specific permitted facilities which can provide some relevant data near the spill site, such as basic water quality, biological monitoring data and/or facility information.
- Community-based monitoring programs, such as:
  - Streamkeepers training program, a comprehensive education and awareness program supported by Fisheries and Oceans Canada to protect and restore local aquatic habitats (Pacific Streamkeepers Federation 2003); and
  - The Atlantic Coastal Action Program, a unique community-based program initiated by Environment Canada to help Atlantic Canadians restore and sustain local watersheds and adjacent coastal areas (ACAP 2008).

However, challenges and gaps still exist in the baseline data, particularly in acquisition, integrity, sharing and uncertainties. For example, the British Columbia baseline data could not address species' population levels within the Burrard Inlet, which would be helpful for determining species most at risk and essential for quantifying impacts of a spill event. Stable legislative and financial mechanisms are lacking in driving long-term data acquisition and management at both federal and provincial levels.

Access to baseline data and data sharing are still limited among government, industry and academia, which constrains oil spill response research and practices (Lieske et al. 2011; Marty and Potter 2014). *Uncertainties unavoidably exist and come from a variety of sources during data acquisition, processing and manipulation, leading to the need for quantifying the impacts and developing mitigation methods.*

Comprehensive baseline assessments of natural resources and socioeconomic entities are important for informing environmental and economic impact studies, supporting contingency planning and response decision-making, and facilitating accurate monitoring after a spill has occurred.

In addition, most of those existing sources of baseline data are not well coordinated, accessibility of the data varies and geographic coverage can be spotty, particularly for remote areas. Besides further extending the baseline information, there is a strong need for a thorough examination of available data applicable to establishing a defensible baseline dataset for high-risk aquatic systems adjacent to crude oil shipment routes, whether by marine tanker, pipeline, rail or road. One possible place to start might be a national directory of monitoring information with links to databases, GIS maps and reports.

7.1.5 Sensitivity and vulnerability

7.1.5.1 Sensitivity

Sensitivity is regarded as one of the central concepts in ecosystem protection (Holt et al. 1995; Tyler-Walters and Jackson 1999). It is axiomatic that all ecosystem features have either evolved (in the case of biotic features) or been formed (in the case of abiotic features) within a certain range of environmental conditions.

Sensitivity can be measured using one or more indicators (of species, communities and habitats) that respond to oil spills. These responses are potentially nonlinear and are likely to include interactions among stressors (Adler and Inbar 2007). In this context, sensitivity does not inherently assume the characteristics of fragility or intolerance with which it is often associated. There is no implied judgement that an increased association between the indicator and the stressor reduces a feature's probability of persistence. Nevertheless, as exposure to a chronic perturbation or stress increases, the persistence of that feature is diminished.

Zacharias and Gregr (2005) defined sensitivity as the degree to which features respond to stresses, such as spills, which are deviations in environmental conditions beyond the expected range.

7.1.5.2 Vulnerability

Vulnerability is the likelihood of exposure to a relevant external stress factor, combined in some way with the exposure (duration, magnitude, rate of change) to that stress. Zacharias and Gregr (2005) provided a quantitative methodology for identifying vulnerable areas based on valued ecological features, defined as biological or physical features, processes or structures deemed by humans to have environmental, social, cultural or economic significance.

Responding to an oil spill is extremely challenging in any environment, especially those regions where extreme weather prevails (Pilipenko et al. 2013). For example, the offshore operating season in the Arctic, and therefore the period when it would be possible to clean up an oil spill, is restricted to four to five months by darkness, heavy ice and extreme cold (Reich et al. 2014). These severe conditions would make it impossible to attempt an oil spill cleanup for half of the time during the operating season and 100% of the time during the winter. In this intervening time, the Arctic environment would be extremely vulnerable to any possible oil spill event. Due to the low temperature and harsh climatic conditions, the natural attenuation rate is extremely low in this region (Margesin and Schinner 2001). Given the Arctic region has limited biodiversity, damage to some vital species can lead to widespread changes that cascade through all components of the social-ecological system (Chapin et al. 2004).

7.1.5.3 Vulnerability analysis

> Vulnerability is defined as the probability that a feature will be exposed to a stress (e.g., oil spills) to which it is sensitive (Adger 2006; Metzger et al. 2006).

When responders are making decisions regarding the hierarchy of vulnerable areas to be safeguarded after an oil spill, they need to compare the biological impact and recovery potential, the relative value of the population among other impacted populations and the technical possibilities to help the population. *Incorporation of vulnerability analysis into risk assessment has been increasingly adopted in governmental initiatives, programs and practices*. For example, in 2013, Transport Canada conducted a nationwide risk assessment to determine the risks associated with ship-source spills in Canadian waters south of 60° north latitude and in the Arctic (Transport Canada 2015d). Vulnerabilities have been considered as inputs to risk assessment. On the other hand, *growing efforts have been made to develop more effective methods to classify and evaluate vulnerability to oil spills.* For example, Reich et al. (2014) developed a model of environmental vulnerability to determine the relative vulnerability of broad geographic regions to spilled oil. The model was based on the underlying vulnerability of habitats and representative species present in each region and season assessed. It can be applied to any geographic area of interest and provide a simple, yet comprehensive and expandable methodology for determining baseline environmental vulnerability of large geographic regions. Ihaksi et al. (2011) presented an index-based method that can be used to make decisions concerning which populations of classified natural organisms should be primarily safeguarded from a floating oil slick with oil booms. Olita et al. (2012) proposed a new model for evaluating the hazard of oil slicks contacting shorelines based on the geomorphology of the intertidal area. The hazard index layer can be used as a solid basis to assess the risk and support oil spill response decision-making. Recently, Li et al. (2014a) developed a Monte Carlo simulation-based two-stage adaptive resonance theory mapping model to classify a given site into distinguished zones representing different levels of an offshore oil spill vulnerability index (OSVI). Integrating Monte Carlo simulation with the adaptive resonance theory and mapping approach addresses the uncertainties that widely exist with the environmental conditions. The classification results can also provide the least desired number of zones that can sufficiently represent the levels of offshore OSVI in an area under uncertainty and complexity, saving time and budget in spill monitoring and response (Li et al. 2014c). *However, limited studies focused on the Arctic and sub-Arctic environments are reported in the literature. Vulnerability analysis based on field measurement and integrated with spill modeling and response decision-making are again lacking.*

7.1.6 Preparedness and contingency planning

A management strategy or contingency plan is a set of instructions that outlines the steps that should be taken before, during and after an emergency. It helps minimize potential damage to human health and the environment by ensuring a timely and coordinated response (Chen et al. 2012).

7.1.6.1 Preparedness and response regime

In Canada, the designation of the lead agency for a spill event may be based on legislation, an interagency agreement, a Cabinet decision and/or custom or precedent. There can be more than one lead agency represented under a unified command, as well as the party that is taking responsibility for impact mitigation (e.g., cleanup and response management) and generally referred to as either the spiller or polluter. **Table 7.3** shows a list of the lead agencies in Canada for different types of oil spills based on the *National Environmental Emergencies Contingency Plan* (Environment Canada 1999):

Table 7.3 *Lead agencies for different types of oil spills*

Federal Legislation on Oil Spills	**Lead Agency**
Deposition of oil into migratory bird habitats (*Migratory Birds Convention Act*)	Environment Canada
Oil pollution from ships (*Canada Shipping Act*)	Department of Fisheries and Oceans; Transport Canada
Cleanup, sampling and analyzing oiled wildlife	Environmental Conservation Service
Oil loading and unloading from ships (*Canada Shipping Act*)	Canadian Coastal Guard
From loading facilities connected to oil production platforms in Canadian Atlantic	National Energy Board

For example, for marine oil spills, Transport Canada is the administrative agency that ensures an appropriate level of preparedness is available for any oil spill incidents occurring within prescribed time standards and operating environments. The Marine Oil Spill Preparedness and Response Regime, established in 1995, is built on a partnership between government and industry (Transport Canada 2013). The regime is designed to ensure that marine shippers pay for spill preparation, response and cleanup. The regime also includes requirements for rigorous contingency planning. The regime is equipped to handle up to 10,000 tonnes of oil spilled in Canadian marine waters. The Canadian Coast Guard monitors and, where necessary, augments or assumes management of the response when it is in the interest of the public.

Privately-funded certified Response Organizations (RO) have the responsibility to respond to oils spills from vessels with which they have arrangements and when contracted to respond. Ship owners are required to have such an arrangement with one or more ROs, depending on the intended destination(s) of the ship and the area covered by each RO. However, there is no legal obligation to enact the arrangement and engage the services of the RO. Alternative arrangements could be made using other resources, if deemed appropriate. Below 60 °N, Canadian waters have been divided into two principal areas: west and east coasts, with an RO established for each. In addition, two further ROs have been established to cover specific parts of the eastern coast region. Each RO has a Response Plan establishing the resources and strategies needed to respond to a range of spill scenarios within its jurisdiction (ITOPF 2013).

Although it is prudent to have some level of preparedness for a worst case spill, the primary focus of the ROs should be preparing for the types of spills that are likely to occur within their area of response. The challenge is how to determine what level of preparedness is appropriate for each area of response. Transport Canada commissioned risk assessments for marine spills in Canadian waters (WSP 2014a, b) as mentioned earlier. These reports estimated the risk of pollution from marine oil spills to specific sectors of the Canadian coast (Pacific, Atlantic, Estuary/Gulf of St. Lawrence and the Great Lakes/St. Lawrence Seaway System). The results can be used as a valuable base for ROs to determine the level of preparedness and develop their response strategies.

No comprehensive national framework is in place for training and exercises for ship-source oil spill preparedness and response in Canada that involves all key stakeholders. Although Canada's preparedness, at the national level, is within an oil spill preparedness and response regime, it still lacks sufficient capability to address and manage the risks existing along the coast line, particularly within the Great Lakes and the St. Lawrence Seaway (Transport Canada 2013). This lack of capability may be the reason why Canada's current regime has been questioned sometimes in terms of providing the best approach to mitigating the impacts of potential future spills (Marty and Potter 2014; Rise 2014).

7.1.6.2 Technical preparation

Sound preparedness and contingency planning should rely on knowledge of oil spills and the associated impacts and technologies for response and cleanup. Technical preparation involves not only an examination of spill risks, but also thorough analysis of the nature of the spill events that might occur (source, oil type, spillage rate, location and timing) and the way in which the nature and impacts of spills may change over space and time. For example, Silliman (2014) stated that many environmental factors affect the fate of spilled oil sands products in aquatic environments because bitumen, a large component of oil sands products, has a density greater than fresh water. By analyzing specific factors in areas at risk, responders can better prepare for and expect submergence of oil sands product spills.

If areas identified have low salinity, rough sedimentation, high turbidity, strong sunlight exposure, high temperatures, and strong currents that cause a high risk of submergence, the response teams in these areas should have submerged oil recovery equipment readily available for rapid deployment (Soomere 2012). According to the Joint Review Panel for the Enbridge Northern Gateway Project (JRP 2013a), the advances in technology and modern pipeline design, materials, construction and operating practices would greatly reduce environmental risks from pipeline spills.

A spill of any oil product could have serious effects in any environment. Compared to lighter crude oils, heavier oils and diluted bitumen usually take longer to degrade naturally. The information about oil spill fate, influencing factors and impacts can directly guide the development of contingency plans and the pipelines' design, location and management systems to minimize the potential volume released and keep oil from reaching waterways (Ramseur et al. 2014; Taylor et al. 2014).

Insufficient information could lead to difficulties in making sound contingency planning and response decisions. Many recent publications and conferences, such as the 2015 AMOP Technical Seminar (Environment Canada, 2015c), have revealed knowledge gaps and research needs especially related to the fate and behaviours of diluted bitumen, as well as their implications to response methods under different spill and environmental conditions (especially in cold regions or waters). Also refer to the relevant discussions in Chapter 9.

7.1.6.3 Contingency planning

Oil spill prevention planning requirements are determined by the potential source of the spill, which for transported oil primarily include storage facilities, vessels, pipelines, rail cars and trucks. The designated federal agency must assess the capacity of the responsible party to effectively respond to a spill, which may include providing oversight of response plans, maintaining contingency plans at various levels and personnel training (Ramseur et al. 2014). Transport Canada (2013) proposed an Area Response Planning model that includes a national risk assessment, an identification of area of response, a regional risk assessment, a response requirement, an area response plan, a certification and a continuous improvement plan. *Moving from static national standards to a risk-based model represents an important shift for the Canadian Regime.* The more rigorous planning process inherent in this model may strengthen the links between the public and private elements of the regime and build public confidence in Canada's ability to respond to an oil spill. Provincial governments are also playing a more important role in oil spill contingency planning. For example, the British Columbia Ministry of Environment (2014) recently introduced the preparedness and response guidelines for land-based oil spills, particularly from heavy oil pipelines. The large volume of technical information and stakeholder feedback gathered by the Ministry suggested that world leading practices for oil spill prevention, response and recovery systems to manage and mitigate the risks and costs of heavy oil pipelines are highly desired.

Mathematical models and computer tools have been effectively applied to facilitate contingency planning, although significant amounts of high-quality data, computational resources and maintenance efforts are usually required. *Integration with state-of-the-art risk/readiness assessment and geomatic analysis methods has recently been gaining interest and research efforts.* For example, Etkin et al. (2011) recommended a risk-based approach to contingency planning and spill risk management that takes into account the complex factors on both the probability and consequence sides of the risk equation. The approach may include relevant cost-benefit and cost-effectiveness analyses of spill response measures to help plan for the most beneficial strategies to reduce impacts on sensitive natural and socioeconomic resources. Etkin et al. (2013) further suggested that the determination of scope of a contingency plan should be based on the risk of spills within the geographic area that the plan is intended to cover. Lamarche et al. (2013) developed a new cartographic system, based on Google Earth, to support the planning effort in the event of an incident. It allows users to access the system on stand-alone or portable devices, providing a more efficient planning and response tool for spill responders and the responsible party. A variety of geomatic analysis tools and GIS-aided management systems have been increasingly used by Canadian ROs, such as Eastern Canada Response Corporation and Canadian Coast Guard. Taylor et al. (2014) reported that, in 2011, the Regional Association of Oil and Gas Companies - Latin America and the Caribbean developed the *Oil Spill Response Planning and Readiness Assessment Manual* and its assessment tool, the Readiness Evaluation Tool for Oil Spills (RETOS™). The tool provides a general guide to industry and governments to assessing their level of contingency planning and readiness management in relation to pre-established criteria, which are commonly agreed upon by the involved institutions and consider international best management practices. *These criteria are not intended to reflect or add any legal or regulatory requirements. However, their voluntary use by governments and industry can help guide improvements for management of oil spill preparedness and readiness.*

7.1.6.4 Legal requirements and assessment

The responsibility for drawing up contingency plans at a local level, for example, for an individual facility, port or stretch of coastline, and at a larger district or national level, will be dependent on the relevant domestic administrative arrangements. The plan holders should be involved from the outset if plans are to be realistic and practical. Responsibility in the US for ensuring that all plans are compatible usually falls to a national agency, either the US Coast Guard for marine shorelines or the US EPA for inland spills (US Coast Guard 2001). In Canada, to associate industry with government, a legislative framework has been created by an amendment of *the Canada Shipping Act 2001* (Minister of Justice 2001). See Section 7.1.6.1 for details about the lead agencies responsible for various types of oil spills in Canada.

Meanwhile, to guide and enhance response preparedness for transboundary spill events, a number of international contingency plans and legal instruments have also been developed, such as Canada-United States Joint Inland Pollution Contingency Plan, Canada-United States Joint Marine Contingency Plan and the International Maritime Organization (IMO)'s International Convention on Oil Pollution Preparedness, Response and Co-operation (OPRC) (IMO 1990; Environment Canada 1999; Martini and Patruno 2005).

7.1.6.5 Training, drills and education

Training programs should be developed for all response levels and include marine and shoreline response teams and interested parties (US Coast Guard 2001). Regular and realistic exercises will help to ensure that contingency arrangements function properly and that the roles and responsibilities of all parties are thoroughly tested and understood. Equipment should be mobilized and deployed regularly to assess its availability and performance. Such exercises also ensure that contact details and equipment listings are current (Doerffer 2013). *Plans should be periodically reviewed and, if appropriate, amended in the light of lessons learnt from exercises or actual incidents.* All those involved need to be made aware of any changes to the plan (Fingas 2012). Nuka (2010) recommended that field exercises and drills be conducted for training and practice purposes. They can provide valuable information on how well the response equipment perform, the limits to the response systems posed by real-world conditions and the cooperation among various personnel and response organizations. *However, exercises are still inherently artificial as the equipment and vessels are pre-assigned and the personnel are pre-notified or even pre-positioned. An unannounced true spill response drill is sometimes necessary to test the operator's response capacity to contact, move and deploy the whole response team.*

Meanwhile, education through social media is being used and should be further encouraged in order to improve the way the community is informed and engaged during oil spills about the situation and how decisions are made. Proper education can help the involved communities improve their attention to preparedness, agility in responding to spills and recovering ability from spills (Merchant et al. 2011). Johnson (2014) suggested a strategy to provide education to local communities in order to help the public understand oil spills and their impacts.

Recommendation: Educational outreach to enhance literacy and promote preparedness and responses should be a key part of the training.

7.2 Response Decision Support

The response to an oil spill usually consists of a series of dynamic, time-sensitive, multifaceted and complex processes subject to various constraints and challenges (Chen et al. 2012). *The success and effectiveness of a response must rely on how efficiently the information (location, oil properties, weather, currents, etc.) and response resources (devices, manpower, money, etc.) can be used and how optimally the decisions and actions can be made.* Even though the policy or regulations focusing on framework or infrastructure are relatively consummate, inadequate decision support may be one of the major challenges that limit the efficiency of spill response. In the past decades, many models have been developed mainly focusing on individual oil spill response activities, including early warning and detection, spill simulation, cost-benefit analysis, risk and impact assessment, cleanup technology selection and cleanup optimization and performance evaluation (Christoph 2013; Lamarche et al. 2013; Paul et al. 2013; Li et al. 2014b,c; Silliman 2014). *However, to date, the integration of the above into an integrated response decision support system is still lacking.* This section will review the current status of research and practice in the area of oil spill response decision making.

7.2.1 Early warning

A reliable, integrated system of early warning and real-time monitoring can significantly improve the effectiveness and efficiency of oil spill emergency response. Similar to medical diagnosis, such a system is able to identify, diagnose and react promptly to minimize the oil discharge into the environment at an early but critical stage of the emergency (Li et al. 2014a).

7.2.1.1 Spill imaging and analysis

Most existing satellite methods of oil spill monitoring tend to be economical, but cannot eliminate the need of systems for early detection and direct monitoring. The integration of *in situ* and remote monitoring hardware with pollution analysis software is of necessity and has been gaining attention. Barenboim et al. (2013) proposed an automated monitoring system for oil spills in waterbodies. It consists of a remote sensing subsystem using fluorescent LIDAR, a network of automatic monitoring stations and an oil pollution identification subsystem based on hydrocarbon contents, alteration of radioactivity and water conductivity. The system provides an efficient tool for early warning and monitoring of oil spills from oil and gas facilities. Rapid distribution of aerial images helps responders at both tactical and strategic levels. In addition, aerial imaging systems that can share information over low cost data links greatly enhance response capabilities by providing real-time information to response teams.

Recent technology advancements enable aerial images to be communicated over low cost data links to stakeholders at different geographic locations within minutes of acquisition. Sweeten et al. (2012)

incorporated a proof-of-concept test into an emergency response drill that confirmed the ability to transmit images to stakeholders and responders rapidly during oil spill response events.

<u>Recommendation:</u> Comprehensive and in-depth analysis of real-time spill images, along with baseline and historic data, are highly desired to provide more effective and meaningful information for spill response decision-making in a timely and effective manner.

7.2.1.2 Early warning indicators

One efficient way of improving the ability to prevent and reduce major oil spill events and impacts is to use early warning indicators. **Table 7.4** categorizes the typical early warning indicators and compares their strengths and weaknesses. The use of indicators can be seen as a regulatory requirement and/or a means to avoid unwanted events. Investigation reports of accidents, such as Longford (Hopkins 2000) and Texas City refinery (US Chemical Safety and Hazard Investigation Board 2007), recommended the use of indicators. Øien (2010) compared the different approaches for developing early warning indicators and suggested that people should be flexible with respect to the choice of methods and preferably use more than one method. One challenge with the establishment of early warning indicators for potential minor events is that these events are not included in the current quantitative risk analysis used in the offshore petroleum industry (Skogdalen et al. 2011). *Most existing response systems lack or are weak in effective early warning function/ability to identify, diagnose and react promptly to minimize the oil discharge into the environment at an early but critical stage of the emergency. Furthermore, it is challenging to incorporate the selected indicators into the early warning and real-time monitoring systems and into the spill response decision-making processes.*

Table 7.4 *Summary of early warning indicators and their strengths and weaknesses*

Early warning indicator	Description of approach	Advantages	Disadvantages	References
Safety performance-based indicator	• Describes the safety level within an organization, activity or work unit • Starts with a set of factors that have potential effects on safety • Becomes not only useful for describing safety levels, but also applicable for early warning	• Is favorable when it comes to practicality, simplicity and documentation • Is very relevant as an early warning	• The risk significance and the relative importance between the chosen influencing factors are unknown	Jennings and Schulberg (2009); Skogdalen et al. (2011); Christoph et al. (2013);
Risk-based indicator	• Utilizes risk models as bases, and the development of risk models are part of the method • Regards risk control as the main function of the risk indicators • Becomes preferred with sufficient data • Particularly focuses on organizational risk indicators in the case of early warning	• Provides indicators for major accidents • Easily determines the risk significance • Depends on either accident investigation or occurred events • Indicates potential scenarios without the occurrence of accidents	• It is rather resource intensive, especially for organizational risk indicators, which are desirable since they are most relevant as early warnings	Khan et al. (2002); Pula et al. (2005)
Incident-based indicator	• Depends on detailed analysis of incidents or accidents • Assumes that if the contributing factors are efficient, then neither the incident nor accident have been analyzed nor similar ones have occurred • Mainly focuses on identifying and measuring the factors that contribute to the incident or accident with the use of indicators	• Closely relates to major accidents • Easily communicates with stakeholders based on a factual incident or accident	• Requires very thorough review and documentation • The risk significance and relative importance of the underlying causes are unknown	Jennings and Schulberg (2009); OGP (2011)
Resilience-based indicator	• Questions capability of recognizing, adapting to, and coping with unexpected events by providing specific approaches to manage risk in a proactive manner • Indicates the engineering resilience in organizations and safety management approach with methods, tools and management approaches under complexity	• Focuses on positive signals with failures that may be lack of data • Does not rely on information from occurred events and the indicators are relevant as early warnings	• The risk significance and relative importance of the influencing factors are unknown	Hollnagel and Woods (2006); Øien et al. (2010); Paltrinieri et al. (2012)

7.2.2 Response technology screening and evaluation

7.2.2.1 Technology standards

The DWH oil spill revealed a variety of regulatory failures in terms of implementing a regulatory regime, which mandates adequate safety and cleanup technologies in deepwater oil exploration (Bush 2011). To help address the problems, Best Available Technology (BAT) standards are being advocated (Hout et al. 2014; Leifer et al. 2015). In fact, BAT standards have been adopted by some agencies since 1990 and Alaska is among the first. In early 1990, following the EVOS incident in Prince William Sound, Alaska's Department of Environmental Conservation (ADEC) established regulations establishing new oil discharge prevention and contingency planning statutes, which require BAT standards and rigorous technical and economic assessment of BAT (ADEC 1993). However, such an assessment requirement only applies for mechanical oil spill response equipment (Shepherd, 2014).

> Under Alaska state law and ADEC regulations, each blowout prevention contingency plan for marine waters in Alaska must mandate adequate secondary relief well capacity, or similar blow-out prevention and response tools in Cook Inlet. Such plans must include BAT standards "consistent with the applicable" statutory criteria, including: a) whether each technology is the best in use in other similar situations and is available for use by the applicant; b) whether each technology is transferable to the applicant's operations; c) whether there is a reasonable expectation each technology will provide increased spill prevention or other environmental benefits; d) the cost to the applicant of achieving BAT, including consideration of that cost relative to the remaining years of service of the technology in use by the applicant; e) the age and condition of the technology in use by the applicant; f) whether each technology is compatible with existing operations and technologies in use by the applicant; g) the practical feasibility of each technology in terms of engineering and other operational aspects; and h) whether other environmental impacts of each technology, such as air, land, water pollution, and energy requirements, offset any anticipated environmental benefits (ADEC 2015).

In promulgating a BAT regulatory standard, *regulators must identify the best available technology to adequately respond to the particular risks associated with each industrial category. The identification should be based on scientific understanding of the effectiveness and technical/economic constraints especially in cold and harsh environments.* Consequently, regulators must proactively investigate the safety records of oil industry members, the safety regulations and standards, and the industries that are interested in advancing cleanup technology. However, industry usually tends to bypass the standards to reduce the costs (Prendergast and Gschwend 2014). Economic variance can affect the viability of a BAT standard as increased technology requirements often necessitate increased expenditures by industry. Therefore, the oil industry may consider replacing the BAT standard with other strategies to avoid excess costs (Hout et al. 2014). Meanwhile, depending on the location of a spill and weather conditions, response technologies may encounter various constraints to effectiveness (Andrade et al. 2013), especially in Canadian harsh environments where rough weather, high seas, poor visibility, high wind, freezing temperature and ice conditions prevail (Chen et al. 2012). *There have been difficulties in selecting the BAT according to both equipment capacity and working conditions.* Laborde et al. (2015) proposed a framework to develop an oil spill response gap map model based on high resolution historical data at large spatial and temporal scales. The model would show how often environmental factors exceed the operational capacity for *in situ* burning, booming-skimming and dispersant application in a web-based GIS environment.

7.2.2.2 Screening and performance evaluation

A spill response strategy often starts with the identification of appropriate technologies that accommodate the site-specific environmental conditions and increase the probability of a favourable outcome. Numerous factors must be considered for the selection of oil spill response procedures for use in contingency plans and emergency response operations. These factors include but are not limited to the probability of an oil spill, the possible volume, type and properties of crude oil or refined product that might be spilled, environmental factors influencing the fate and behaviour of the hydrocarbons that could be released, the sensitivity of the most valued ecosystem components (VECs) to oil pollution, the potential impacts from the application of oil spill countermeasures, and the time needed for habitat recovery (Board of Ocean Studies & Marine Board 2014). Leschine et al. (2015) introduced a scenario analysis for oil spill contingency planning and response technology screening for vessels, pipelines, tank farms, berthing docks and many other oil-industry infrastructures. Liao et al. (2012b) proposed an oil spill emergency preparedness system that recommends the BAT based on a comparison with similar cases. *Still one of the key challenges in selecting and developing suitable response strategies and cleanup technologies is insufficient knowledge about their technical limitations, influencing factors and ecological impacts, especially related to some emerging concerns, such as diluted bitumen, aging or subsea pipelines, spills to freshwater ecosystems and Arctic conditions. Furthermore, there is a need for new or updated regulations to govern the application of those response technologies based on the improved knowledge.* Further discussion about influencing factors and performance evaluation for response technologies are provided in Chapter 6 and later in this chapter.

7.2.3 Spill physical and numerical simulation

Besides the gaps in modeling oil spills as discussed in Chapter 5, *challenges also exist in how to use modeling tools to more effectively and dynamically support response decision-making* (Chen et al. 2012; Li et al. 2012a, 2014b; Li 2014). *The linkage between modeling of oil slicks (weathering and trajectory) and cleanup processes (e.g., in-situ burning and skimming) is lacking, as well as their dynamic coupling with ecological/ environmental risk assessment to provide decision-makers more accurate and comprehensive information. Furthermore, harsh environments prevailing in northern regions and the Arctic can pose large amounts of uncertainty and difficulties in using the traditional physical and numerical simulation models and their integration with the corresponding response simulation and decision support systems.*

7.2.4 Net Environmental Benefit Analysis (NEBA)

Net Environmental Benefit Analysis (NEBA) has become widely used to assess oil spill countermeasures, both active (e.g., *in situ* burning and mechanical recovery) and passive (e.g., monitoring of natural attenuation processes). NEBA can help determine whether or not additional environmental damage could be caused by specific response actions (Fritt-Rasmussen et al. 2013). NEBA can provide decision-makers with a reliable strategy for deciding what response options are appropriate at a specific spill location based on the analysis of environmental tradeoffs that may occur from the use of the various responses (Coelho et al. 2013; Coolbaugh et al. 2014).

The generic NEBA framework is outlined in IPIECA (2000). A typical NEBA process involves: a) review of previous spills and experimental results that are relevant to the area and to possible countermeasures; b) assessment of likely environmental outcomes if the proposed countermeasures are implemented compared to outcomes if the area is left to recover naturally; and c) comparison and weighing of advantages and disadvantages of various potential responses with those of natural cleanup. The NEBA process can be used to establish the most important resources at risk before or in an oil spill based, for example, on their status as protected species, ecosystem service or relevance, economic value or human use (Le Floch et al. 2014; Prince 2015).

The determination of priorities will depend on the preparation of a list of local environments at risk, the results of predictive oil weathering and trajectory models, and *in situ* or remote monitoring data, etc. NEBA accounts for the nature of the spilled oil and changes it may undergo during weathering and spreading, which may influence the level of environmental, biological and socioeconomic effects (Daling et al. 2014). However, *NEBA can only process environmental variables and does not account for other considerations in the strategy-forming process. A strategy that is environmentally or ecologically ideal but does not recognize political or legal factors or operational feasibility ultimately may not be implemented (Coelho et al. 2013). This should be better addressed in the NEBA.*

NEBA tends to be an integral part of contingency plans because post-spill decisions are best and most quickly made in light of pre-spill analyses, consultations and agreements involving all of the appropriate organizations and parties (Daling et al. 2014). Use of NEBA in contingency planning offers several advantages, including extended timeframes for analysis, consideration of spill scenarios covering a wide range of environmental factors (e.g., seasonal changes in species diversity and ice cover), time for identification and collection of scientific data and stakeholder involvement (Cox 2014). NEBA can also facilitate the identification of potential conflict areas and possible solutions through consultation before any spill occurs. *Other important considerations during NEBA include the logistical constraints that are likely to be encountered during oil spill response operations, which will influence the efficacy of current countermeasure strategies* (Bejarano and Mearns 2015).

Cumulative impacts refer to the effects of an action that are added to or interact with other effects in a particular place (e.g., an oil spill site) and within a particular time (US EPA 1999). The combination of these effects and any resulting environmental changes caused by response actions should be considered in a cumulative impact analysis, which has been incorporated into environmental impact assessment processes. *When introducing cumulative impact analysis to NEBA for oil spill response, difficulties may be encountered when identifying/quantifying cumulative impacts of response actions (e.g., application of dispersants), especially for long time periods (Paul et al. 2013; Davies and Hope 2015).*

Regardless of what and how response method(s) are applied, there will be some level of environmental impact. Many studies have conclusively shown that the application of aggressive cleanup operations may delay the rates of habitat recovery by causing additional damage beyond the oil spill itself (Judson et al. 2010; Kirby and Law 2010). For example, in the aftermath of the EVOS incident, excavation and washing of rocks to remove surface and subsurface oil were shown not to offer a net environmental benefit because the procedures altered shore structure and delayed biological recovery (US NOAA 1990). The recent DWH spill involved around 47,000 people and 7,000 vessels during *in situ* burning, mechanical recovery and application of dispersants, yet long-term side effects of those activities, especially some caused by the use of dispersants, have been reported (Graham et al. 2011). *In fact, a response strategy that provides protection for one environmental resource (e.g., chemical dispersion of oil slicks to protect seabirds) may increase risks to another* (e.g., toxicity of dispersed oil to fishes in the water) (Graham et al. 2011; Payne et al. 2012; Paul et al. 2013). *Decision-makers need to select the optimal response strategy based on the protection of prioritized environmental resources and the countermeasures that offer them the greatest protection, which always lead to some level of trade-off.* The value (effectiveness and impact) of a particular method will depend on the situation, including the type and properties of oil spilled, weather conditions, organisms and ecosystems that are impacted and availability of response support.

A NEBA process can help identify the relevant factors affecting the effectiveness of options and select the best response strategy. However, *prioritizing response options in NEBA usually involves human inference and judgement regarding making the trade-off (Prince 2015).* Qualitative evaluation approaches, including questionnaire surveys, are usually used and unavoidably introduce uncertainties into the results due to incomplete information and subjective judgement based on personal knowledge, experience and opinion (Reynolds 2014).

<u>Recommendation:</u> More unbiased measures and better understanding of the influence of human judgment are required in NEBA and subsequent decision-making processes. Furthermore, socioeconomic factors play an important part in response decisions and should be reflected in the NEBA process in terms of impact on a region's environment, its economy and the wellbeing of its people.

Many oil spill countermeasure technologies (e.g., chemical agents including dispersants and facilitation of oil mineral aggregate formations) may not be fully understood in terms of their environmental and ecological impacts, and their effectiveness in harsh environments such as ice conditions (Payne et al. 2012; Coelho et al. 2013). Until sufficient information is available on the population dynamics of VECs, the fate and environmental effects of oil and the efficacy of various response technologies, the effectiveness of NEBAs will vary and outcomes will be uncertain (Fitzpatrick et al. 2012; Coolbaugh et al. 2014). *However, application of NEBA is still necessary to assess some newly emerged concerns (e.g., dilbit), countermeasures (e.g., use of biosurfactants as dispersants) and special environmental conditions (e.g., ice coverage, permafrost and peat lands).*

In terms of damage assessment, an ecosystem services approach has been suggested (Menzie et al. 2012; NRC 2013). It can account for an event's impact on all aspects of human wellbeing and can help remediate the damage to natural resources caused by oil spills. Chapters 4 and 8 present the definition and detailed discussion about ecosystem services modeling.

Although NEBA is much desired in the contingency planning stage before a spill, it has also been used to choose the intensity of the response countermeasure, as well as the decision on when to conclude the response (DeMicco et al. 2011). Decisions are typically made based on potential environmental and socioeconomic impacts of the spill, the potential impacts of the cleanup operation and the possibility and ability of natural or human-enhanced recovery of the impacted environment. The 2012 report of the American Petroleum Institute (API), *Spill Response in the Arctic Offshore* (Potter et al. 2012), identified where a range of different cleanup intensities and conditions might be appropriate. It was noted that the most intense efforts to remove oil are appropriate in areas with high levels of human activity or environmental sensitivity, the risk from oil is high and the impact from intense cleanup measures is low. By contrast, monitoring may be sufficient in situations where the spilled oil poses little risk, the potential for natural oil degradation and natural recovery are high and the risks posed by cleanup efforts are high. Another example from the API report showed that, where areas adjacent to the spill site are highly sensitive to oil and the oiled area is only moderately sensitive to cleaning, the appropriate cleanup efforts may include removing most of the visible oil but allowing traces of oil to remain.

7.2.5 Performance evaluation and post-event management

7.2.5.1 Performance evaluation and impact assessment

The oil types, applied response methods, performance and environmental impacts of some major oil spills in Canada and the US are summarized in **Table 7.5**. The summary presents significant variations of performance and impacts of similar response options in different spill events. Post-event comparable studies are lacking to help develop more comprehensive quantitative methods for response performance evaluation in a holistic manner. Consequently lessons from the past spill responses should be better analyzed and reflected in planning and decision-making processes for future spill responses. Also, *effective environmental monitoring and impact assessment practices should be in place, using the most appropriate scientific techniques, to enable the response, conservation and scientific communities to properly assess the real significance of spills and subsequent response activities and to learn lessons for future events. The requirements for improved on-site and post-incident monitoring and assessment continue to increase. Although most risks can usually be estimated during or right after spill response, the variability of the situation may require some degree of on-site or post-event assessment to* *continuously assess the risk of oil spill and response activities (*Leong 2012). Such variability can include, but not be limited to, weather changes and subsequent work activities, etc. On-site and post-event assessment usually includes visits to key risk areas, direct observation, data collection and analysis, questionnaire survey and interview and long-term site monitoring (Dix et al. 2011; Shupe et al. 2014). Bostrom et al. (2015) applied a mental models survey approach to assess public thinking about oil spills and oil spill response. The decision model considered controlled burning, public health and seafood safety. The results illustrated opportunities to reframe discussions of oil spill response in terms of trade-offs between response options, and new possibilities for assessing public opinions and beliefs during events.

7.2.5.2 Adaptive management

Adaptive management, as a systematic process, has been widely used to continually improve management policies and practices by adjusting subsequent actions based on both past lessons learned and advanced knowledge from new scientific and socioeconomic information on the systems being affected (Rost et al. 2014; Kulapina et al. 2015). The key steps usually include learning and reducing uncertainties, using learned knowledge to change policy and practice, focusing on improving management effectiveness, applying trial management and being formal and systematic (Cluzel et al. 2012; Hausberger et al. 2012). *The application of adaptive management, especially with integration of risk analysis, has been limited in the oil spill response field.* Peltier et al. (2014) developed a new approach that used multiple indicators, including oil slick drifting, to provide monitoring information on dolphin populations and to setup adaptive management strategies. *Adaptive management should be further encouraged to continually improve management policies and practices by adjusting subsequent actions based on learning from past events and new knowledge development.*

Table 7.5 *Major oil spills in North America and their response performance*

Oil Spill Case	Oil Type	Date	Amount (US gallon)	Responses and Performance	Key Impacts	References
Nova Scotia Uniacke G-72 Oil Spill, Nova Scotia, Canada	Mud, gas and condensate	February 22, 1984	126,000	• Well crews evacuated • No immediate response • Well recapped 10 days later	• Strong hydrocarbon odour was present as far as 10 km away • Oiled seabirds and seals were observed • No evidence of condensate on the shoreline	Gill et al. (1985)
Exxon Valdez Oil Spill, Alaska, USA	Crude oil	March 24, 1989	11-38 million	• Controlled burning (with ship and boom) - 113,400 L of oil reduced to 1,134 L of removable residue • Mechanical cleanup (with boom and skimmer) - only 10% oil recovered • Skimmer: low efficiency (thick oil, heavy kelp, plenty of permanent container, bad weather, etc.) • Chemical dispersants ineffective due to lack of wave energy • Shoreline washing • Bioremediation of shorelines	• Immediate effects - the deaths of 100,000 to as many as 250,000 seabirds, at least 2,800 sea otters, and many other animals • Long-term effects: more losses of species than expected • Bioremediation was somewhat effective in accelerating biodegradation as a cleanup option	Morris and Loughlin (1994); Boehm et al. (2014)
Pine River Oil Spill, British Columbia, Canada	Light crude oil	August 1, 2000	260,400	• 118,800 gallons removed from the river • Vacuum oil and set up containment booms of 12, 24 and 28 miles from the rupture • 119,560 gallons removed from soil • Removal of large woody debris from river channel due to it being coated with oil	• Extensive mortality of fish and some wildlife • Water supply to the District of Chetwynd was ceased and the use of many groundwater wells nearby the river was discontinued • Disruption of the river channel and destruction of fish habitat by seasonal flooding following the removal of woody debris that stabilized the river morphometry	Anderson and Schwab (2012); Chung et al. (2012)
Terra Nova Oil Spill, Newfoundland, Canada	Waxy crude	Nov. 2004	43,650	• 5% oil recovered	• An estimated 10,000-16,000 direct kills of birds	McGrath (2014)

Wabamun Lake Oil Spill, Alberta, Canada	Heavy Bunker C fuel oil	August 3, 2005	343,000	• 185,000 gallons of Bunker C and Imperial Pole Treating Oil removed • Early response by sorbent booms (ineffective) • containment boom (inadequate quantity) • Later response by SCAT process and cleanup of individual shore segments based on geomorphology and degree of oiling • Extensive removal of shoreline oiled reed bed vegetation and mechanical recovery of oil from reed bed water column and sediments	• Residents were told to stop cleaning wildlife and to completely avoid use of all lake water and well water, even for watering gardens and lawns • Access to the lake for recreation and fishing was limited for months following the spill • Extensive damage to reed beds caused by oiled vegetation removal and recovery of oil and tar balls • Mortality of reed bed fish and wildlife, and reduction of nesting habitat for Western Grebe • Residual oil and tar balls in shoreline and marsh areas for several years • Evidence of oil contamination of whitefish spawning shoals at concentrations sufficient to impair embryo survival	Newbrey et al. (2012); Martin et al. (2014)
Deepwater Horizon Oil Spill, Gulf of Mexico, USA	Crude oil	20 April, 2010	210 million	• 33 million gallons recovered • Initially: ROVs, 700 workers, 4 airplanes and 32 vessels • Involved 47,000 people and 7,000 vessels in total • Chemical dispersants - Corexit (1.07 million gallons on water surface & 721,000 US gallons underwater) • *In situ* controlled burning (13 million US gallons) • Over 60 open water skimmers (33,000,000 US gallons or 120,000 m^3 of tainted water removed) • Extensive shoreline remediation, including shaping shorelines to direct oil away from sensitive areas and oil recovery from beaches and coastal wetlands	• Most impacts were on marine species – by November 2, 2010, 6,814 dead animals, including 6,104 birds, 609 sea turtles, 100 dolphins and other mammals • Actual number of mammal deaths due to the spill may be as much as 50 times higher than the number of recovered carcasses • Use of dispersant made oil sink faster and more deeply into the beaches, and possibly groundwater supplies • Beach erosion and disruption of plant and animal life-cycles were observed due to oil toxicity and cleanup actions	Allan et al. (2012); White et al. (2012); Barron (2012); NRC (2013)

Kalamazoo River/ Enbridge Pipeline Spill, Michigan, USA	Cold Lake Blend (with benzene diluent)	July 26, 2010	819,000	• Over 1.1 million gallons of Line 6B oil recovered • Excavation and dredging	• Eighty miles of shoreline and adjacent lands were contaminated • Submerged oil was assessed and recovered at over 25 locations • Over 100 residents were relocated due to air quality (benzene) concerns • Residual oil in sediments producing sheen when disturbed • Extensive severe habitat damage and destruction due to removal of riparian vegetation, construction of roads on riparian lands up to the river banks, removal of islands that had been over-washed by oily water, and continual disturbance and removal of contaminated sediments	Dollhopf and Durno (2011); McGowan et al. (2012)
Lac-Mégantic Rail Disaster, Quebec, Canada	Bakken oil	July 6, 2013	26,455	• Removed oil and damaged rail cars from downtown Lac-Mégantic • Excavation of 57,250 m^3 contaminated soils • 49,494,000 L of oily water and oil were recovered and treated till December 19, 2013. • Run-off water management - oil and water recovery trenches and pumping stations • About 100,000 L spilled into the Chaudière River – shoreline cleanup	• Heavily contaminated with benzene causing heat and toxic conditions • Most-contaminated areas might never be habitable • 30 km stretch of the Chaudière River has residual oil in sediments and along the banks	Ecosocialist Network (2013); Lacoursière et al. (2015)
Gogama Oil Spill, Ontario, Canada	Synthetic crude oil	March 7, 2015	Over 264,000	• Containment booms installed • Skimmers and vacuum trucks deployed	• The spill contaminated a nearby lake, river and soil • The municipal water system was impacted by oil	Canadian National Railway Company (2015)

7.2.6 Risk assessment

7.2.6.1 Spill risk assessment

> The main components of a relative risk assessment of oil spills are:
> - Estimation of the probability of various sizes of spills based on past and projected future incident rates;
> - Vulnerability of the environment to oil spill impacts; and
> - Selection of the oil spill scenario(s) to be assessed; e.g., maximum most probable discharge and/or worst-case discharge.
>
> The assessments are conducted on a regional and seasonal basis by oil type. The level of detail used depends upon the spatial and temporal scope of the assessment and the availability of data.

Risk assessment underpins all preparation and planning for oil spill response and includes the assessment of both the likelihood of a spill occurring and the consequences or effects caused by a spill (Maritime New Zealand 2006). Substantial research has been done and progress made to develop analysis tools and evaluate risks of oil spills across the world and especially in many maritime countries, such as Canada, US, Norway, United Kingdom and Australia (Turner 2010). Refer to the discussion about oil spill risks and case studies in Chapter 8.

WSP (2014a,b) have examined the potential frequency of spills in Canadian waters and the potential consequences associated with these spills. Potential spill frequencies were estimated using a combination of Canadian and worldwide spill statistics. Risk values generally increased in coastal areas and the overall highest risk was observed for small size spills due to their high frequency. Much of the conceptual foundation for these methods is provided by the Washington Compensation Schedule (Washington Administrative Code 173-183), which provides a relative impact score for oil spills, considering sensitivity of the locations oiled, relative density and seasonal distributions of sensitive biota, and factors related to oil type. The methods used in these reports are similar to those developed and demonstrated by Etkin (2012a), Reich et al. (2014) and Li et al. (2014a).

The general approach used by WSP (2014a,b) in their assessment of spills in Canadian coastal waters was as follows:

- Coastal waters were divided into four main sectors which were in turn divided into smaller subsectors for a maximum number of 77 zones;
- Shipping densities, as well as vessel types and size distribution, in each zone were estimated;
- Oil spill frequencies for ships were obtained from the most recent 10 years of worldwide data;
- The behaviour of oil spills (surface area over time) was estimated from simple transport and fate models which depend on the oil type, the spill size and location characteristics;
- The environmental sensitivity index (ESI) was calculated based on physical, biological and human metrics, which were further mapped to illustrate their spatial distribution in each zone; and
- The overall ESI was determined using a spreadsheet calculation and mapped to present its spatial distribution using GIS tools (**Figure 7.6**).

The key findings of the WSP (2014a) report on spills in southern Canada were as follows:

- The largest marine traffic volumes are in the Pacific sector where the probability of small size fuel spills is the highest. The zones with the highest probability of a large spill occurring were the waters around the southern tip of Vancouver Island, the Cabot Strait including southern Newfoundland, the eastern coast of Cape Breton Island and the Gulf of St. Lawrence and the St. Lawrence River;
- ESI results showed that the zones of highest potential impact were in the Estuary and Gulf of St. Lawrence, as well as in the southern coast of British Columbia including Vancouver Island. Higher ESI scores were observed in near-shore zones compared with intermediate and deep sea zones;

- The highest relative risk values were for small spills due to their higher frequency of occurrence. The risk of large spills is generally low in Canada. The risk generally increases in near-shore zones compared with deep sea zones with the exception of the Pacific sector where US traffic may increase deep sea probabilities. The increase in risk in near-shore zones is related to an increase in environmental sensitivity; and
- The Estuary and Gulf of St. Lawrence, the St. Lawrence River, the southern coast of British Columbia, as well as three subsectors in the Atlantic sector, are at the greatest risk from large oil spills. For the rest of the study area, the risk posed by spills over 10,000 m^3 were much lower. Risk is higher from small and medium spills in every sector, especially spills in the 100 to 999 m^3 range. These smaller spills can also cause significant damage and are likely to happen much more frequently than the larger spills.

These results can be used to tailor spill preparedness for each sector and subsector. *It would be useful, as a first step, to evaluate the current level of preparedness under the Marine Oil Spill Preparedness and Response Regime in light of relative risks in order to identify deficiencies.*

WSP used a similar methodology to assess the relative risk of oil spills in Canadian Arctic coastal waters (WSP 2014b). Physical Sensitivity Indicators (shoreline type, wetlands, ice coverage), Biological Resource Indicators (ecologically and biologically significant areas and bird distribution and Human-Use Resource Indices (coastal population, tourism, national/international freight tonnage) were combined to produce an overall ESI for each of 18 subsectors. Spill frequencies were very low compared to southern Canada because of the current low amount of marine tanker traffic. The higher ESI scores occurred in the southern Arctic subsectors, including in the south of James Bay, the south of the Beaufort Sea and at the Mackenzie River Delta. Because the current probability of oil spills is low, relative risks were also low throughout all subsectors.

The WSP assessment of oil spills in Arctic waters did not include prediction of future risks due to increased traffic associated with the opening of routes due to climate change. The assessment also did not appear to account explicitly for the difficulty inherent in cleanup of Arctic spills, which would potentially produce more long-term risk.

Figure 7.6 *Overall ERI for crude oil spills South of the 60th Parallel. Image from WSP (2014a)*

Etkin (2012a) and Li et al. (2014a) proposed new modeling approaches to calculate the probability and/or vulnerability of oil spills by considering environmental conditions, shipping routes, incident cause, vessel type and/or nearby ecological reserves with uncertainties reflected in the system. The approaches were applied to the Cook Inlet vessel traffic and the southern Newfoundland offshore areas, respectively, where concerns of oil spillage exist due to shipping operations and potential impacts on the sensitive environment of the area.

Recently, Reich et al. (2014) assessed the spill risk in Alaska/Arctic and identified the three highest relative risk regions within the scope of their study for maximum probable spills and worst case spills as shown in **Table 7.6**. They pointed out that the relative risk model was highly data-intensive. Therefore, the quality of the results was dependent on the quality of input data. They cautioned that some environmental vulnerability data inputs were known to be of poor quality and should be updated. In particular, bottom habitat and submerged aquatic vegetation data coverage were lacking for much of the area assessed. Sensitivity testing of the model suggested that the number of species used for the study was sufficiently robust, but the addition of more species could refine the risk scoring. This would be important, for example, if species of high traditional use value to aboriginal people were a priority for assessment. Reich et al. (2014) also pointed out that incident rates and potential spillage volumes forecasted for 2025 were subject to considerable uncertainty. Notwithstanding the limitations of the assessment, the results identified broad regions of Alaska with high relative risk, with implications for spill prevention and preparedness.

Table 7.6 *Summary of the relative risk rank and regions. Data from Reich et al. (2014)*

Relative Risk Rank	Max Probable Current Risk	Worst Case Current Risk	Max Probable 2025 Risk	Worst Case 2025 Risk
1	Southeast Alaska	Southeast Alaska	Beaufort Sea	Beaufort Sea
2	Aleutians	Kodiak/Shelikof Strait	Aleutians	Aleutians
3	Kodiak/Shelikof Strait	Cook Inlet	Southeast Alaska	Southeast Alaska

7.2.6.2 Environmental/ecological risk assessment

The general environmental/ecological risk calculation is expressed as the probability of spills multiplied with the potential impacts on environmental or ecological systems (US EPA 1999, 2004; NRC 2013). In general, the first step of risk assessment is hazard identification, which determines the qualitative nature of the potential adverse consequences caused by the action or contaminant. The second step is dose-response analysis, which determines the relationship between dose/frequency of action and the probability or the incidence of effect (dose-response assessment). The third step is exposure quantification, which measures the amount of a contaminant (dose) that individuals and populations will receive. And the last step is risk management, including coordinated and economical application of resources to minimize, monitor and control the probability and/or impact of risks (Board of Ocean Studies 2014; Li 2014).

Many assessment methods and practices for oil spill events have been reported. For example, French-McCay (2002) developed and validated an oil toxicity and exposure model (OilToxEx) for estimation of impacts to aquatic organisms resulting from acute exposure to spilled oil. The author further proposed a coupled oil fate and effects model for the estimation of impacts to habitats, wildlife and aquatic organisms resulting from acute exposure to spilled oil. The physical fate model estimated the distribution of oil (as mass and concentrations) on the water surface, on shorelines, in the water column and in the sediments. The biological effects model estimated exposure of biota of various behaviour types to floating oil and subsurface contamination, resulting percent mortality and sublethal effects on production (somatic growth). Impacts were summarized as areas or volumes affected, percent of populations lost and production foregone because of a spill's effects (Liu et al. 2009). Recently, Etkin (2012b) developed a simple and defensible model to provide a relative quantitative measure of the environmental and socioeconomic impacts of a pipeline or facility spill as a function of key location-specific attributes. The model was intended to reflect significant differences in the sensitivity of different types of environments to spill-related damage without requiring a complex site-specific environmental impact assessment. Stephenson et al. (2015) studied hypothetical spills of dilbit in the Kitimat River and concluded that the potential for chronic ecological risk was the greatest for wildlife species occupying the floodplain or riparian habitat and having relatively small home-range sizes.

7.2.6.3 Health risk assessment

Health risk assessment is used to provide individuals with an evaluation of their health risks and quality of life. The main objectives include assessing human health, estimating the level of health risk and providing feedback to participants to motivate behavioural change to reduce risk. The results can reflect the impacts of oil spills and response activities on human health and therefore aid in decision-making as to whether or not and to what degree responses should be conducted (Crosby et al. 2013; Nicholls, et al. 2014; Bostrom et al. 2015).

Baars (2002) estimated the health risk for people involved in beach cleaning, sunbathing and swimming on the coast of Brittany, France, due to the wreckage of the oil tanker *Erika* in 1999. The results suggested that the risks were limited only to people who had bare-hand contact with the oil. Aguilera et al. (2010) reviewed the possible consequences of exposure to spilled oil on human health. Barenboim and Saveka (2012) introduced the biological impacts of individual petroleum hydrocarbons into the determination of the risk of oil spills for biota and humans. Michigan Department of Community Health (2014) evaluated the health risk associated with an oil spill on the Kalamazoo River and found that chemical levels found in surface water were not expected to cause long-term harm to people's health. It was also deemed that the concentrations of hydrocarbons found in fish from the Kalamazoo River and Morrow Lake would not harm people's health. Yee et al. (2015) carried out a Human Health Risk Assessment (HHRA) to assess both potential acute and chronic risks to human receptors in the unlikely event of a full bore pipeline break. The model was tested by a hypothetical spill with the proposed pipelines used for transporting oil extract from the Alberta oil sands to refineries or to coastal terminals for international export. The results showed that risk management strategies targeting the protection of the exposure pathways with relatively high contribution to human health risk (e.g., consumption of below ground and root vegetables and fish ingestion) during the remediation would be important to reduce the risk.

An emerging concern has been raised on the psychosocial impacts of a major oil spill. Grattan et al. (2011) used a community-based participatory model to conduct the standardized assessments of psychological distress (mood, anxiety), coping, resilience, neurocognition and perceived risk on residents of fishing communities who were indirectly impacted (n = 71, Franklin County, FL) or directly exposed (n = 23, Baldwin County, AL) to coastal oil. They found the residents of both communities displayed clinically significant depression and anxiety but no significant differences between community groups. They further pointed out that current estimates of human health impacts associated with the oil spill might underestimate the psychological impact in Gulf Coast communities that did not experience direct exposure to oil. Income loss after the spill might have a greater psychological health impact than the presence of oil on the immediately adjacent shoreline. Gail et al. (2014) compared the psychosocial impacts caused by the 2010 DWH oil spill and the 1989 EVOS based on surveys of local residents collected a certain period of time (12 and 18 months, respectively) after each of the spills. The analysis revealed similarly high levels of psychological stress, tied to renewable resources, concerns about their economic future, worries about air quality and safety issues regarding seafood harvests in oiled areas.

It is valuable to incorporate a comprehensive examination of ecological and human health risks of oil spills into contingency planning and response decision-making (Cao and Fan 2013; Crosby et al. 2013; Bostrom et al. 2015). It would allow spill contingency planners and decision-makers to determine optimal risk-based response strategies, calculate the costs and benefits under different scenarios and choose the best scenario (or make the optimal decisions) to guide response actions (Gala et al. 2009; Etkin et al. 2011; Etkin 2012a; Fernandes et al. 2013). Linkov et al. (2006) suggested that decision analytical methods could incorporate risk assessment into integrated frameworks. A key attribute of the methods is the ability to engage stakeholders, providing for an opportunity for a shared understanding of the issues, and the importance of particular assumptions and model or data results on the assessment of alternatives (von Stackelberg 2013).

7.2.7 Cleanup process simulation and control

Process control is defined as an engineering discipline that deals with mechanisms and algorithms for maintaining the output of a specific engineering process within a desired range (Jing et al. 2012, 2015). *For oil spills, the knowledge and prediction of dynamic response processes to the variations of environmental conditions and operational factors are critical to ensure an optimal operation of the response process. A clear understanding of the mechanism of a response process (e.g., booming, in situ burning, skimming, dispersion and bioremediation) will help to quantify the direct relationships among the inputs (e.g., number and types of skimmers) and outputs (e.g., recovery rate), as well as the indirect relationships, such as the time-series correlation* (Jing et al. 2015). Modeling of oil behaviour, effects and fate, along with the influence of spill response measures (e.g., skimming or dispersion), has been recognized as an essential component and foundation of successful process control strategies (Li et al. 2014b). *A numerically simulated response process can provide the decision-makers with a dynamic means to optimize oil spill recovery and cleanup operations. Particularly with the real-time aid of process simulation and control tools during spill response actions, the response efficiency and effectiveness can be promoted and the overall time and cost of recovery can be minimized.*

7.2.7.1 Gaps in cleanup process modeling

In dealing with an oil spill event, responders always require fast and accurate estimates of the spill to make timely and effective decisions in deploying skimmers, applying dispersants or conducting other response activities before, during and after the spill event. However, *complexity and dynamics inherently exist during oil spill response processes emanating from the fate and transport of spilled oil, existing climatic and oceanic conditions, operation of cleanup equipment, as well as their interactions, all of which cause significant challenges in response decision-making. Traditional physics-based spill models are weak in providing a good solution.* A few studies have explored the possibility of simulating oil recovery processes based on empirical oil weathering models and artificial equipment performance settings (Buist et al. 2011; El-Zahaby et al. 2011; You and Leyffer 2011; Zhong and You 2011), but *technical and knowledge gaps persist in how to obtain accurate and timely forecasting results under varying environmental conditions. This is especially true in harsh environments where the window of opportunity for spill response is significantly shorter, and more efficient decisions and actions are highly recommended.* Chen and his group (Jing et al. 2012; Li et al. 2012a, 2014b,c, 2015) proposed a set of simulation-based dynamic nonlinear programming approaches to optimize the number and operation of oil skimmers during a spill in a fast, real-time and cost-efficient manner based on the consideration and modeling of oil weathering processes. *Nonetheless, the modeling of response processes when using different cleanup techniques, such as booming, skimming, in situ burning, dispersant application and bioremediation, still face many challenges due to the lack of background data, high nonlinearity and various uncertainties from oil properties and weather conditions.*

7.2.7.2 Special considerations for harsh environments

Cold and harsh environments in northern Canada and the Arctic are usually characterized by a wide range of wind speed and direction, limited visibility, low temperature, rough water surface, ice coverage, etc., posing substantial challenges for oil spill cleanup process simulation and control (Oskins and Bradley 2005; Keller and Clark 2008). For example, considerable amounts of fixed or floating ice may occur in the winter in both inland waters and offshore areas (Cleveland 2010). The presence of ice is a key factor affecting the ability to respond to a spill, as well as the modeling efforts (DeCola et al. 2006). The physical distribution and condition of spilled oil under, within or on top of the ice plays a critical role in determining the most effective response strategies at different stages in the ice growth and decay cycle. As pointed out by the National Energy Board of Canada's "State of Knowledge Review of Fate and Effect of Oil in the Arctic Marine Environment" (Lee et al., 2011), it is needed to understand the influence of these environmental variables/factors and the influence of various levels of ice coverage on oil fate and behaviours and the associated environmental impacts. A vast amount of basic information is available from the previous laboratory, mesocosm and field studies, as well as lessons learned from the past spills. However, *knowledge gaps still exit on the fate and behaviour of oil in water in ice conditions (solid, slush and frazil ice) and during active periods of formation and breakup of annual and multi-year ice, as well as the impacts on ecosystems. Consequently, the effects of applications of the different response methods under Arctic conditions are hard to forecast and manage in a more timely, eco-friendly and cost-effective manner.* The recent report by Arctic Oil Spill Response Technology Joint Industry Programme (AOSRT JIP 2014) provided a comprehensive review in this regard.

In-depth knowledge and modeling tools for oil fate and transport and effective response technologies are lacking for oil spills in ice and harsh conditions. Existing models have insufficient ability to accurately predict how oil and ice interact and then how oil transforms and moves where ice is present. Most mathematical equations used to simulate oil cleanup/recovery are likely based on empirical approximations and assumptions and are subject to time step and grid limitations. Furthermore, current response technologies are either ineffective or require more scientific and field validation in dealing with oil in ice conditions. These challenges should be addressed to support more effective response decision-making and operations.

<u>Recommendation:</u> Research is needed to develop physical and numerical models for simulating, predicting and optimizing response processes and evaluating their individual and collective effects on response decision and effectiveness, particularly in terms of accuracy and adaptability to different environmental conditions. The dynamic links with spill modeling and decision-making should also be realized.

7.2.8 Response operation optimization

The response to an oil spill is a dynamic, time-sensitive, multifaceted and complex process subject to various constraints and challenges. It is dependent on a variety of factors, including quantity and properties of the spilled oil, location, environmental conditions and availability and utilization of response resources at various degrees of oil weathering (Ornitz and Champ 2003). *Response operations usually need to be undertaken within a limited time window and improper decisions may compromise the efficiency of oil recovery and waste resources. It is highly desirable to develop and implement an optimized strategy to better coordinate different types of operations.* You and Leyffer (2011) developed an approach for oil spill response planning with integration of the physiochemical evolution of oil slicks. The approach includes a dynamic oil weathering model and can simultaneously predict the optimal coastal protection plans and oil spill cleanup schedules with different types of mechanical, burning and dispersant application equipment. The results demonstrated the importance of integrating an oil transport and weathering model in response planning. Zhong and You (2011) addressed the optimal planning of oil spill response operations under the constraints of economic and responsive criteria, with consideration of oil transport and weathering processes. A multi-criteria, multi-period linear programming model was developed that minimizes the total cost and response time-span and simultaneously predicts the optimal time trajectories of the oil slick's volume and area, transportation profile, usage levels of response resources, oil spill cleanup schedule, and coastal protection plan. Li et al. (2012a, 2014c) proposed a simulation-based nonlinear optimization approach to provide sound decisions for skimming spilled oil in a fast, dynamic and cost-efficient manner, which especially targeted harsh marine environments. The model was further integrated with the optimization method to determine the optimal strategy to achieve the maximum oil recovery within constraints of time and resources. The approach was tested using hypothetical case studies showing its capability of efficiently incorporating the process simulation and optimization into the same modeling framework to improve skimming effectiveness. Efforts are being made to incorporate these approaches into existing modeling software or new decision systems with user-friendly interfaces to become effective tools for onsite use and training by responders.

Recommendation: In general, response decision-support systems are rare and only present limited degrees of integration between oil spill modeling, cleanup process simulation and/or risk assessment, but their dynamic and interactive features need to be significantly enhanced, and more field validation efforts are urgently required to increase the confidence for implementation.

Uncertainty, which is one of the major hindrances to improving the efficiency of cleanup process simulation and control, may arise from a variety of sources. Such sources include, but are not limited to, incomplete information, errors in sampling, subjective judgment, random variations of and dynamic interactions among operating factors, approximations and assumptions in measurement, and changes of environmental conditions (Huang et al. 2001; Lin et al. 2009; Liu et al. 2009). *Uncertainties lead to difficulties in developing optimization models for supporting decision-making in oil spill response and impair confidence of decisions.*

7.2.9 Information technologies for response decision making

7.2.9.1 Geomatics, remote sensing, and geographical information systems

Geomatics (or geomatic technology or geomatic engineering) is a hybrid field of gathering, storing, processing and presenting geographic information or spatially referenced information (Zhu et al. 2013; Song et al. 2014). The techniques of geomatic analysis, remote sensing and GIS have been widely used in oil spill response. The Central Gulf of Mexico Ocean Observing System (CenGOOS), along with remote sensing and GIS, were adopted in monitoring and forecasting the DWH spill (Howden et al. 2011; Li et al. 2012b). Morović and Ivanov (2011) discussed the properties of synthetic aperture radar (SAR) imagery as the most reliable source of oil spill information and the possibilities of a combined SAR-GIS approach for oil spill monitoring and management for the protection of the Adriatic Sea. Pan et al. (2012) used multi-source remote sensing data, including MODIS data, and advanced SAR images to study the aftermath and delineate the extent of the 2006 Lebanon oil spill. Dollhopf et al. (2014) introduced a multiple-lines-of-evidence approach for assessment and recovery of submerged oil by integrating with a robust GIS tool. The approach helped optimize the assessment and recovery, inform the decision-making related to transitions and endpoints, and improve the cleanup efficiency while limiting the long-term ecological damages from the recovery activities.

7.2.9.2 Data mining and artificial intelligence

Knowledge Discovery (KD) effectively uncovers hidden but subtle patterns from large and diverse datasets and outperforms traditional statistical techniques. Data mining, a major stage in the KD process, is the analysis of datasets that are observational, aiming at finding out hidden relationships among datasets and summarizing the data in a manner that is both understandable and useful to the users. Many artificial intelligence (AI) tools have been used for data mining, such as neural networks, fuzzy logic, ant colony algorithms and genetic algorithms. *Given these features, data mining and AI tools have received increased interest and efforts in addressing the complexity and dynamics of oil spill and response operations and seeking optimal solutions for risk assessment and decision-making* (Cai et al. 2009; Akinyokun and Inyang 2013). Some new methods, such as fuzzy neural network (Cao and Fan 2013; Inyang and Akinyokun 2014) and predictive Bayesian model (Echavarria-Gregory and Englehardt 2015), have been developed and applied to assess oil spill risks and characterize their patterns.

7.2.9.3 Results visualization

Preferably, an integrated oil spill response decision support system would include visualization of not only past and current situations, but a dynamic probability envelope for the future spill positions and the associated risks, time and costs under different response scenarios, much as is done in the hurricane/typhoon and flooding forecasting community (Sanyal et al. 2010). However, *present oil spill visualization systems are generally based on producing either a snapshot map of representative oil spill particle trajectories or a movie of an evolving point cloud of particles* (Kang et al. 2013; Hou and Hodges 2014). Furthermore, as geomatic technologies become more powerful and usable over desktops and even mobile platforms (e.g., smart phones, tablets), oil spill visualization systems should use GIS standard formats for output data to allow web-based access for emergency response personnel (Yu and Yin 2011). *Standardization within a GIS can allow spill trajectories to be linked to existing index systems (e.g., environmental or ecological sensitivity index) that classify sensitive coastal areas by their degree of exposure and vulnerability.*

Fernandes et al. (2013) described recent updates of the oil and inert spill modeling component of MOHID model, including interfacing with meteorological and oceanographic data and the integration with decision support systems. This system revealed a good stability and strong performance in visualization of weathering processes and properties. The rich image resources of satellite remote sensing Google Earth was selected as the client during constructing the system. The system solved data exchange and data storage of KML between Google Earth and Oracle by connecting them, which realized the visualization of the oil spill system. Hodges et al. (2015) introduced methods to integrate existing oil spill models, servers, connections to online data services and visualization tools to support response decision-making. To improve deepwater oil spill emergency response, Wei et al. (2015) built a high-resolution hydrodynamic data field and a 3D visualization system based on oil behaviour and fate.

The oil spill response community will greatly benefit when current technical challenges and knowledge gaps are overcome to enable the coupling of advanced modeling and visualization techniques to address questions such as:

- How to integrate a dynamic spill modeling system with remote sensing, GPS and GIS to turn real-time information into real-time decisions and then visualize them;
- How to combine oil fate and transport modeling, environmental risk/impact assessment and cleanup process simulation and optimization with information technology to achieve the best response efficiency while minimizing time and costs; and
- How to visualize the levels of uncertainties within models to evaluate their risk.

7.3 Summary

This chapter reviewed the current development and practice of oil spill prevention and response decision-making in Canada and beyond. Prevention and preparedness have been emphasized as the key factors to proactively reduce the potential damage of oil spills. With a high level of knowledge, many potentially high-risk activities can be anticipated and may be mitigated or prevented. Cutting-edge monitoring and oil analysis technologies, as well as advanced vulnerability assessment and contingency planning methods, can help identify and even prevent unexpected oil spills in an efficient, timely manner. Baseline data of environmental and ecological conditions before spills take place in areas of high spill probability are critical in support of spill preparedness and response decision-making. A well-structured response regime, an established spill contingency plan and existence of active programs for training, drills and education are critical for a country or region to effectively combat oil spills and minimize the damage to the environment and danger to human health.

Responses to an oil spill can be highly dynamic, time-sensitive, multifaceted and complex due to uncertain or changing information (location, oil properties, weather, currents, etc.) and response resources (devices, manpower, money, etc.). A successful response operation usually starts with an accurate detection of an oil spill through imaging analysis and early warning. The selection of BATs and the precise prediction of oil trajectory to combat the oil spill also play important roles in terms of saving cost and time. NEBA and risk assessment tools usually offer the decision-makers quantitative information to evaluate the damage and to prioritize the response technologies. Cleanup processes should be simulated and optimized simultaneously in order to improve the response effectiveness within a limited time window. With the aid of advanced techniques, such as geomatic analysis, AI and computer visualization, oil spill response decision support systems should be capable of not only integrating spill and cleanup modeling and risk assessment but recommending, and graphically presenting in the most simplistic format, optimal decisions and corresponding impacts under different scenarios to responders and stakeholder before or during a spill. In addition, post-event assessment is recommended to deal with changing conditions, such as weather and subsequent work activities. It should be noted that the efforts of integrated oil spill response decision-making have been limited due to the complex, dynamic, and uncertain nature of oil spills. More efforts toward the improvement of oil spill preparedness and decision-making are highly desirable, particularly for some emerging challenges such as dilbit spills, derailments and harsh environments.

7.4 Research Needs and Recommendations

7.4.1 High Priority Research Needs

- Research is needed to develop modeling methods to simulate, predict and optimize individual and collective cleanup processes (e.g., booming, in situ burning, skimming, dispersion and bioremediation) and their effects individually and collectively for supporting response decision making.
- Research is urgently required on development and demonstration of integrated oil spill response decision support systems (DSS). Such systems should be capable to integrate monitoring and early warning, spill modeling, vulnerability/risk analysis, response process simulation/control, system optimization, and visualization in a dynamic and interactive manner. Response decision making and implementation are challenged by harsh environments in northern regions and Arctic waters which has a short window of opportunity and can pose large amounts of uncertainty and difficulties in using traditional modeling and response methods.
- Research investment is needed for trial tests and field validation of new prevention and decision-making methods to demonstrate feasibility, increase confidence for implementation and improve response capabilities.
- Research is needed to better quantify uncertainties, evaluate their propagation and mitigate their impacts throughout spill response systems and decision-making processes. Uncertainty is one of the major hindrances to improving the efficiency and integrity of spill modeling and decision making tools and then the confidence and effectiveness of response decisions.
- Further research is desired on environmental forensics (e.g., new biomarkers and fingerprinting methods), remote sensing and in situ measurement, and biological monitoring to improve spill prevention and decision-making.

- Special research efforts should be given to the harsh and Arctic environments and some other emerging concerns (e.g., diluted bitumen, aging/subsea pipelines, and railcars) for improving effectiveness and confidence of prevention and response strategies and decisions.

7.4.2 Medium Priority Research Needs

- Concerns over acquisition, integrity, sharing and uncertainties of baseline data make oil spill contingency planning and response decision-making less able to meet response needs. (refer to Chapter 4)
- Innovative research should be strongly encouraged to develop more cost-efficient and eco-friendly response technologies (refer to Chapter 6). Meanwhile, there is a need for updated regulations to govern the use of response technologies (e.g., dispersants) especially for their Arctic and subsea applications, which should be based on improved knowledge and better understanding of their long-term impacts.
- Oil leakage from routine operations and discharges of hydrocarbons with wastewater (e.g., produced water, ballast water, bilge water and quench water) in the oil and gas industry is not given sufficient attention in comparison with accidental spills in terms of research and policy development. Quantitative evaluation of cumulative effects of long-term leakage and/or discharge of persistent and toxic oil components (e.g., PAHs) and development of in situ advanced treatment and recovery methods are recommended.
- Most response systems lack effective early warning functions/ability to identify, diagnose and react promptly to minimize oil discharge into the environment at the early and critical stage of the emergency. Incorporation of early warning indicators for potential events into real-time monitoring, quantitative risk analysis and response preparedness is recommended.
- Oil leak detection systems need to be further developed to detect spills rapidly after an incident. More comprehensive and reliable in situ and remote detection methods are needed. Research and implementation of autonomous, remotely operated detection devices (e.g., AUVs and ROVs) technologies should be encouraged.

7.4.3 Low Priority Research Needs

- Analysis of cumulative impacts remain a challenge for NEBA of oil spill response options. Influence of human judgment and socioeconomic factors should be more effectively reflected in the NEBA process. There is also a need to assess the NEBA against emerging issues of concerns (e.g., dilbit), countermeasures (e.g., bio-dispersants) and special environmental conditions (e.g., ice coverage, permafrost and peat lands) to identify knowledge gaps for decision making.
- It is critical to properly assess the real significance of spills and subsequent response activities and to develop lessons learned in preparation for future events. The requirements for improved onsite and post-incident monitoring and assessment should be better defined. Adaptive management, as a systematic process, is encouraged to continually improve management policies and practices by adjusting subsequent actions based on learnings from past events and new knowledge development.
- There is no comprehensive national framework in place for training and drilling exercises for ship-source oil spill preparedness and response that involves all key stakeholders. Most current exercises are artificial as the equipment and vessels are pre-assigned and the personnel are pre-notified or even pre-positioned. Unannounced spill response drills are sometimes necessary to test the operator’s response capacity to contact, move and deploy the whole response team.
- Education through social media is being used and should be further encouraged in order to improve the way the community is informed and engaged during oil spills about the situation and how decisions are made. Educational outreach to enhance literacy and promote preparedness and responses should be a key part of the training..

CHAPTER 8: RISKS FROM OIL SPILLS

Abstract

This chapter provides a review of the important factors affecting the consequences of selected oil spill case studies and presents lessons learned from each spill. Uncertainties and research needs revealed by each spill case are presented. The strengths and weaknesses of relative risk assessments are discussed and recommendations are made to improve the current practice of risk assessment in Canada.

A review of selected oil spill cases illustrated that each case had a unique combination of site-specific factors. There were different combinations of factors that either increased or decreased the overall impacts of each spill. The conclusions arising out of examination of the case studies are listed below.

- Delayed response was a critical factor affecting the consequences of all the oil spill case studies. Notwithstanding the importance of weather, remote locations and technological challenges, human error (at an individual and organizational level) was a dominant factor across all case studies. Absent or inadequate planning, insufficient integration, inadequate training, poor communication, insufficient capacity (personnel and equipment), poor or no information sharing, and lapses in regulatory oversight were noted for most, if not all, spill case studies.
- The consequences of oil spills cannot be predicted simply on the basis of the type of crude oil, although in general, spills of light crude had greater acute effects. Long-term effects were dependent upon a combination of the type of crude oil, characteristics of the receiving environment (including season) and effectiveness of cleanup.
- The lack of pre-spill baseline data seriously limits the ability to predict or monitor long-term effects of crude oil spills on populations and communities of aquatic organisms.
- Major advances in the development and validation of spill response technologies are seriously limited by the inability to conduct controlled field experiments with oil.
- Standard accepted methods have not been established for post-spill monitoring and validating the efficacy of oil spill response protocols and operational endpoints (How clean is clean?).
- Effects of oil spill cleanup on aquatic ecosystems can be significant.
- Aquatic ecosystem resilience to shocks from oil spills is the key to the maintenance of ecosystem services. The presence of long-term stresses may tax the capacity of ecosystems to be resilient to shorter-term shocks.

A review of relative risk assessments for coastal areas of Canada and Alaska and risk assessments done in support of Environmental Impact Assessments (EIAs) generated the following conclusions:

- The data needed for input to risk assessments in Canada are often either absent or widely scattered among government agency, industry and academic sources;
- Information needed for reliable environmental sensitivity indices is very limited for large portions of Canada;
- Input from Indigenous peoples and interested parties is required to produce reliable and credible information to be used for environmental sensitivity indices;
- Assessments of the risks of hypothetical pipeline spills are likely underestimated given the assumption that it would take only a few minutes to recognize a pipeline breach and deploy shut-off valves; and
- The level of sophistication of risk assessments conducted in support of EIAs varied substantially between regions.

High-priority recommendations arising out of these conclusions are:

- Collect and evaluate baseline information from high-risk, poorly-characterized areas in Arctic coastal areas and in freshwater systems (e.g. inland rivers with multiple pipeline crossings, the Great Lakes, the Gulf of St. Lawrence);
- Conduct controlled field experiments on oil spills at a variety of sites for the development and verification of current and emerging spill response countermeasures;
- Conduct long-term research into effects of different crude oil types on populations of aquatic biota, including follow-up research at the site of old spills;
- Conduct a program of research on resilience of aquatic ecosystems;
- Develop national guidance for monitoring of oil spills to ensure that information gathered is reliable, adequate, credible and consistent. The guidance should include provisions for adjustment in response to specific characteristics of the receiving environment and should provide details on operational endpoints which identify when cleanup and remediation can cease;
- Include studies of the relative effectiveness of response measures in all investigations of significant oil spills in Canada;
- Pre-approved funding should be put aside for research and monitoring of ‘spills of opportunity’;
- To support the development of improved spill response guidelines, build a comprehensive national database for the fate, behaviour and effects of various types of oil spilled and the efficacy of current and emerging oil spill countermeasures over a range of environmental conditions;
- Investigate the socioeconomic impacts of oil spills in support of assessment of effects on ecosystem services;
- Conduct regional risk assessments in areas of concern to provide further guidance for policy and planning;
- Establish a ‘standard of practice’ regarding the assessment of risk of oil spills in support of EIA in Canada which includes updated and refined assessment methods and a re-examination of appropriate spill scenarios; and
- Integrate traditional knowledge and information about traditional uses of resources into development of sensitivity indices used for risk assessment.

Introduction

To cover the range of potential spill scenarios that Canada may encounter in the future, this chapter examines the risks arising from oil spills into aqueous environments in two main sub-sections: oil spill case studies and reviews of risk assessments of hypothetical spills.

The case studies clearly illustrate that each spill incident is a unique combination of site-specific factors. These factors include: the type of oil; the mechanism of release; the volume of the spill; the weather/hydrology conditions at the time of the spill; the vulnerability of the habitats; the sensitivity of the biota; and the effectiveness of applicable spill response options. The impact of a spill is often influenced by the degree to which the oil reaches shorelines and sediments, as well as the physical-chemical characteristics of the oil (e.g., tar balls, liquids trapped under cobbles, oil mixed with sand, ‘pavement’, etc.). The interactions of various physical-chemical forms of oil with shorelines and sediments influence environmental persistence, bioavailability, toxicity and net environmental benefit of countermeasure strategies applied. In each of the case studies and risk assessments reviewed in this chapter, different combinations of factors either increased or decreased the overall impacts.

The case studies were selected to present combinations of geography, oil type and environmental factors that influenced the response, outcome and knowledge gained:

- Marine environments:

- The *Arrow* tanker spill of heavy fuel oil in Chedabucto Bay, NS.
- The Baffin Island Oil Spill (BIOS) Project involving deliberate release of crude oil into the Arctic environment.[1]
- The *Exxon Valdez* tanker oil spill (EVOS) of medium crude oil into cold, pristine conditions with intensive shoreline intervention, in Prince William Sound, AK.
- The Deepwater Horizon (DWH) spill of light crude into the deep subsurface and shoreline environments of the chronically oil-impacted Gulf of Mexico, with unprecedented subsurface application of dispersant.

- Freshwater environments:
  - A pipeline spill of sour light crude into the Pine River, BC.
  - A derailment spill of a type of Bunker C oil (HFO 7102) into Wabamun Lake, AB.
  - A pipeline spill of dilbit into Talmadge Creek and the Kalamazoo River, MI.
- Recent Canadian spills in 2015:
  - The *Marathassa* Intermediate Fuel Oil (IFO) spill in English Bay, Vancouver, BC.
  - Nexen Long Lake pipeline bitumen emulsion spill near Ft. McMurray, AB.

For each case study, the important factors affecting the consequences are identified. Lessons learned are then listed. Finally, a list of research needs illustrated by the case study are identified and presented in **bold**.

The risk subsection reviews: 1) predictive relative risk assessments conducted in support of policy and planning (Transport Canada's review of Canada's preparedness and response for ship-source spills); 2) risk assessment in support of EIAs prepared as part of the regulatory approval process for proposed projects (e.g. the Northern Gateway Pipeline); and 3) risks from crude-by-rail transport. Reviews included evaluation of the risk assessment methods used, the key factors contributing to risk, and the primary uncertainties associated with the prediction of risk from oil spills. Recommendations for the improvement of risk assessment based on the Panel's findings are presented in **bold**.

8.1 The Arrow Spill

On February 4, 1970, the aging tanker *Arrow* encountered severe weather as it entered Chedabucto Bay, NS. She ran aground on Cerberus Rock, a well-known navigational hazard. Severe weather hampered attempts to off-load her cargo of Bunker C crude oil (Table 2.2) and on February 8, the tanker split into two releasing about two-thirds of her cargo (10,000 tonnes of oil) into the icy waters of Chedabucto Bay, much of which took the form of an oil-in-water emulsion that affected 300 km of coastline. Retrieval of the remaining oil from the wreck was completed on April 11, 2015, using pioneered techniques subsequently used in other tanker accidents (Maritime Museum of the Atlantic 2015).

The *Arrow* spill provides a long-term case study of reliance on natural attenuation (defined in Chapter 3). Only 48 km of the approximately 305 km of oiled shoreline were cleaned (Owens 2010). Cleanup primarily involved manual and mechanical removal of oiled coarse sediments, typically contaminated to a depth of 25-100 cm and occasionally as much as 200 cm (**Figure 8.1**). The average volume of oiled sediment generated by manual cleanup was approximately an order of magnitude less than mechanical removal using bulldozers and front-end loaders; this had implications for waste management. In terms of long-term impacts, mechanical removal of oiled beach material resulted in retreat of the beach crest at some locations for periods up to 10 years (Owens 2010).

[1] *In addition to the information summarized in this report, the Panel notes a recent report by the Arctic Oil Spill Response Technology Joint Industry Programme (AOSRT 2014), which provides a comprehensive literature review and recommendations regarding the assessment of environmental impacts of Arctic oil spills.*

Figure 8.1. Testing the use of lime during shoreline clean-up of the Arrow spill. *Image courtesy of Ed Owens.*

Time-series measurements of petroleum-derived hydrocarbons in the water column of Chedabucto Bay demonstrated that concentrations returned to pre-spill levels within a year (Levy 1972). Time-series measurements in 1970, 1973 and 1976 showed a dramatic reduction in shoreline oiling, with 75% of the heavily oiled shoreline cleansed by 1973, even in sheltered areas with low wave energy (Owens 2010). By 1992, approximately 250 km of oiled shoreline were cleaned naturally, of which about 70 km were sheltered environments where physical processes such as wave action and abrasion would have played only a minor role in weathering and degradation (Owens et al. 1993; Owens 2010). The coastal waters of northern Chedabucto Bay are rich in clays and these clays can interact, albeit slowly, with shoreline oil suggesting that the formation of clay-oil emulsions (also referred to as clay-oil flocculation, oil-mineral aggregates or OMA (Chapters 2 and 6) played a significant role in the natural removal of shoreline oil and subsequent biodegradation (Owens 2010).

Twenty years after the spill, Vandermeulen and Singh (1994) studied two beach sites in Chedabucto Bay and found that both contained a spectrum of degraded petroleum residues, from seemingly unaltered to severely weathered residues. The authors noted that the relatively permeable nature of the Chedabucto Bay sediments permitted stranded oil to become sequestered and protected within shore sediments (**Figure 8.2**). The authors concluded that persistence was a direct function of beach sediment permeability, sediment grain size and the depth to which entrapped tar residues penetrate. Persistence was an inverse function of the depth and frequency in which sediments were reworked during tidal incursions. The authors noted that the oil residues trapped within the spaces of protected sand-gravel lagoons and deep cobble/boulder beaches would be the primary long-term source of hydrocarbon movement to pore water and surface water. The chemistry of some of the sequestered residues still closely resembled the original spilled oil (Vandermeulen and Singh 1994). In contrast, the surface-stranded Bunker C residues progressively weathered to tar via exposure to oxidation, photooxidation (Chapters 2 and 6) and physical weathering by wave action, sediment scouring and tidal washing.

Thirty-five years later, most of Chedabucto Bay was oil-free, but the areas with surface oil distribution had changed little since mapping in 1992, and some areas of Black Duck Cove (a low-wave energy site) still had residues on coarse-sediment beaches and within fine-grained sediments at an adjacent protected lagoon (**Figure 8.2**, Owens et al. 2008). Exposed highly biodegraded and photooxidized surface asphalt pavements observed in the upper intertidal and supratidal zones in 1992 were being eroded by wave action at slow but observable rates. Subsurface oil that filled the pores below the boulder surface layer was associated with the presence of finer sediments, limiting the downward migration of the oil. Analysis of samples from these environments showed that the oil close to the surface was extensively degraded relative to subsurface oil recovered at depths beneath the surface layer of boulders, cobble and fine sediment where the composition of residual oil was similar to the original spilled material. The authors suggested that the more deeply buried residues in the cobble-boulder areas would likely remain until the sediment was disturbed by major storms as a result of landward barrier migration. These observations on oil persistence supported those from a previous study in the 1990s (Vandermeulen and Singh 1994). Owens et al. (2008) noted that residual oil in the fine-grained sediment of the lagoon area of Black Duck Cove was extensively biodegraded. The authors suggested that this indicated that if unweathered oil is released from the cobble areas into the lagoon, it would be rapidly degraded.

High wave energy may strand oil in the supratidal zone but also removes the oil on shores by erosion. A hurricane removed a sandy beach in Nova Scotia being studied by researchers, and winter storms may have been the most effective mechanism for the removal of stranded oil on rocky shorelines following the EVOS (K.Lee, pers. comm.)

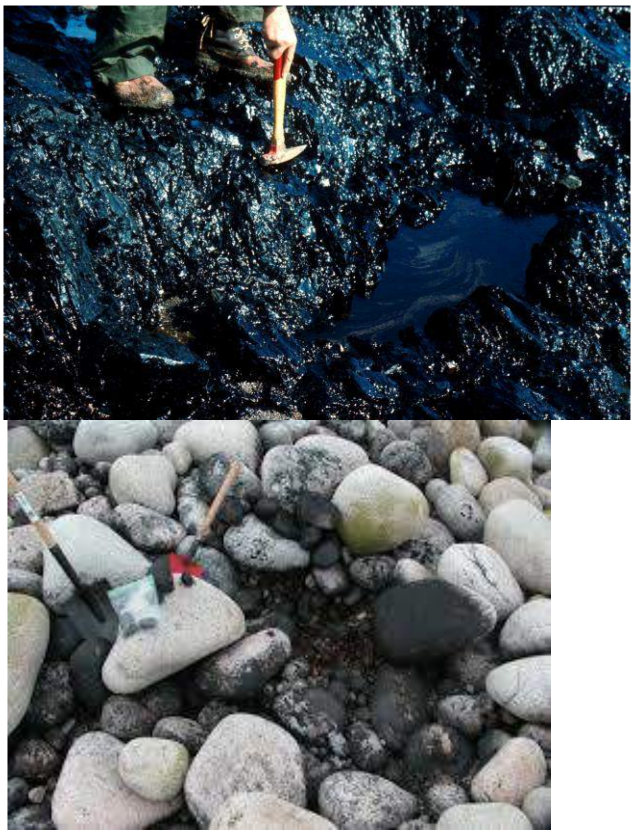

Figure 8.2 Comparison of oil on the shoreline immediately after the Arrow oil spill in Chedabucto Bay, NS and thirty-five years later*. Left: Cobble/boulder beach in 1970 immediately after the spill. Image courtesy of DFO. Right: Interstitial oil residue in Black Duck Cove in 2005. Image from Owens et al. (2008)*

The shorter-term effects of the *Arrow* spill were acute fauna mortality from exposure to the more toxic (and shorter-lived) components of the oil, as well as physical smothering of waterfowl. Certain deposit-feeding polychaetes had a high tolerance for living in sediments contaminated with the Bunker C oil, and their feeding activity accelerated the weathering rate of oil through various processes, including bioturbation and digestion (Gordon et al. 1978a). Other intertidal organisms appeared to be more susceptible. Thomas (1978) observed that within the first six years after the spill, effects included extensive mortalities of the attached algae *Fucus* on rocky shores and mortality of clams and marsh grasses in lagoons. Species diversity was generally lower at oiled sites.

The longer-term ecological risks of the *Arrow* were largely a function of the weathering and release of hydrocarbons from the oil sequestered within beach materials. Longer-term effects were investigated by Lee et al. (1999) in 1993 and 1997, when oil was evident as asphalt pavements, stain on rocks, surface sheen and liquids trapped within sediments at some low-energy sites, such as the lagoon in Black Duck Cove.

Lee et al. (1999) conducted tests at a representative site in Black Duck Cove to determine the toxicity of residual oil to fish (winter flounder), invertebrates (amphipods, sea urchins and grass shrimp) and bacteria. They found that while much oil remained in the sediment, it was of low toxicity in most cases (except for significant mortality in an amphipod survival test) as it had undergone significant biodegradation (Lee et al.1999) and photooxidation processes (Prince et al. 2003). Habitat recovery was indicated by field observations of diverse benthic invertebrate communities within the sampling area (Lee et al. 2003), including green crabs (*Carinus maenus*), soft-shelled clams (*Mya arenaria*), common periwinkles (*Littorina littorea*), amphipods (e.g. *Gammarus oceanicus*) and worms (e.g. *Nereis* sp., *Arenicola* sp.). Exposure to elevated concentrations of bulk remaining oil within the sediment at the site to the flora and fauna has been reduced by burial at depth and dilution by storm events over the years. Tissue hydrocarbon concentrations in *Mya* had declined to levels where residents were harvesting clams from the study area, part of which had become a public park.

Wang et al. (1994) noted that after 22 years of weathering in the environment, most saturated hydrocarbons and polycyclic aromatic hydrocarbons (PAHs) in *Arrow* oil samples had been lost. The analysis of biomarker compounds by GC/MS were required to link residual oil samples to the *Arrow* cargo oil as traditional fingerprint methods could not provide detailed information of the source, characteristics and fate of the spilled oil.

In conclusion, the *Arrow* spill provides a valuable example of the fate and effects of spilled oil and the relative merits of cleanup versus natural attenuation for heavily oiled coarse-grained beaches in mid-latitude environments. Natural processes, including the interaction of oil and fine mineral particles that enhanced the physical dispersion processes, were effective in significantly reducing shoreline oiling such that residual risks appear to have been minimal.

8.1.1 Important factors affecting the consequences of the Arrow spill

8.1.1.1 Oil properties and behaviour

- Severe weather and turbulence resulted in both rapid dispersion of the oil and deposition onto shorelines and lagoon areas.
- Formation of OMAs contributed to relatively rapid natural attenuation of shoreline oiling.

8.1.1.2 Effect of the environment on fate and behaviour

- The presence of cobble/boulder beaches and lagoons with fine sediments provided areas where oil was sequestered and persisted.
- Storms buried and then re-exposed some of the spilled oil.
- Oil under aerobic surface conditions biodegraded at a much faster rate than oil sequestered within sediments with limited oxygen availability and water/nutrient exchange.
- Bioturbation by benthic organisms enhanced oil biodegradation rates.

8.1.1.3 Oil toxicity

- Acute mortality was associated with exposure to the more toxic (and shorter-lived) components of the oil, as well as physical smothering.
- Reductions in chronic effects were correlated to the weathering of the residual oil (including biodegradation) and the episodic release of buried oil within beaches as the result of storm events.

8.1.1.4 Spill response

- The application of active spill response operations was limited by the lack of availability of spill response measures and logistic constraints linked to inclement weather conditions.
- Mechanical removal of oiled sediments generated up to 10 times more solid waste than manual removal.
- Removal of large volumes of coarse-grained sediment without replacement resulted in beach retreat.
- Oil was naturally removed in low-wave-energy environments where fine particles created OMAs that enhanced physical dispersion and biodegradation of the oil.
- The persistence of residual oil was generally inversely correlated to shoreline energy level (e.g. from waves, tides and ice) with oil remaining longer in low energy environments.

8.1.2 Lessons learned from the Arrow spill

- Delayed response due to adverse weather and oil spill response preparedness increased the volume (due to water-in-oil emulsification processes) and extent of spilled oil.
- Over time, natural attenuation can effectively mitigate the environmental impacts caused by oil spills in the marine environment.
- Socioeconomic effects can be both short- and long-term; short-term effects include loss of income among fishermen. Long-term effects are largely aesthetic, and these can cause loss of amenities (e.g., beach use) and tourist income.

8.1.3 Research needs related to the Arrow spill

Recommendation: Further assessment of cumulative effects of the residual oil in Chedabucto Bay should be conducted. The assessment should evaluate species and indicators relevant to all stressors of concern (from all sources) within a defined study area appropriate to the current and predicted future location of stressor sources. The assessment should establish clear thresholds of effect for each indicator such that the incremental contribution of the residual oil to overall cumulative risk can be better understood.

Recommendation: An assessment of the residual effects of the *Arrow* spill on ecosystem services would provide useful information for incorporation into net environmental benefit analysis (NEBA), as well as input to future risk assessments.

8.2 The Baffin Island Oil Spill Project (BIOS)

The BIOS project was conducted from May 1980 to August 1983 in the eastern Arctic at Cape Hatt, on the northern end of Baffin Island (Sergy and Blackall 1987). Information from the study and others, such as the Balaena Bay study[2] were intended for planning, approval and operational phases of hydrocarbon development in the Arctic (Lee et al. 2011).

The BIOS Project consisted of a shoreline study and a near-shore study that involved controlled releases of crude oil. Its primary objective was to determine if the use of dispersants in the Arctic near-shore would reduce or increase the environmental effects of spilled oil and to determine the relative effectiveness of other shoreline protection and cleanup techniques. The secondary objective was to determine the chemical and physical fate of oil in Arctic near-shore and shoreline areas (Sergy and Blackall 1987).

[2] Conducted in 1974-1975 with the principal objectives of assessing the impact of an offshore oil well blowout on the thermal regime of the Beaufort Sea and developing potential countermeasure techniques (NORCOR Engineering Research Ltd. 1975).

The shoreline of the study area consisted of steep, rocky promontories separating coarse sand, gravel and cobble beaches. Open water occurred for about 65 days per year. Tides ranged from 1 to 2 m and the mid-summer mean maximum air temperature was about 7 ^{o}C (Sergy and Blackall 1987). Pre-spill analysis of water, sediment and benthic fauna confirmed that there were very low background petrogenic hydrocarbon concentrations (Cretney et al. 1987a, b, c).

Three bays of similar coastal morphology and sedimentology were selected as test areas. Oil fate was monitored in the intertidal and shallow subtidal zone in the water column, intertidal beach sediments, subtidal sediments and the tissue of selected benthic invertebrates (Boehm et al. 1987; Humphrey et al. 1987a, b; Owens et al. 1987). The measurement of biological effects focused on the small and less mobile subtidal benthic flora and fauna (Sergy and Blackall 1987). The experimental approach was not suitable for the direct measurements of effects on fish, sea birds and marine mammals.

8.2.1 The near-shore study

The near-shore study compared the consequences of dispersing an oil slick close to shore with the consequences of allowing the oil to beach and leaving it to natural attenuation. Two experimental discharges of 15 m^3 of weathered (8% by weight) sweet medium crude oil (Venezuela Lagomedio) were released at each site over a period of six hours or half a tide cycle. Corexit 9527 was the dispersant used in a volumetric dispersant/oil ratio (DOR) of 1:10 (Lee et al. 2011).

The surface slick release began at high tide and under the influence of an onshore wind. The oil was carried up and deposited on the beach by wind and wave action as the tide receded. The oil remaining on the water surface after completion of the full tidal cycle was collected with skimmers. Booms were deployed to prevent cross-contamination between test and reference areas and were left in place for several weeks to contain oil sheen (Sergy and Blackall 1987). The dispersed oil release was achieved using a subsea diffuser pipe placed on the bottom just outside the study area. The currents provided the mixing and movement patterns required to distribute the oil throughout the study area (Sergy and Blackall 1987).

A pycnocline is a boundary layer separating two layers of different densities. A large density difference between surface waters and deep ocean water prevents vertical mixing. Formation of pycnoclines may result from changes in salinity or temperature. Because the pycnocline zone is stable, it acts as a barrier for surface processes.

The untreated surface slick was stranded in the intertidal zone in a manner representative of an accidental spill of moderate severity (Sergy and Blackall 1987). Relatively stable conditions were reached after about 48 hours, when oil on the beach was no longer being refloated in large quantities. During this 48-hour period, about one-third of the oil was recovered from the water surface by skimming, one-third remained stranded on the beach and one-third was evaporated or dissolved in sea water (Sergy and Blackall 1987). Over the next two years, the original amount of stranded oil was reduced by about 70%. Sergy and Blackall (1987) commented that this rate of natural shoreline cleaning was surprisingly high, given the short period during which it could occur and the protected nature of the shoreline. Biodegradation was considered to have removed only minor quantities of stranded oil; the majority of oil removal was attributed to physical processes. Oil residues were highly visible on the beach after two years; however, the distribution of oil was very patchy. The majority of the oil remaining on the beach was incorporated into an asphalt pavement. Some of the oil from the beach was transported by runoff and wave action to the adjacent subtidal sediments; however concentrations were still relatively low after two years (Boehm et al. 1987). *In situ* biodegradation could not be confirmed; therefore it was considered a negligible factor in the removal of sedimented subtidal oil at the low concentrations encountered (Sergy and Blackall 1987).

Concentrations of oil in the water column were low beneath the initial slick and only trace amounts were measured over the subsequent two years.

The subsea discharge of oil/seawater/dispersant was swept by currents through the designated study areas. Oil contacted bottom sediments and organisms from the shoreline to a depth of 15 m. Within a few days the oil was distributed throughout the surface waters of Ragged Channel, including the reference site. The subtidal benthos received average exposures of 300 mg/kg, 30 mg/kg and 3 mg/kg in the two study Bays and the reference Bay, respectively (Boehm et al. 1987). Concentrations of oil in the water column were diluted to near background levels within a period of days. There was minimal recoalescence of oil on the water surface and negligible oiling of intertidal sediments.

Conditions in the immediate vicinity of the subsea release caused benthic organisms to be exposed to high concentrations of toxic aromatic hydrocarbons, which would otherwise have been rapidly lost to surface evaporation (Sergy and Blackall 1987). The dispersed oil was introduced at greater water depths than would likely be the case of a surface oil slick. Sergy and Blackall (1987) noted that in many Arctic coastal areas, the often present and well-pronounced pycnocline would suppress the downward mixing of oil to productive benthic depth zones. The high, short-term exposures to the chemically-dispersed oil produced acute behavioural and physiological effects in a wide variety of animals and, in a few species, a short-term reduction in abundance (Sergy and Blackall 1987). Responses included the emergence from the sediment and/or immobilization of infaunal and epibenthic invertebrates. Recovery and reburial occurred in the two weeks following the spills. No behavioural changes were observed at the other study sites, which were exposed to very low levels of dispersed oil.

Heterotrophic bacteria in the water column were not affected by the surface oil slick and only temporarily affected by the chemically-dispersed oil. Effects on bacteria living in subtidal sediments were also minor (Bunch 1987).

There was no major large-scale mortality of benthic infauna to either oil release. After the two-year post-spill monitoring period, there was no evidence of large-scale mortality of subtidal benthic biota attributable to either the chemically-dispersed oil or the oil-contaminated beach. There were few changes in the populations or community structure of infauna, epifauna or macroalgae (Cross and Thomson 1987; Cross et al. 1987a; Cross et al. 1987b). There were no measured biological effects in the intertidal zone due to the absence of Arctic intertidal life.

There were indications that exposure to the persistent oil residues in subtidal sediments (from both spills) was responsible for medium term (1-2 year) sublethal effects, but only in a few species. For example, there were effects on condition in the bivalve *Macoma calcaerea* and decreases in density of the polychaete *Spio* spp. (Cross and Martin 1983).

Exposure to even low concentrations of chemically-dispersed oil resulted in a rapid and significant uptake by subtidal benthic fauna, particularly the filter-feeding bivalves (Humphrey et al. 1987a). Bioaccumulation was observed over a relatively large area due to the extensive vertical and horizontal movement of the oil cloud. The water column was only a short-term source of oil exposure. Body burdens of filter-feeding bivalves were reduced within two weeks and those of all organisms were reduced considerably within the first year. On a longer term but very localized basis, deposit-feeding benthos living in contaminated sediments had elevated body burdens two years post-spill. In some cases an uptake-depuration balance appeared to exist.

Indirect effects of bioaccumulation were not part of the scope of the BIOS Project. Sergy and Blackall (1987) suggested that tainting may occur in shellfish harvested for human consumption. They also suggested that bioaccumulation may be of ecological significance in concentrated feeding areas for birds and mammals that use benthic biota as a food source. They stated that critical habitat for resource species (e.g. fish, birds and mammals) should be protected from oil of any type, and particularly from floating and beached oil slicks.

8.2.2 The shoreline study

The shoreline study evaluated options for cleanup of oiled shorelines by comparing cleanup methods to natural self-cleaning. Small plots (20-40 m^2) were used in the intertidal and backshore zones of the test beaches (Sergy and Blackall 1987). The same Lagomedio crude was used as for the near-shore study. Oil was deposited mechanically. Both emulsified and non-emulsified oil were used in paired plots (**Figure 8.3**). After application of oil, the plots were left for 24 hours prior to initiation of cleanup tests. This was assumed to represent minimal response time.

Figure 8.3. Shoreline study test plots during the BIOS project. *Image courtesy of Ed Owens.*

Wave energy was the dominant factor in the removal of oil from exposed beaches. On the partially exposed beach, the majority of oil was removed within the first open water season and by the end of the second season less than 0.03% remained.

Rising tides removed large quantities of oil on sheltered beaches over the first two days, after which relatively stable conditions prevailed. Oil was less persistent in the fine-grained sediments than on the pebble-cobble beach, where oil residues were still visible four years post-spill (Sergy and Blackall 1987). Climate and soil conditions played major roles in the fate of oil in the backshore plots. Significant amounts of oil remained in surface and subsurface sediments after three years; however there was considerable change in the composition of the oil due to weathering and biodegradation (Sergy and Blackall 1987).

Cleanup techniques evaluated were based on the operational realities of the eastern Canadian Arctic (Lee et al. 2011). Small labour force and the impracticability of disposing of large volumes of contaminated materials were the primary limiting factors; therefore, the emphasis was placed on the selection of techniques that would either have low labour or simple waste disposal requirements. The methods chosen were: *in situ* combustion; mechanical mixing of contaminated sediments; application of chemical surfactants to disperse stranded oil (BP1100X and Corexit 7664); and application of a solidifying agent to the stranded oil.

Chemical solidification was effective in stabilizing the oil but very labour intensive. Low-pressure flushing by sea water of oiled fine-grained beach sediments did not reduce oil concentrations. Burning also proved ineffective as even high-temperature igniters failed to sustain combustion on oiled cobble beaches. Application of commercial fertilizers to the plots increased bacterial numbers and degradation of oil on fine-grained backshore sediments but not on those of coarse material (Eimhjellen and Josefson 1984). Based on the experimental design (i.e., pseudoreplication), methodologies available (e.g., lack of genomic analysis to study whole microbial community responses) and the type/amount of data collected that limited statistical rigour, Sergy and Blackall (1987) could only suggest that biodegradation, enhanced or natural, was unlikely to be a factor of quantifiable significance except over a long period of time.

Wave energy was insufficient to mix surfactant and oil on very sheltered beaches; therefore, this treatment was ineffective in these areas. The use of surfactants quickly reduced the amount of oil present on the surface of cobble beaches partially exposed to waves. Sergy and Blackall (1987) concluded that surfactants would be most effective on small sections of coast where stranded oil might otherwise have a severe short-term impact or where long-term persistence was not desirable. Furthermore, consideration of the effects of flushing the oil from the beach into adjacent near-shore waters would be required.

Mechanical mixing of oiled intertidal and backshore areas reduced the total hydrocarbon concentrations in surface sediments, but in many cases at the expense of increasing subsurface concentrations (Sergy and Blackall 1987). The technique could be applied where the objective is to reduce contamination of surface traffic, to prevent or reverse asphalt pavement formation, or, in the backshore, to increase rates of weathering and to enhance biodegradation.

8.2.3 Important factors affecting the consequences of the experimental BIOS spills

8.2.3.1 Oil properties and behaviour

- One-third of the near-shore undispersed oil spill evaporated.
- Wave action was the primary mechanism for removal of oil from beaches.
- The majority of the residual oil on the beaches was incorporated into asphalt pavements.

8.2.3.2 Effect of the environment on fate and behaviour

- Rising tides removed large quantities of oil on sheltered beaches over the first two days, after which relatively stable conditions prevailed.
- Oil was less persistent in the fine-grained sediments than on the pebble-cobble beach, where oil residues were still visible four years post-spill.
- Biodegradation was considered a minor factor, but the evidence was inconclusive, especially in light of findings from recent studies using ‘genomic’ techniques.
- Oil persisted for long periods of time on low-energy beaches and backshore areas and in nearby seabed sediments.
- Climate and soil conditions played major roles in the fate of oil in the backshore plots.

8.2.3.3 Oil toxicity

- Biological impacts from both near-shore spills (dispersed and undispersed) were relatively minor and effects were short-term with no evidence of large-scale mortality of subtidal benthic biota and few changes in community structure of infauna, epifauna and macroalgae.
- Exposure to the persistent oil residues in subtidal sediments (from both dispersed and udispersed near-shore spills) was responsible for medium-term (1-2 year) sublethal effects, but only in a few species.
- The subsurface injection of dispersed oil caused benthic organisms to be exposed to high concentrations of toxic aromatic hydrocarbons that would otherwise have been rapidly lost to surface evaporation; responses included the emergence from the sediment and/or immobilization of infaunal and epibenthic invertebrates. Recovery and reburial occurred in the two weeks following the spills.

8.2.3.4 Spill response

- Skimming removed approximately one-third of the undispersed surface oil spill.
- Chemical solidification was effective in stabilizing the oil but very labour intensive.
- Low-pressure flushing by seawater of oiled fine-grained beach sediments did not reduce oil concentrations.
- Burning was ineffective as even high-temperature igniters failed to sustain combustion on oiled cobble beaches.
- Application of commercial fertilizers to the plots increased bacterial numbers and degradation of oil on fine-grained backshore sediments but not on those of coarse material.
- Wave energy was insufficient to mix surfactant and oil on very sheltered beaches; therefore, this treatment was ineffective in these areas.
- The use of surfactants quickly reduced the amount of oil present on the surface of cobble beaches partially exposed to waves.
- Mechanical mixing of oiled intertidal and backshore areas reduced the total hydrocarbon concentrations in surface sediments, but in many cases at the expense of increasing subsurface concentrations.

8.2.4 Lessons learned from the BIOS project

- According to Sergy and Blackall (1987), the BIOS Project provided no major ecological reasons to prohibit the use of chemical dispersants on oil slicks in near-shore areas similar to the experimental sites. Despite the high exposure of benthic organisms to chemically-dispersed oil, there were no major population- or community-level consequences. However, for use in areas where benthic organisms (such as filter-feeding bivalves) are consumed by wildlife or humans, the authors raised concerns over bioaccumulation.
- Sergy and Blackall (1987) stated that chemical dispersion may be the only alternative in situations where the immediate protection of shoreline and near-shore habitats is of primary importance or where a shoreline cleanup operation is environmentally less desirable. They further suggested that where practical and effective application methods and dispersant formulations are available, it would seem appropriate to give pre-spill approval for dispersant use along sections of Arctic coastline with ecosystems typified by the Cape Hatt site.
- Exposure to low-level oil residues in the sediments did not cause significant changes in the subtidal benthic populations over a two-year period following the spill.
- Oil residues persisted for long periods of time on low-energy beaches and backshore areas and in nearby seabed sediments; therefore, cleanup decisions should consider the implications of long-term oil residues to shoreline users and the potential for chronic bioaccumulation or sublethal effects in subtidal benthos.
- The results confirmed that Arctic beaches can be cleaned of oil by natural processes, despite the short open water season, and that this can occur very quickly on beaches exposed to moderate wave action.
- Sergy and Blackall (1987) stated that the BIOS findings show that natural cleaning of oil-contaminated beaches can be an environmentally acceptable option for low-priority shorelines similar to those at Cape Hatt. Response efforts would be more effectively directed toward areas of greater importance and sensitivity, such as shores adjacent to communities, wildlife breeding and staging areas and traditional hunting and fishing camp locations.
- Of the cleanup methods studied, two—surfactant flushing and mechanical mixing—produced an immediate reduction in the quantity of oil on the beach surface. These might be desirable where the objective is to reduce contact between oil and wildlife that frequent the shoreline.

- Washing with surfactant could also be considered as a means to prevent oil-sediment consolidation (asphalt pavement) in the intertidal zone.

8.2.5 Research needs based on the BIOS project

<u>Recommendation:</u> The fate and behaviour of oil (dispersed and undispersed) released due to a subsea blowout in the Arctic requires much more study. Models to predict the trajectory of dispersed oil in open water and under ice are needed. The models will require real-time high resolution meta-data of oceanographic properties to provide emergency response support (Lee et al. 2011).

<u>Recommendation:</u> The relative risks of bioaccumulation across trophic levels in Arctic subtidal communities should be assessed and the results of the assessment used to set research priorities. Risks should be estimated for organisms which consume subtidal benthic species, as well as the benthic species themselves.

<u>Recommendation:</u> The comparative risks of undispersed and dispersed oil spills under Arctic conditions to fish, sea-birds and marine mammals should be assessed. The risk scenarios should include subsea use of dispersants.

<u>Recommendation:</u> Future experimental spill in any environment must use statistically rigorous procedures involving randomized and replicated plots.

8.3 Other Arctic Oil Spill Field Trials

8.3.1 Review of conclusions arising from experimental spills in ice covered waters

Dickins (2011) reviewed research into the behaviour of oil spills in ice covered waters. The Dickins review is comprehensive and provides a base upon which to develop research programs in the Canadian Arctic. At the time of the review, Dickins, noted that the SINTEF Oil in Ice Joint Industry Partnership Program conducted between 2006 and 2009 in the Norwegian Barents Sea, was the most comprehensive Arctic oil spill research program completed. The field trials component of this program was between 2008 and 2009. The SINTEF projects have investigated: oil distribution and bioavailability; fate and behaviour of oil spills in ice; *in situ* burning (ISB) of oil spills in ice; mechanical recovery of oil spills in ice; use of dispersants; and chemical herders on oil spills in ice. Field trials have demonstrated that oil spilled in ice conditions was significantly thicker than in open water, and the final area of spilled oil was much wider in open water (Lee et al. 2011). Thus, oil contained in ice and snow would be thicker and more easily burned or otherwise recovered. Furthermore, containment in ice reduces wave action, and relatively slow weathering in the Arctic environment can provide time for spill response, extending the window of opportunity for mobilizing response activities and enhancing the effectiveness of certain response measures such as burning and skimming (Dickins 2011).

Lee et al (2011) provided a summary of conclusions drawn from experimental oil spills in the Arctic:

- Low water and air temperatures in addition to ice-covered waters generally result in greater oil equilibrium thickness due to smaller contaminated areas and reduced spreading rates;
- Ignitability is enhanced in cold temperatures and ice due to the greater persistence of lighter and more volatile components of petroleum hydrocarbons;
- Ice has a dampening effect on waves; therefore, the sea conditions in areas of the Arctic may be significantly less severe than most open ocean areas, thus allowing for easier marine operations;
- Ice can naturally contain spilled oil and act as a barrier to spreading. The natural herding properties of oil then enhance the effectiveness of ISB by thickening the slick;

- High ice concentrations (7/10 or more) tend to immobilize and encapsulate most spilled oil quite rapidly, particularly from a subsea blowout;
- Ice encapsulated oil is effectively isolated from weathering and allows for a longer window of opportunity to carry out cleanup activities. Effective combustion at a later date is possible because the oil remains unweathered; and
- Most of the Arctic shoreline has a seasonal fringe of fast ice that acts as an effective natural barrier against oil contamination on the coastline in winter.

Lee et al. (2011) also provided a summary of some of the challenges and limitations associated with response to oil spills in the Arctic:

- Oil trapped on or under ice in moving pack ice is difficult to measure because crews cannot maintain continuous operations with immediate means of evacuation;
- Skimming operations can be hindered due to the slow spreading and flow of oil in leads and openings in pack ice;
- Moving vessels during response operations can cause rapid spreading of oil, creating a thinner, less easily recoverable or ignitable slick; and
- Crude oils with pour points of 0 °C or less tend to gel.

8.3.2 Research needs regarding spills in Arctic conditions

According to Dickins (2011), future advances in the ability to respond to spills in ice will require a new approach to permitting experimental spills in the Canadian Arctic. Lee et al. (2011) stated that Arctic field trials could be used to address research questions, such as:

- Remote sensing systems to detect, monitor and map the transport and spreading of oil in ice and below ice;
- Weathering of oil in cold water conditions;
- Development and verification of oil-in-ice drift and fate models;
- Improved mechanical response, such as skimmers, pumping systems for viscous oil and the removal of oil from ice and water;
- ISB in broken ice;
- Oil dispersion enhancement by dispersants and enhanced OMA formation;
- Bioremediation of oil stranded on shorelines;
- Characterization of water-soluble components and biological effects on Arctic species; and
- Development of operational endpoints for spill cleanup operations.

Two major initiatives have been recently funded to address some of these oil spill response knowledge gaps in the Arctic:

The Arctic Oil Spill Response Technology Joint Industry Programme (JIP) was initiated in 2012 and is currently ongoing. It represents a collaboration of ten international oil and gas companies to enhance industry knowledge and capabilities in the area of Arctic spill response, as well as to increase understanding of potential impacts of oil on the Arctic marine environment under the management of the International Association of Oil and Gas Producers. The JIP (described at: www.arcticresponsetechnology.org) has several specific projects each focusing on a different key area of oil spill response:

- Project 1 - Fate of Dispersed Oil under Ice: The project will provide important information for dispersants use in ice-covered marine environments and develop a tool to support contingency planning.

- Project 2 - Dispersant Testing under Realistic Conditions: The project will define the operational criteria for use of dispersant and mineral fines in Arctic marine waters with respect to oil type, oil viscosity, ice cover (type and concentration), air temperatures and mixing energy (natural, water jet and propeller wash). Another objective is to identify the regulatory requirements and permitting process for dispersant and mineral fines use for each Arctic nation/region.
- Project 3 - Environmental Impacts from Arctic Oil Spills and Oil Spill Response Technologies: The project will improve the knowledge base for using "Net Environmental Benefit Analysis" (NEBA) for response decision-making and ultimately facilitate stakeholder acceptance of the role of EIA in oil spill response plans and operations.
- Project 4 - Oil Spill Trajectory Modeling in Ice: The project will advance the oil spill modeling for oil spills in ice-affected waters by evaluating ice trajectory modeling approaches and integrating the results into established industry oil spill trajectory models.
- Project 5 - Oil Spill Detection and Mapping in Low Visibility and Ice: The project will expand remote sensing and monitoring capabilities in darkness and low visibility, in pack ice and under ice. This project is split into two elements: surface remote sensing (i.e. satellite-borne, airborne, ship-borne and on-ice detection technologies) and subsea remote sensing (i.e. mobile-ROV or AUV based and fixed detection technologies).
- Project 6 - Mechanical Recovery of Oil in Ice: The project will evaluate novel ideas for improving efficiency of mechanical recovery equipment in Arctic conditions.
- Project 7 - *In Situ* Burning of Oil in Ice-Affected Waters. State of Knowledge: The project aims to raise the awareness of industry, regulators and external stakeholders to the significant body of knowledge that currently exists ISB.
- Project 8 - Aerial Ignition Systems for *In Situ* Burning: The project will develop improved ignition systems to facilitate the use of ISB in offshore Arctic environments, including ice when the presence of sea ice restricts use of vessels as a platform for this response option.
- Project 9 - Chemical Herders and *In Situ* Burning: The project will advance the knowledge of chemical herder fate, effects and performance to expand the operational utility of ISB in open water and in ice-affected waters.
- Project 10 – Field Research: Results from previous research projects show that many of the advances in our state of knowledge about Arctic response technology were gained through controlled field experiments with oil. This project will pursue opportunities for large scale field releases for validation of response technologies and strategies.

Within Canada, the Churchill Marine Observatory was established in July 2015, with research infrastructure funding is provided through the Canada Foundation for Innovation’s Innovation Fund, Aboriginal Affairs and Northern Development, the Province of Manitoba and collaboration with the universities of Calgary and Victoria. This facility will be a dedicated multi-disciplinary research facility for study on the impact of oil spills in sea ice, as well as the investigation issues facing arctic marine transportation.

Recommendation: The effects of climate change on ice cover and ice behaviour in the Canadian Arctic is an important issue requiring investigation.

Recommendation: Explicit research questions regarding effects on marine biota require further study and validation both for spills under ice-covered conditions and in open-water conditions.

Recommendation: Effects of cleanup activities on Arctic biota require study in order to support comprehensive and reliable NEBA.

Recommendation: If future multi-disciplinary field trials are allowed in the Canadian Arctic, they should be collaborative and incorporate the concerns and knowledge of Indigenous peoples.

8.4 The Exxon Valdez Oil Spill (EVOS)

On March 24, 1989, the *Exxon Valdez* altered its course from shipping lanes to avoid floating ice and struck Bligh Reef in Alaska's Prince William Sound. The grounding was caused by a series of human errors committed by its crew members, including the master; however broader safety issues associated with inadequate policies and procedures within the Exxon Shipping Company, as well as the U.S. Coast Guard were identified by the NTSB (1990). Specific policy and procedure issues included: failure of the Exxon Shipping Company to provide a fit master and a rested and sufficient crew; the lack of an effective Vessel Traffic Service; inadequate personnel training; deficient management oversight; and the lack of effective pilotage services (NTSB 1990).

The remote location, accessible only by helicopter, plane or boat, made government and industry response efforts difficult, as did severe weather with high winds, which came about two and half days later. About 42,000 tonnes of Prudhoe Bay crude oil (Alaska North Slope medium crude oil; Table 2.2) was released into the ocean affecting an area of about 28,000 km^2. The dispersant Corexit 9580 was applied on the day of the spill, but there was not enough wave action to mix the dispersant with the oil in the water (Chapter 6). Some of the surface oil was burned, reducing 113 m^3 of surface oil to a removable residue; however, unfavourable weather prevented further burning. Booms and skimmers (Chapter 6) were deployed for mechanical recovery, but skimmers were not readily available during the first 24 hours, and thick oil and kelp tended to clog the equipment. A major storm 2.5 days after the spill led to extensive mousse formation. About 20-30% of the spilled oil evaporated, was diluted or dispersed into the water column or photooxidized (Chapter 2) (Wolfe et al. 1994). Within three weeks, less than 25% of the oil remained on the sea surface.

Immediate effects of the spill included large-scale seabird mortality (estimates vary but average about 250,000 comprising over 90 species), as well as the deaths of about 1,000 to 5,500 sea otters (Platt and Ford 1996; Ballachey et al. 2014). Twenty-two killer whales died. One pod of highly-exposed killer whales lost seven members within a week of the spill, including three adult females, and an additional seven or eight members of this pod died over the next two years (Spies et al. 1996). Other species affected directly by mortality included river otters, harbour seals and bald eagles, plus unknown numbers of herring, salmon and other fish species (Ballachey et al. 2014).

About half of the oil was distributed along the shoreline and inter- and subtidal areas as far as 970 km from the spill site (Owens 1991; Wolfe et al. 1994)). About 782 km of Prince William Sound (about 16% of shoreline) and 1,315 km of Gulf of Alaska (about 14% of shoreline) were oiled to some degree (Owens 1991; Neff et al. 1995).

Shoreline cleanup included manual removal and the use of surfactants and high-pressure hot water (Chapter 6). The cleanup focused on the intertidal zone, including removal of tar mats, mousse and subsurface deposits, as well as sediment relocation and biostimulation to enhance microbial degradation. An assessment in 1990 showed that most remaining deposits were isolated from the biological environment (with the exception of exposure pathways leading from mussels to sea otter (Chapter 4); therefore, only a few larger deposits of subsurface oil were relocated to the middle and upper intertidal zones where it was subject to wave and tidal action and natural cleaning. Less intrusive cleanup efforts continued through the summer of 1991 involving mostly manual removal and bioremediation. Although biostimulation on an unprecedented scale (48,600 kg N in various nutrient formulations applied at 1,400 different sites) initially accelerated oil removal from shoreline surfaces (Atlas and Hazen 2011), after a few years even the deliberately untreated ('set-aside' or control) sites were equivalent in terms of residual oil load (Pritchard et al. 1992).

The aggressive cleanup methods had significant effects. For example, high-pressure washing (**Figure 8.4**) removed all of the macroalgal and mussel communities in some areas, extending the time to recovery of intertidal communities (State of Alaska 1993). Furthermore, the high-pressure washing, while removing oil from the upper and mid-intertidal zone where its effects were somewhat restricted to relatively tolerant organisms, such as barnacles, rockweed and mussels, transported the remobilized oil into the lower intertidal and shallow subtidal zones where the oil was placed into contact with relatively more sensitive organisms, such as hard shelled clams and crustaceans (State of Alaska 1993). The physical features of the shoreline were also affected; e.g., silty sediments were washed out of the beach areas and into the water. Most of the animals that normally lived in these beach areas required a certain mix of fine-grained sediments; therefore, many would not return until the beach sediments had stabilized (Shigenaka 2014).

Figure 8.4 Cleanup workers spray oil-covered rocks on Prince William Sound with high-pressure hoses. *(Photo Courtesy of Exxon Valdez Spill Trustee Council)*

Eight years after the spill, removal of oil was attempted on armoured portions of beaches in Prince William Sound using high-pressure injection of a surfactant (Brodersen et al. 1997). The cleaning was conducted at the request of the local subsistence-use community. Cleaning resulted in a mean reduction of 62% at treated areas with further reduction occurring in the following year. However, newly visibly oiled sites were exposed by winter storms the year after the cleanup.

Shigenaka (2014) stated that despite the unprecedented scale, duration and cost of the response, modeling of the fate of the spilled oil estimated that the cleanup itself removed only a small portion (a little more than 10%) of the spilled oil from the environment. By far, the largest part of the total was naturally weathered or degraded (**Figure 8.5**).

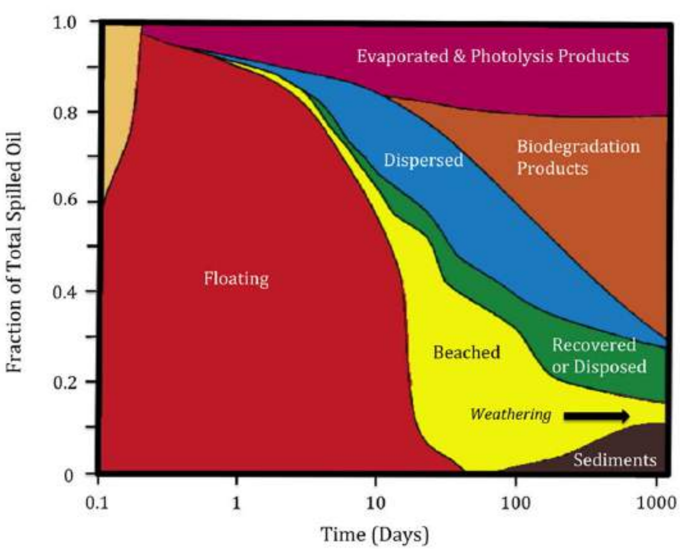

Figure 8.5. Modeled fate of the spilled Exxon Valdez oil with time. *The portion recovered by the cleanup is in green (after 1,000 days). Reprinted with permission from Wolfe, D.A., Hameedi, M.J., Galt, J.A., Watabaytashi, G., Short, J., O'Clair, C., Rice, S., Michel, J., Payne, J.R., Braddock, J., Hanna, S. and D. Sale. 1994. The fate of the oil spilled from the Exxon Valdez. Environmental Science and Technology 28: 561–568. Copyright (1994) American Chemical Society.*

The *Exxon Valdez* Oil Spill Trustee Council (EVOSTC) has adopted an official list of resources and services injured by the spill as part of its Restoration Plan. This list includes fish and wildlife resources that "experienced population-level or chronic injury from the spill" (EVOSTC 2014). The list is divided into six categories (**Table 8.1**). The EVOSTC Restoration Plan was first adopted in 1994 when it was created as guidance for the expenditure of public funds.

Table 8.1 Exxon Valdez Oil Spill Trustee Council List of Resources and Services injured by the Spill

Recovering	Recovered	Not Recovering	Recovery Unknown	Human Services
• Designated wilderness areas • Intertidal communities • Killer whales – AB Pod • Sediments	• Archaeological resources • Bald eagles • Barrow's goldeneyes • Clams • Common loons • Common Murres • Cormorants • Dolly Varden • Harbour seals • Harlequin ducks • Mussels • Ink salmon • River otter • Sea otters • Sockeye salmon	• Marbled murrelets • Pacific herring • Pigeon Guillemots • Killer whales – AT1 population	• Kittitz's murrelets	• Commercial fishing • Passive use • Recreation and tourism • Subsistence

Some authors maintained that the persistent, residual oil in unconsolidated sediments of the intertidal zone continues to contaminate invertebrates to the extent that some vertebrate consumers (including fish, otters and seabirds) are still being exposed to toxic oil concentrations (Peterson et al. 2003; Ballachey et al. 2014). In contrast, other authors have concluded that the Prince William Sound ecosystem has effectively recovered from the EVOS (Harwell and Gentile 2006).

There appears to be a consensus that continued contamination of subtidal areas is not a concern (Ballachey et al. 2014). The authors noted that some of the estimated 55,000 kg of oil remaining in mid- and upper-intertidal habitats may persist at some sites for several decades and that some of the residual oil is largely unweathered because it exists in anaerobic patches where biodegradation is slow (Figure 2.3; Chapter 3). This estimate is for subsurface oil in the upper two-thirds of the intertidal zone. Inclusion of the lower one-third and surface oil would substantially increase this estimate (Short et al. 2004).

Potential chronic effects to the pink salmon population have been linked to direct embryo mortality in the first five years after the spill and continuing exposure to residual oil. Ballachey et al. (2014) summarized the results of several field and laboratory studies of pink salmon, and concluded that these studies "provided compelling evidence of chronic impacts to pink salmon from oil persisting in intertidal habitats". They cited evidence including: 1) observations of elevated embryo mortality in the five years following the spill; 2) identification of the exposure mechanism from contaminated beaches to spawning gravels; and 3) measured effects on fitness following embryonic exposures under laboratory conditions. They concluded that the group of pink salmon studies they reviewed provided "unprecedented evidence that exposure of embryonic life stage (*sic)* to low level PAHs (in ppb) from persistent oil can have a population level effect". Ballachey et al. (2014) also concluded that chronic exposure to oil and possibly latent effects of acute exposure appeared to have decreased survival and constrained recovery of the sea otter population in Prince William Sound for more than two decades.

Not all authors agree that population-level effects on pink salmon persisted. In a detailed review of studies of effects on pink salmon in Prince William Sound, Brannon et al. (2012) concluded that problems with experimental design and methods called into question the potential for population-level effects. Brannon et al. (2012) stated that there was no evidence that weathered oil increased toxicity, either in the form of total PAH or as HPAH (high molecular weight PAH) leachate. They went on to state that field evidence suggested that "well-weathered oil deposits in the actual areas impacted by the EVOS do not represent a continuing and increasing threat of interstitial toxic water to pink salmon eggs incubating in adjacent streams". Further, the authors examined studies of growth rate of juvenile pink salmon in Prince William Sound and concluded that the assumptions necessary to discern growth effects either were not met or contained uncertainties about their validity. As discussed in Chapter 4, the tributaries to Prince William Sound produce so many juvenile fish that any deficit in production in tributaries affected by the spill did not appear to affect total abundance.

The effect of spatial scale may underlie much of the debate regarding effects on pink salmon. Hatchery production of pink salmon in Prince William Sound is comparable in numbers with wild stock production. Hatchery production was not affected by the EVOS, and effects on wild stock production were negligible at the scale of Prince William Sound as a whole. However, pink salmon spawning streams that bisected beaches that were heavily oiled by the EVOS were subject to mortality and sublethal effects on embryos, as stated by Ballachey et al. (2014).

Herring have been the focus of extensive studies since the EVOS because they were commercially harvested in Prince William Sound and their numbers showed large declines within a few years of the spill. The herring population was still very low in 2014 with no commercial fishery present; however, the role of the spill in the decline and lack of recovery of herring, relative to other factors, including disease, predation and recruitment, is unclear and, according to Ballachey et al. (2014), is unlikely that it will ever be completely understood.

> *"If the Exxon Valdez experience has taught us anything, it has emphasized the importance of variability as both a key feature of biological communities and a critical consideration to integrate into assessment of disturbance and recovery. As we inevitably consider oil spill scenarios for the Arctic, they are framed against the background of change that is occurring at unprecedented rates"* (Shigenaka 2014).

Peterson et al. (2003) emphasized that there can be delayed population reductions and cascades of indirect effects that postpone recovery. For example, harlequin ducks appeared to be affected via the energetic costs of metabolizing PAHs, leading to lower body mass and elevated overwintering mortality. According to a study by Iverson and Esler (2010 cited by Ballachey et al. 2014), full recovery of the harlequin duck population would require from 16-32 years under best-case and worst-case scenarios, respectively. Peterson et al. (2003) pointed out that there were also cascade effects from the cleanup actions. For example, the removal of *Fucus* stands with their associated community of grazers, such as limpets and periwinkles, led to initial blooms of green algae and opportunistic barnacle growth with declines in invertebrates associated with the *Fucus* canopy. After regrowth of the *Fucus*, there was another mass mortality in 1994, probably caused by simultaneous senility of a single-aged stand. All of this extended the recovery process for a decade or more.

The Shigenaka (2014) analysis concluded that the intertidal biota of Prince William Sound had recovered, at least in terms of the metrics used in the analysis (attainment of parallel temporal trends in abundance), after an initial six-year period. This conclusion applied to infauna, algae and invertebrates living on the surface of rocky substrates. The authors emphasized that their conclusions were for intertidal populations only.

The *Exxon Valdez* Oil Spill Trustee Council (2015), Harwell and Gentile (2006) and Shigenaka (2015) all note that while the spill and cleanup clearly caused significant ecological effects for months to a few years post-spill, *natural variability and the occurrence of multiple anthropogenic stressors not associated with the spill are now making the detection of any potential residual effects of the spill very difficult.* In addition, current natural and human stressors may be hindering recovery of some resources initially injured by the spill. The passage of time and the evolution of science have shifted the purpose and utility of the Injured Resources and Species List. "The Council recognizes that the complexities and the difficulties in measuring the continuing impacts from the spill result in some inherent uncertainty in defining the status of a resource or service through a specific list and the Council's focus has accordingly expanded to a more ecosystem approach" (EVOSTC 2015).

The inherent natural variability of biological communities complicated interpretation of monitoring data following the spill (Shigenaka 2014). A new statistical approach to analysis was designed, which acknowledged that: unoiled reference sites may be biologically different from oiled sites at the time of impact, thus rendering absolute convergence of conditions in the recovery phase less useful; and conditions at both oiled and unoiled locations are likely influenced by a host of factors not related to the spill disturbance (Shigenaka 2014). The new approach analysed long-term datasets for patterns of abundance. The underlying assumption was that in the absence of spill effects, sites would respond similarly to climate, ocean conditions or other determinants of biological communities in a defined study region.

The risk of oil spills must be assessed against the backdrop of responses to large-scale phenomena. The Shigenaka (2014) analysis noted that results across three independent experimental studies revealed a strong correlation of biological metrics in Prince William Sound with cycles of the Pacific Decadal Oscillation (PDO). For example, mussels and molluscs appear to respond positively to warmer cycles of the PDO whereas rockweed shows greater abundance during cool phases. The author stated that in recent years, linkages between changes in Alaskan biological communities and conditions and large-scale atmospheric, oceanic and climatic shifts have grown more numerous.

The use or interpretation of data in support of specific values or policies is called 'normative science', and, according to Landis (2007), normative science can explain at least some of the differences in interpretation of data related to long-term effects of the EVOS. According to Landis, ecosystem health, ecosystem integrity, ecological significance and recovery are constructs that incorporate values and policies. "Separation of science from policy or at a minimum a transparent acknowledgement of the science-policy interaction is clearly necessary to obtain a clear picture of the ecological system under investigation" (Landis 2007). Landis suggested two alternatives for dealing with normative science: 1) to stop using terms such as ecological significance, integrity and recovery (in the Clementsian context)[3]; or 2) to understand that ecological policy is a complex and multi-component decision-making process that cannot be summarized in metaphorical clichés, such as ecosystem health. If a policy goal is being discussed or supported, it should be clearly defined and obvious to the reader. Landis (2007) asked

[3]*Clementsian ecology is based on assumptions of steady-state equilibrium and development of predictable and specific climax communities, which have fallen out of favour given the complex and dynamic properties of ecosystems.*

whether controversies such as those surrounding long-term effects of the EVOS are really debates about policy rather than scientific merit.

8.4.1 Important factors affecting the consequences of the Exxon Valdez spill

8.4.1.1 Oil properties and behaviour

- Evaporation occurred at lower rates due to low temperature.
- Natural dispersion was wind driven and very widespread.
- Stranding was widespread on shorelines.
- Remobilization of oil deposited on shorelines occurred by tidal and wave action.

8.4.1.2 Effect of the environment on fate and behaviour

- Biodegradation was slow but significant at the ambient temperatures present in Prince William Sound.
- Oil persisted in unconsolidated sediments of the intertidal zone.
- Some persistent oil remained in a relatively unweathered state due to low oxygen conditions in sediments.
- Wave exposure enhanced the weathering of non-sequestered residual oil.

8.4.1.3 Oil toxicity

- Acute toxic effects of floating oil from the spill included large-scale seabird and sea otter mortality.
- Chronic toxicity caused mortality-related damage to the social structure of a killer whale pod. Indirect effects may have postponed recovery of some species (e.g., energetic costs of metabolizing PAHs caused lower body weight and higher winter mortalities in harlequin ducks). Long-term effects of residual oil on pink salmon were caused by exposure of early life-stages and may have been limited to sub-populations using spawning streams that bisected beaches that were heavily oiled.
- Intertidal biological communities recovered relatively rapidly from the combination of oil toxicity and the effects of cleanup activities, although there was a mass mortality of *Fucus* in 1994 (associated with simultaneous senility of a single-aged stand), which extended recovery of areas affected by the mortality by a decade or more.

8.4.1.4 Spill response

- Limited regional response capability and the remoteness of the location with no ground access delayed the response.
- Severe weather following the spill limited some response options, such as ISB and use of dispersants, so that the spread of the surface oil was increased and more oil was entrained into intertidal sediments on affected shorelines.
- Aggressive shoreline cleanup methods, such as high temperature and pressure washing, impaired site recovery rates due to mortality and removal of indigenous species and habitat destruction.

8.4.2 Lessons learned from the Exxon Valdez spill

- Challenges inherent in oil spill response in northern, remote areas prone to adverse weather increase the probability that oil released from near-shore tanker accidents will rapidly disperse and reach shorelines over a wide area.

- Some response measures can be difficult or impossible to implement because of weather and sea conditions (e.g., the use of dispersants or ISB).
- Aggressive shoreline cleanup methods, such as high-pressure washing, can impart substantial negative effects on biological communities, including indirect and cascade effects, and can delay recovery.
- Cleanup removed a small proportion of the spilled oil (about 10%).
- Weathering and biodegradation were of primary importance with respect to the nature and extent of residual oil.
- Altering the physical features of a beach or shoreline can significantly affect the recovery of impacted plants or animals. Physical recovery and stabilization of a site are necessary for biological recovery.
- Long-term, population-level effects are difficult to study and the results can be controversial, which emphasizes the critical need for baseline data on natural resources, as well as consensus-based definitions of monitoring endpoints.
- The inherently high degree of natural variability found in systems such as Prince William Sound can limit or preclude the use of standard or traditional statistical methods. Risks of oil spills in the Arctic must be framed against the background of large-scale oceanic and climatic phenomena and changes that are occurring at unprecedented rates (Shigenaka 2014).
- NOAA found that so-called 'set-aside sites' that were oiled but intentionally left uncleaned have been critical to the NOAA monitoring program's ability to determine impacts due to oiling alone and those due to cleanup, and to enable scientifically rigorous interpretation of data.
- Normative science may have played a role in the debate regarding long-term, population-level effects of the spill. This is not surprising given the high social, economic and cultural value of the receiving environment. The consequences of being wrong about the interpretation of data can be ecological and societal. Therefore, both consequences should be identified and considered in a transparent manner.

8.4.3 Research needs related to the Exxon Valdez spill, in the Canadian context

<u>**Recommendation:**</u> **The most commonly-used suites of biological metrics for Canadian receiving environments (e.g. intertidal or subtidal community metrics) should be examined across broad gradients of natural factors and over longer time-frames to establish the relative roles of local, regional and global factors. Research should be conducted on a range of species and/or communities with various levels of resilience and should focus on identified high risk marine environments (note: WSP and SL Ross, 2014a,b).**

The relative role of local, regional and global factors in determining the natural variability of biological metrics is poorly understood, particularly at the population and community level. Factors, such as climate and oceanographic variability, overexploitation and invasive species, may overwhelm any signal of subtle, long-term effects of residual oils. However, the incremental stress produced by exposure to oil may contribute to 'tipping points' for species whose resilience has already been challenged by other stressors. Furthermore, future field studies should incorporate multiple study areas (both reference and treated) to enable determination of experimental error, which might mitigate the effect of natural variability affecting scientific conclusions.

8.5 Deepwater Horizon (DWH) Blowout

The DWH offshore oil drilling rig was situated in the Macondo oil prospect in the Mississippi Canyon, a valley in the continental shelf of the Gulf of Mexico. The well over which it was positioned was 1,522 m below the surface and extended 5,486 m into the geological formation under the seabed. On the night of April 20, 2010, a surge of natural gas blasted through a concrete core recently installed to seal the well.

The natural gas travelled up the rig's riser to the platform where it ignited, killing 11 workers and injuring 17. The rig capsized and sank on the morning of April 22, rupturing the riser, through which drilling mud had been injected to counteract the upward pressure of oil and natural gas. Without any opposing force, Macondo light crude oil (Table 2.2) began to discharge into the Gulf (Britannica Online 2015).

Several unsuccessful attempts were made to slow or stop the flow of oil, a technically challenging task given the extreme depth of the blowout. A cap was successfully placed in June that greatly reduced the flow, but didn't eliminate it. The well was permanently sealed with the successful completion of a relief well on September 19, 2010. The spill is considered the largest accidental marine oil spill in the history of the petroleum industry. The estimated volume released varied from about 430,000 to 500,000 tonnes (McNutt et al. 2012; Fingas 2013; Chapter 6). According to satellite images, the spill directly affected 180,000 km^2 of ocean (**Figure 8.6**). Response measures included over 1,300 km of containment booms to either corral the surface oil or function as barriers to protect coastal areas, shrimp/crab/oyster ranches or other ecologically sensitive areas. About 7,000 m^3 of two different Corexit chemical dispersants were used, including about 2,920 m^3 injected into the subsurface oil plume at the wellhead during the spill (Chapter 6). Oil was removed from the water surface via ISB, in addition to physical recovery (e.g., booming and skimming).

Figure 8.6 Oil from the Deepwater Horizon oil spill approaches the coast of Mobile, Alabama, May 6, 2010. *Image from US Navy.*

According to the Federal Interagency Solutions Group (2010), the expected mass balance was: 17% of the oil was collected as it was released from the well; 5% was burned; and 3% was skimmed from the surface for a total of 25% (**Figure 8.7**). The fate of the 75% of the oil not collected, burned or skimmed was estimated as follows:

- 13% dispersed naturally;
- 16% dispersed with Corexit;
- 23% evaporated or dissolved; and
- 23% other mechanisms such as stranded on shorelines or sinking to the seafloor.

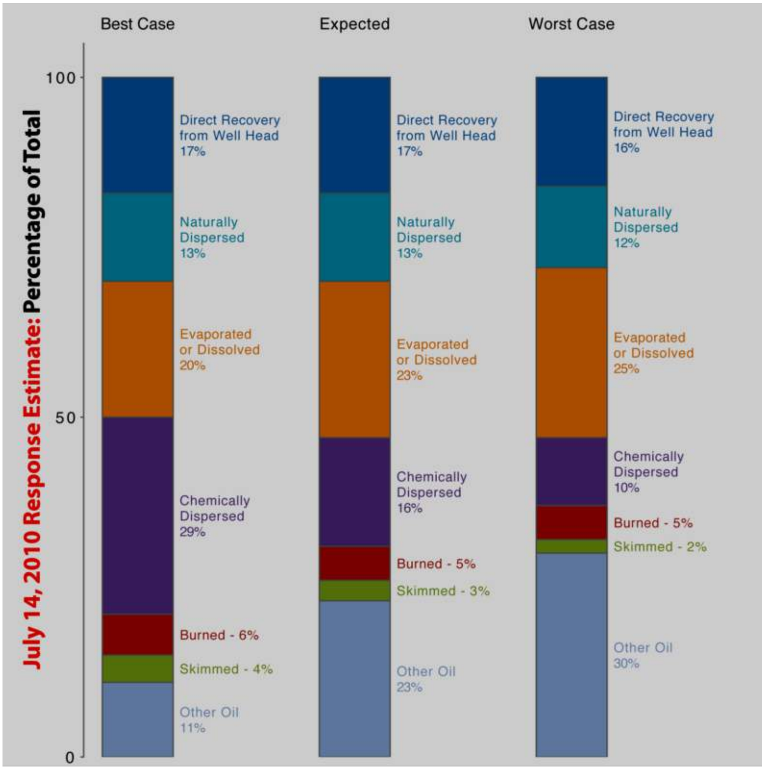

Figure 8.7. Oil budget estimates expressed as percentages of the cumulative volume of oil discharged through July 14, 2010. *These estimates served as a guide for the response to the Deepwater Horizon blowout. Image from Federal Interagency Solutions Group (2010).*

A more recent review of the mass balance concluded that of the total amount of oil released, about 6 to 7% of the oil was burned *in situ*, about 12 to 15% of the oil was skimmed, and about 6 to 26% (best estimate about 10%) of the oil arrived onshore (Fingas 2013). Fingas estimated that 50 to 55% of the oil remained in the water column.

Subsequent results have shown that sinking played a more important role than previously thought. Valentine et al. (2014) suggest that about 318,000 m^3 of submerged oil from the subsurface plume may have been trapped in deep ocean intrusion layers at depths of about 1,000-1,300 m. Based on spatial, chemical, oceanographic and mass balance considerations, they calculated that between 4-31% of oil sequestered in the deep ocean was deposited in patches to deep sea sediments. The pattern of contamination points to deep ocean intrusion layers as the source and was most consistent with dual modes of deposition: 1) a 'bathtub ring' formed from an oil-rich layer of water impinging laterally upon the continental slope (at a depth of ∼900–1,300 m); and 2) a higher-flux 'fallout plume' where suspended oil particles sank to underlying sediment (at a depth of ∼1,300–1,700 m). Independently, Chanton et al. (2015) also calculated that a large proportion of the 'missing' Macondo oil has been partially buried in deep sea sediments in the Gulf of Mexico. The precision of these estimates is still debated due to sample heterogeneity. Furthermore, natural oil seeps, with a fingerprint similar to the Maconda oil, also contributed to uncertainty within the oil budget. In terms of shoreline impact assessments, it was difficult to distinguish tar mats or tar balls originating from the spill from those originating from seeps.

8.5.1 Dispersant use

During the spill response, approximately 6.9 million litres of Corexit were applied, 4 million litres of Corexit 9527 and 9500A at the surface and 2.9 million litres of Corexit 9500 via subsurface injection (Federal Interagency Solutions Group 2010).

One of the controversial aspects arising from the DWH oil spill response operation was the injection of dispersants at the wellhead located at 1,500 m depth. Monitoring programs identified the presence of a plume of oil at a depth between 1,100 and 1,200 m below the surface (Camilli et al. 2010; Reddy et al. 2011). While the plume was initially thought to be direct evidence of dispersant effectiveness, a number of studies suggested that the subsurface dispersants had little impact in dispersing the spill or preventing oil from reaching the surface (e.g., Paris et al. 2012; Peterson et al. 2012). They argued that the turbulence in the jet of gas and oil from the well head was sufficient to induce massive dispersion. Both processes likely occurred. In addition to changes in oil droplet size (Johansen et al. 2013; Brandvik et al. 2013), evidence supporting the benefits of the subsurface dispersant application included aerial photographs taken during the DWH oil spill that showed a loss and gain in the magnitude of the surface slick following subsurface dispersant injection and its shutdown.

The trade-offs regarding the use of dispersants are the subject of debate since the dispersants may also enhance the bioavailability of the spilled oil or be toxic on their own. In a recent review of the pros and cons of dispersants, Prince (2015) concluded that in most cases, the potential environmental costs of dispersant use are likely outweighed by the much shorter residence time of dispersed oil in the environment. Notwithstanding this conclusion, the debate continues.

The fate and effects of the dispersants with associated dispersed oil within the water column of the Gulf of Mexico is the subject of considerable uncertainty. Kujawinski et al. (2011) found that the concentration of dioctyl-sodium sulfosuccinate or DOSS (a key ingredient of these dispersants) was sequestered in deepwater hydrocarbon plumes at 1,000-1,200 m water depth and did not intermingle with surface dispersant applications. They also found that the concentration distribution was consistent with conservative transport and dilution at depth and it persisted up to 300 km from the well, 64 days after deepwater dispersant applications ceased. Thus, the surfactant does not appear to have been rapidly biodegraded. This finding agrees well with the laboratory results reported by Campo et al. (2013) , who showed that at 5 °C DOSS degraded slowly by only 61% in triplicate microcosms by day 42.

While Corexit 9500 and Corexit 9527 are ranked within the low to moderate toxicity level for aquatic species (George-Ares and Clark 2000), a level of sensitivity remains over their application. Evidence from studies with invertebrates and fish have shown that oil dispersed as small droplets in the water column was more bioavailable, and therefore more toxic, than the oil alone (Chapter 4). However, while the results of laboratory studies have raised much media attention over the high risks of dispersant use, ecological relevance must be considered. Following its dilution in an ‘open sea’ environment, it is unlikely that the dispersants would be present in concentrations toxic to pelagic organisms (Kujawinski et al. 2011; Lee et al. 2013). Nevertheless, caution must still be taken as most toxicological studies have been based on short exposure periods (e.g. 96 h LC50 tests with standard ‘regulatory’ reference test organisms). Many of the long-term Natural Resource Damage Assessment (NRDA) studies on the long-term effects of oil and chemically-dispersed oil on trophic level dynamics in the Gulf of Mexico have not yet been released, and no community/population level studies have been conducted on chronic effects of the chemically-dispersed oil on deepwater organisms.

Microbial communities in the Gulf of Mexico rapidly responded to the spill, including in deepwater plumes (Atlas and Hazen 2011). Redmond and Valentine (2012) showed that the deepwater microbial community was very different from the surface microbial community, reflecting the colder temperatures at the plume depth, as well as exposure to natural oil seeps in the Gulf and possible leakage from other oil wells in the area. The authors suggested that the high natural gas content of the spill may have provided an advantage to specific taxa, notably *Colwellia* and to a lesser extent *Oceanospirillales* (Chapter 3).

8.5.2 *Deposition and effects on shorelines*

A review by Michel et al. (2013) of the extent and degree of shoreline oiling stated that about 1,770 km of shoreline was affected consisting of 51% beaches, 45% marshes and 4% other shoreline types. Simulations of oil transport from the footprint of the spill on the water surface showed that the mass of oil that reached the shorelines was between 9,000 and 27,200 tonnes, with an expected value of 19,960 tonnes (Boufadel et al. 2014). It should be noted that this predicted mass is much lower than estimated by Fingas (2013). Shoreline cleanup was authorized on 550 km of shoreline. Two years after the spill, oil remained on 687 km of the shoreline but to a much lower degree (e.g., the authors reported that the heavily oiled category declined from 360 km to 6.4 km using the Shoreline Cleanup and Assessment Technique (SCAT)). The bulk of the oil stranded during a three-month period when many of the beaches were in an erosional state that led to burial of the oil. In addition, oil was stranded high in the supratidal zone due to high water levels and wave activity. The oil was buried, exposed and remobilized multiple times in some areas. Removal of deeply buried oil required extensive mechanical and manual excavation and sieving. In the lowest intertidal/near-shore subtidal zones, some of the oil/sand mixture accumulated in the near-shore subtidal zone forming extensive submerged oil residue mats. Elsewhere, the oil/sand residues adhered to relict[4] marsh platforms composed of clay and peat at the toe of sand beaches—these mats that were exposed only during the lowest of tides and/or buried by beach accretion were difficult to remove. In marshes, the oil tended to strand along the marsh edge and spread no more than about 10-15 m inland. Some of the most heavily oiled marshes were cleaned using: intensive manual and mechanical raking and cutting to remove the oiled vegetation mats and wrack (Chapter 6); careful removal or reduction of the thick oil layers on the substrate; and limited application of loose organic sorbents.

Microbial communities on oiled shorelines showed a distinct response to the contamination, both in terms of overall bacterial numbers and on the abundance of known oil degraders. Kostka et al. (2011) showed that bacteria in Pensacola Beach sands were on average two to four orders of magnitude more abundant in the presence of oil contamination, and high cultivatable counts as well as nucleic acid-based analyses supported the premise that the majority of bacteria in the oiled sands were active. The authors noted that the native microbial communities responded fairly quickly to oil contamination and suggested that conditions in subtropical sands (temperature, oxygen supply and nutrients) appear to favour a broader diversity of hydrocarbon degraders that might render biostimulation (via nutrient addition) unnecessary.

The impacts of the oil spill on shoreline vegetation were variable. Along some heavily oiled shorelines, there was nearly complete flora mortality. Moderate oiling had no significant effect on some species (e.g. *Spartina;* cord-grass) but significantly lowered live above-ground biomass and stem density of others (*Juncus;* rushes) (Mendelssohn et al. 2012). Since the spill, some recovery has been noted (Mendelssohn et al. 2012). However, there were concerns about whether some shorelines would revegetate naturally before shoreline erosion occurred. Biber et al. (2014) found that there was more rapid removal or degradation of oil along coastlines in Mississippi exposed to higher energy levels. Plant recovery was more rapid in these locations. In contrast, at low-energy locations, oil was still detected in sediments and on plants one year post-spill and plants in these locations exhibited chronic stress, which depressed photosynthesis. Silliman et al. (2012) reported that while rapid salt marsh recovery was observed, there were also permanent marsh area losses. They also observed thresholds of oil coverage that were associated with severity of salt marsh damage; plant death of marsh edges more than doubled rates of shoreline erosion, further driving marsh platform loss that is likely to be permanent. However, in non-eroded areas, marsh grasses had largely recovered. The authors noted that heavy oil coverage on shorelines that were already experiencing elevated erosion because of intense human activities induced a geomorphic feedback that amplified erosion and thus limited the recovery of otherwise resilient vegetation.

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[4] *A group of animals, plants or objects that exists as a remnant of a formerly widely distributed group in an environment different from that in which it originated.*

8.5.3 Effects on fisheries

Near-shore fisheries were vulnerable to the spill both in the spawning grounds in the Gulf of Mexico and in estuarine nursery areas. The spill overlapped with peak spawning periods for several important species, including brown shrimp (*Farfantepenaeus aztecus*), white shrimp (*Litopenaeus setiferus*), blue crab (*Callinectes sapidus*) and spotted seatrout (*Cynoscion nebulosus*) (Mendelssohn et al. 2012). Although the location of the spill was in deep water, currents carried oil into the shallow spawning areas of these species. The short- and long-term effects of this oil (and/or dispersants) on eggs and larvae are still uncertain, but Fodrie and Heck (2011 cited by Mendelssohn et al. 2012) did not find short-term negative effects on juvenile fish associated with inshore seagrass beds. Some evidence of low impact to fish populations was noted at sites distant from the heavily oiled Louisiana coast (Anderson 2014). Although coastal fishes likely have adapted for shifting habitat availability in Louisiana, it is uncertain whether wetland losses due to the spill would have a negative effect on fish production (Anderson 2014). Fishery responses to the spill are difficult to tease out because of high annual variability and the effects of many other anthropogenic stressors (Mendelssohn et al. 2012). Anderson (2014) emphasized the importance of continued monitoring of sediments, plants and animals in oiled areas.

A study of the effects of the spill on spotted seatrout by Brown-Peterson et al. (2014) showed a substantial, but short-term effect on reproductive parameters after the spill compared with historical, pre-spill data. The authors noted that the availability of pre-spill (baseline) reproductive data allowed direct comparisons from the same sites before and after the spill. Important environmental variables, such as temperature and salinity, were similar during most of the months of the reproductive season pre- and post-spill, and the two significant differences in temperature and salinity pre- and post-spill were deemed to be unimportant biologically. The authors acknowledged that other impacts on the spotted seatrout populations in the years between the two sampling events, such as heavy fishing pressure, habitat loss and changes in salinity due to drought and flood conditions, may also contribute to differences in reproductive parameters, "although impacts from DWH seem to be the most parsimonious explanation for the observed differences" (Brown-Peterson et al. 2014). Uncertainty regarding the interpretation of results is increased because measured PAH concentrations in water taken from the sampling sites in 2011 were generally below the 1.03 μg/L detection limit and were not significantly different from pre-spill concentrations. The authors suggest that larval spotted seatrout may have been exposed to oil during the summer of 2010, leading to altered reproductive dynamics in 2011 as the fish reached sexual maturity. Reproductive parameters were returning to pre-spill levels by July, but the effective reproductive season was reduced from the normal six months to three months.

Remedial operations may have caused significant secondary effects. The creation of a 35-km oil prevention berm off the Chandeleur Islands, a unique habitat for neonatal and juvenile lemon sharks (*Negaprion brevirostris*), may have reduced available habitat for the sharks and may also have inhibited sharks pupped on the windward side of the island from reaching the protected sea grass beds on the leeward side (McKenzie et al. 2014). A lack of suitable protected nursery habitat may have, in turn, resulted in a further reduction of lemon shark numbers around the islands. The authors noted that it will be important to continue monitoring the population numbers and the occurrence patterns to determine if the effects are long-term.

8.5.4 Effects on invertebrates

Studies on the impacts of the DWH oil spill on blue crab (Fulford et al. 2014) and oysters (Le Peyre et al. 2014) revealed that effects, if any, were indirect (for blue crab) or the data indicated no significant differences in biomarkers of exposure to PAHs (for oysters). Fulford et al. (2014) found that megalopal (final crab larval stage) settlement patterns were more likely a reflection of climatic conditions and pointed out that cyclic uncertainty in recruitment of decades or longer is important and should be accounted for in interpreting data time series. They also found a low level of larval mortality due to PAH exposure in 2010 in the wild, which was supported by laboratory assays that showed a mortality effect only at PAH concentrations of 1 mg/L or higher. They suggested that direct larval exposure to oil in the pelagic zone may not be the most important point of vulnerability for the crab population. Rather, effects might be indirect, operating at the larval source and, in turn, affecting larval delivery to the near-shore habitat.

The nature of the spill in terms of its magnitude and release at depth raised concerns regarding effects on deepwater coral communities. White et al. (2012) studied coral communities at 11 sites three to four months after the well was capped. Healthy coral communities were observed at all sites greater than 20 km from the well. However, at one site 11 km southwest of the well, coral colonies showed several signs of stress. Of the corals examined at the affected site, 46% exhibited evidence of impact on more than half of the colony, and nearly a quarter showed impacts to more than 90% of the colony. Floc deposited on the corals was traced to the Macondo well via analysis of hopanoid biomarkers (White et al. 2012). The significance of particulate deposition (i.e., mortality caused by smothering) from the failed 'top kill' operation and/or the episodic release oil (with similar biomarker ratios) from natural seepage (which has been reported to occur within the region) has not been fully addressed.

8.5.5 Effects on trophic level dynamics

There is currently much interest within the NRDA process to identify potential community and population level changes, as well as alterations in trophic level dynamics. Graham et al. (2010) found that $\delta^{13}C$ depletion, used as a tracer of oil-derived carbon in mesozooplankton and suspended particulate samples in near-surface and bottom waters from four stations in 8 to 33 m water depth in the northern Gulf of Mexico, corresponded with the arrival of surface slicks from the DWH oil spill and demonstrated that carbon from the spill was incorporated into both trophic levels of the planktonic food web.

Results of *in situ* microcosm experiments performed in North Inlet Estuary, SC, with DWH and a Texas crude oil showed a decrease in chlorophyll *a* in phytoplankton as crude oil concentration increased from 10 to 100 µL/L (Gilde and Pinckney 2012). This change was interpreted as a decrease in biomass rather than chlorophyll due to the short duration of the experiments. Diatom, cyanobacteria, euglenophyte and chlorophyte abundances were unaffected or increased with increased oiling, whereas cryptophyte abundance decreased. The authors suggested that oiling could result in changes in phytoplankton community composition within salt marsh estuaries impacted by oil from the DWH, thereby affecting higher trophic levels, such as zooplankton, which selectively feed on phytoplankton that might be killed by the oil (Gilde and Pinckney 2012).

Tarnecki and Patterson (2015) recently reported a potential shift in the diet (prey including fish, decapods, cephalopods, stomatopods, gastropods, zooplankton and other invertebrates) and trophic position (determined from stable isotope ratio-mass spectrometry analysis of $\delta^{13}C$, $\delta^{15}N$, and $\delta^{34}S$) for red snapper (*Lutjanus campechanus*) from the north-central Gulf of Mexico following the DWH oil spill. Stable isotope data indicated a post-spill increase in red snapper trophic position (^{15}N enrichment) and an increase in benthic versus pelagic prey (^{34}S depletion), that was consistent with observed dietary shifts, likely linked to relative abundance of prey resources.

Indirect effects on the menhaden (*Brevoortia tyrannus*) population in the Gulf occurred due to trophic cascade effects (Jeffrey Short, pers.comm. 2015). The effects began with the death of close to 1 million seabirds due to physical contact with the oil. The mortality of birds increased the abundance of juvenile menhaden—a primary food source for the birds. The menhaden population increased to unprecedented abundance and biomass levels in 2011-2012. However, this was accompanied by a decline in the condition of the fish (and thus their oil content) as they exhausted their food supply. These effects occurred on a much larger spatial and temporal scale than direct toxicity from the spill. As of 2015, the menhaden population appeared to be recovering.

8.5.6 *Effects on ecosystem services*

An ecosystem services approach can supplement traditional methods of assessing or valuing damage to natural resources by estimating flows of goods and services before and after an event (NRC 2013; reviewed in Chapter 4). The approach focuses not on the natural resources themselves, but on the goods and services these resources supply to people.

> The ecosystem services approach provides a useful framework regarding how to manage human activities (and the consequences of those activities) in order to sustain the ecological structure and function necessary to provide essential services. The approach can be used to inform the public and decision-makers about the connections between human activities and the effects of those activities on ecological services. However, in order to advance the approach beyond generalizations, data are required which describe explicit connections between ecosystems and benefits (economic, cultural and spiritual). These data are fragmentary and scattered among many disciplines.

Ecosystems are subject to natural disturbances, such as floods, droughts and disease outbreaks, as well as human-caused disturbances, including oil spills. Ecosystems are also subject to slowly changing long-term stresses, such as nutrient enrichment and changes in the sediment supply, as observed in the Gulf of Mexico. These long-term stresses can affect the ability of the system to respond to a shock, such as the DWH spill (NRC 2013).

Ecosystem resilience to shocks from oil spills in the context of long-term stresses is key to the maintenance of ecosystem services. In some cases, systems will undergo fundamental shifts in structure and function following disturbances (e.g., changes in trophic structure caused by invasive species in the Great Lakes). Although resilience to preserve ecosystem services is an important concept, the understanding of complex and highly variable systems, such as the Gulf of Mexico (or the Gulf of St. Lawrence) is insufficient to support specific, resilience-based recommendations regarding response to or monitoring of oil spills. If policies and decisions are to be based upon the ecosystem services concept, a large, coordinated, long-term, multi-disciplinary effort will be required.

NRC (2013) summarized the effects of the DWH spill on four key components of the Gulf of Mexico that provide ecosystem services. Their conclusions are presented below.

Wetlands

Acute effects on marshes, where the biota are not expected to recover, appear to be confined to the edges of bays, canals and creeks in a limited subset of the oiled wetlands.

- Where the vegetation has died and root systems have been lost in heavily oiled areas, the erosion of sediment is leading to the conversion of once-productive marshland to open water;
- Subsequent tropical storm activity resulted in additional erosion of oiled marshes; and
- Based on numerous studies that document a rapid recovery from oiling and a relatively low sensitivity of perennial marsh vegetation to hydrocarbons, marsh vegetation can be expected to suffer little or no long-term impairment in areas where roots and rhizomes survived the initial impact of oil fouling. If roots and rhizomes do not survive, then an area will likely not recover on its own due to the loss of habitat by erosion.

These impacts need to be viewed in the context of significant and continuing losses of wetlands in the Gulf of Mexico due to many other stressors, including subsidence, canal dredging, salt intrusion and sediment starvation.

Fisheries

Despite long-term studies and ongoing development of models, the ability to detect spatial and temporal differences in fishery productivity in the Gulf of Mexico is limited. Recent developments in fishery data collection, such as the introduction of vessel monitoring systems in the reef fish fishery, could improve estimates of abundance. However, any mortality or reduction in individual fitness caused by the spill directly or indirectly may take years or, for some species, decades to transfer through the ecosystem and be observed.

The direct value of commercial fisheries to the fisherman is calculated using the dockside value of the catch minus any expenses incurred to capture those fish. The method for evaluating the economic effects of an oil spill on commercial fisheries is derived from either reduced production (due to mortality or fishery closures) or by reduced consumer demand (due to the perception of reduced fish quality or safety).

The immediate economic impact of the DWH spill was a 20% decrease in commercial fish catch for 2010.

Marine Mammals

Bottlenose dolphins were the representative marine mammal examined by the NAS because of the role dolphins play in three ecosystem services—regulating, supporting and cultural. As apex predators[5], dolphin populations serve as important indicators. They are the most studied and among the most popular and charismatic marine mammals. The stranding of hundreds of dolphins in the Gulf of Mexico before, during, and after the spill stimulated considerable public concern. NRC (2013) suggested that if the post-spill mortality event is determined to be linked to the spill, then an opportunity may exist to establish a plan to protect and restore the dolphin habitat and to reduce dolphin mortality due to human activities. Venn-Watson et al. (2015) studied unusual mortality events of bottlenose dolphins (*Tursiops truncates*) in Louisiana, Mississippi and Alabama from 2010 to 2014 and concluded that the rare, life-threatening and chronic adrenal gland and lung diseases identified in stranded dolphins were consistent with exposure to petroleum compounds. The authors suggested that the DWH spill was a contributor to increased dolphin deaths.

Deep Gulf of Mexico

The deep sea area of the Gulf is so vast and sampling is so sparse that gaps in knowledge inhibit the ability to apply an ecosystem services approach in a quantitative way. The NRC (2013) assumed that the primary ecosystem services of the deep Gulf are supporting, e.g., resupply of nutrients. In addition, the NRC (2013) stated that the deep sea area of the Gulf provides the regulatory service of pollution attenuation, e.g. via bacterial degradation. The release of crude oil from the Macondo well at depth created a unique opportunity to study deep sea oil biodegradation.

8.5.7 Important factors affecting the consequences of the Deepwater Horizon Blowout

The huge volume of spilled oil and the length of time it took to stop the release were primary factors in determining consequences. The presence of significant anthropogenic stressors prior to the DWH spill, including degraded or lost shoreline habitats, overexploitation of some fishery resources, salt intrusion, sediment starvation and nutrient influxes leading to algal blooms and oxygen depletion, added confounding factors to the interpretation of the effects of the spill. In addition, the Gulf of Mexico is a highly complex ecosystem subject to major natural cycles.

[5] *An apex predator is a predator residing at the top of a food chain on which no other creatures prey upon.*

8.5.7.1 Oil properties and behaviour

- Dissolution of BTEX and naphthalenes into the water column occurred as the oil moved to the surface from the well.
- There was rapid evaporation of lighter fractions in the floating oil.
- Substantial spreading of surface oil occurred driven by wind and currents.
- Biodegradation along shorelines and within dispersed oil was significant, with a fairly quick response of native microbial degraders to the oil.
- Sinking of physically- and chemically-dispersed oil droplets from mid-column occurred.

8.5.7.2 Effect of the environment on fate and behaviour

- High microbial degradation rates occurred along shorelines and in shallower waters of the Gulf because of subtropical temperatures (Chapter 3).
- Rapid penetration of oil occurred along sand shorelines due to high porosity.
- Repeated burial and exposure of oil occurred (and continues to occur) along shorelines.
- Wave action led to stranding of oil in the high intertidal zone.
- Heavy coating of vegetation along the margins of wetlands and estuarine shorelines including the formation of 'oiled' subsurface mats.

8.5.7.3 Oil toxicity

- Mass acute mortality occurred due to exposure to floating oil.
- Death of vegetation occurred along heavily oiled margins of marshes.
- The extent of chronic toxicity is difficult to determine given multiple confounding factors.
- There may have been trophic level effects, including a shift in the diet of red snapper and a temporary increase in menhaden abundance originating with the mass mortality of predatory seabirds.
- Chemical and biological markers of oil exposure and toxicity were not often included in case studies of oil effects on aquatic biota.
- Extrapolation of laboratory and mesocosm study results to the Gulf of Mexico ecosystem is very difficult.

8.5.7.4 Spill response

- Novel application of dispersants in the deep subsurface was associated with the formation of a deepwater plume.
- Surface application of dispersants had limited effect in reducing oil reaching shorelines.
- Deployment of oil booms, berms and other barriers protected specific shoreline or island areas.
- ISB removed 6-7% of the oil.

8.5.8 Lessons learned from the Deepwater Horizon Blowout

8.5.8.1 Lessons learned according to the USGS (2015)

- Oil was consumed by bacteria, seafood was not contaminated by hydrocarbons or dispersants and the oil budget was by and large accurate. There was consensus that most of the oil was biodegraded. The only part of the oil budget that was later found to be inaccurate was the fraction of oil that was chemically-dispersed versus naturally-dispersed. That information had no impact on public safety, seafood safety or the response effort, but understanding the amount of oil that was dispersed chemically versus naturally is important for future such efforts.

- The scale and complexity of DWH taxed the agencies involved.
- Future oil spill response preparedness should include the following actions:
    - Gathering adequate environmental baselines for all regions at risk;
    - Developing new technologies for rapid precise reconnaissance and sampling to support a timely and robust response effort;
    - Filling large information gaps regarding biological effects of oil, changing climate and other simultaneous drivers of variability in coastal and aquatic ecosystems;
    - Requiring that future oil extraction permits be conditional on having mechanisms in place to rapidly assess flow rate; and
    - Conducting research on the impacts of dispersants and dispersants-plus-oil on a wide range of species and life stages.
- The scale of the spill required unprecedented collaboration among government, academic and industry scientists and engineers. Scientific and engineering information was crucial to guide decision-making for questions never before encountered.
- The lack of peer-reviewed scientific publications from prior marine well blowouts was a significant drawback in addressing many of the issues.
- The event also showed the value of federal partnerships with academic institutions.

8.5.8.2 Other lessons learned (from the RSC Panel's review of the literature)

- Considering the size of the spill, relatively little oil made it to shore and tar balls and tar mats were distributed heterogeneously.
- Receiving environments that are already degraded by human activities (e.g. coastal marshes) have enhanced vulnerability to oil spills.
- Fate and transport of submerged, physically- and chemically-dispersed oil is poorly understood.
- The consequences of deposition of oil to deepwater sediments require investigation.
- The ability to determine effects of oil spills (even those as huge as the DWH) depends upon the availability of pre-spill baseline information, an understanding of natural variability, and an understanding of the effects of multiple anthropogenic stressors.
- Barriers to prevent oil incursion can have unintended consequences (e.g., reduced available habitat for lemon sharks and inhibition of sharks from reaching the protected sea grass beds on the leeward side).
- Natural biodegradation on beaches in warm climates can be rapid and may not require nutrient supplementation, especially if available nutrients are already plentiful enough to support growth on the oil incursion. However, biodegradation will not remove all of the oil components.
- Effects on trophic dynamics via changes in biomass of primary producers and shifts in diet can occur. However, the spatial and temporal scales at which this could occur suggest that effects may not be widespread and/or long-term.
- Oil spill response plans should accommodate and exploit scientific opportunities and oil spill response should incorporate these opportunities.
- Experience of people involved in the response to the spill showed a pressing need for improved analytical procedures for the detection and characterization of oil spill constituents, including standard sample tracking and reporting procedures (Laboratory Information Management linked to sample collection) (Ken Lee, pers. comm.).
- Effects on ecosystem services can be very difficult to establish and quantify, particularly for resources where the ability to detect spatial and temporal differences is limited by lack of data or a lack of fundamental understanding of population or community structure, function and dynamics, or for ecosystem components that have had very little study (e.g., deep sea areas).

- Even if effects on ecosystem services can be quantified, a comprehensive model is needed that incorporates biophysical, social and economic data for the Gulf of Mexico for the long-term (NRC 2013).

8.5.9 Research Needs Related to the Deepwater Horizon Blowout, in the Canadian Context

Recommendation: Research into the consequences of deposition of oil to deep sea sediments in the Arctic, as well as deep sea sediments south of the 60th parallel in Canada would provide part of the required knowledge base for support of decisions regarding offshore oil and gas exploration and oil transport. This is particularly important in light of frontier offshore oil and gas operations moving into deeper waters and emerging interest in the use of dispersants by subsea injection in the case of well blowouts. Offshore drilling in the Arctic and on Canada's east coast will create the potential for impacts on benthic ecosystems and commercial fisheries that have not yet been studied.

Recommendation: In the Canadian context, the current level of understanding of trophic dynamics in identified high-risk offshore and inshore marine habitats requires evaluation in order that critical gaps in understanding are identified.

8.6 Pine River, British Columbia Pipeline Break

On the night of August 1, 2000, a break in an oil pipeline released 952 m^3 of sour crude oil (BC-Light; Table 2.2) into the Pine River in northeastern British Columbia. The Pine River is a major tributary of the Peace River with mean flows in August of about 200 m^3/s (Water Survey of Canada 2015). About half of the oil entered the river and was dispersed downstream. The other half remained on land, contaminating surficial soils and groundwater. The Pine River is a source of drinking water for the town of Chetwynd.

The spill occurred in the vicinity of a previous spill of 30 m^3 of gasoline and 24 m^3 of diesel fuel on August 18, 1994 that caused the mortality of about 150 mature and 1,000 juvenile fish (Goldberg 2011).

8.6.1 Immediate effects, response and cleanup

As a result of the spill, Chetwynd closed its water intake and started exploring alternate water sources. A total of 1,637 dead fish were found 2-50 km downstream, comprised primarily of larger, more visible fish. Most were bottom-feeding species, consisting of 64% mountain whitefish (*Prosopium williamsoni*), 16% slimy sculpins (*Cottus cognatus*) and 5% burbot (*Lota lota*). The remaining fish were surface feeders, consisting of 5% bull trout (*Salvelinus confluentus*), 2% rainbow trout (*Oncorhynchus mykiss*) and 1% Arctic grayling (*Thymallus Arcticus*) (Alpine Environmental and EBA Engineering 2001). It was estimated that 15,000 – 27,900 fish mortalities occurred, based on numbers of fish per kilometer and assuming complete fish-kill in the first 30 km.

The recovery of oil from the river occurred over a period of about two months. According to Alpine Environmental and EBA Engineering (2001), about 91% of the oil was recovered or accounted for as follows:

- 447.5 m^3 entered the river;
- 358 m^3 recovered as liquid oil from the river and spill site prior to soil excavation;
- 89.5 m^3 lost to volatilization (calculated);
- 5 m^3 recovered from the river as liquid oil using absorbents;
- 21.4 m^3 recovered as liquid oil during soil excavation;
- 416 m^3 recovered from the spill site as part of soil excavation; and
- 83.2 m^3 not accounted for (included dissolved, adsorbed in soils along bank and in sediments, trapped in backwaters and eddies, trapped in logjams).

A number of emergency response operations were deemed to have caused detrimental effects on fish and wildlife habitat. These included:

- The alteration of an 115 m-long backchannel from the break site to the river (to stop oil flow into the river) that resulted in the cut off of an oxbow channel that provided abundant fish food and the isolation of a back channel from fish access;
- Bank armouring to prevent erosion and the removal of logjams and riparian vegetation coated with oil removed floodplain habitat available to fish during high flows (Sumners 2001). In this case the contractor also failed to implement the consultant's recommended fish habitat features when installing the armouring;
- The removal of logjams and woody debris structures from the river channel without consultation and approval of regulatory agencies (Department of Fisheries and Oceans-Canada [DFO] and BC Ministry of Environment);
- Rerouting of the river near a tributary by the removal of a logjam diverted flow from a 3.4 km stretch of creek, the Lemoray Meander Loop. The new 1.6 km long channel that formed was unstable, having a steep gradient that resulted in mass erosion with vegetation, soils, gravels and sands washing downstream into spawning habitat—however there was no investigation to access the level of potential impact. While the logjam was eventually rebuilt, it was overwhelmed by the spring freshet in 2001 a 1-in2- or 1-in-3-year event). Sumners (2001) deemed this failure as "catastrophic to the stream channel and the habitat therein". Consulting engineers involved in the project concluded that the magnitude of the changes in the channel prohibited the effectiveness of further attempts at logjam construction; and
- Habitat damage was also caused by the actions of the regulatory agencies which allowed large machinery in the river channel because of the urgency to finish the cleanup work before winter.

Sumners (2001) noted that poor records were kept during the cleanup. In terms of remediating the damage to habitat caused by the initial emergency response operations, at least 13 logjams were rebuilt on advice from a consultant, primarily to maintain the stability of the river. Sumners (2001) expected that where jams were not rebuilt, others would likely form over time; however, the author concluded a net loss of habitat resulted.

8.6.2 Water quality

Visual and olfactory evidence of oil contaminants were evident over an 80-km section of the river following the spill. After three weeks, while concentrations of extractable petroleum hydrocarbons were still detected in waters downstream of the spill site, they were below water quality criteria (Alpine Environmental and EBA Engineering 2001), and few samples contained the more volatile fractions (Amec 2001a). By the end of August (one month later), petroleum hydrocarbons in the water had declined to below detection limits (Amec 2001a) and the presence of sheen was largely restricted to back eddies and other calm water areas along shorelines.

8.6.3 Sediments

Petroleum hydrocarbons accumulated in depositional environments within the river, in areas with soft, muddy sediments along the banks, in back eddies and other calm-water locations (Amec 2001b). There were also high concentrations of organic debris (e.g., branches, leaves and algae) that had accumulated along the shoreline, in front of logjams and attached to sweeper logs (overhanding trees with some limbs and branches submerged during high flows). Six PAH compounds and cadmium were detected in these materials at concentrations sufficient to be a concern for the health of fish and other aquatic biota (Amec 2001b). Heavy rainfall in late August and September mobilized previously stranded oil and oil-contaminated debris and sediments into relatively uncontaminated areas. Higher water levels also scoured some of the more heavily-contaminated depositional areas. The concentration of detectable oil concentrations declined by an average of 71% by October (Alpine Environmental and EBA Engineering 2001).

8.6.4 *Periphyton and benthic invertebrates*

Effects were observed on periphyton and benthic invertebrate communities immediately after the spill. A substantial increase in algal biomass that exceeded the apparent seasonal effects was observed at one sampling station (Alpine Environmental and EBA Engineering 2001). Total abundance of benthic invertebrates declined in August, with substantial recovery by November (Alpine Environmental and EBA Engineering 2001). The benthic invertebrate community structure was also affected. The effects on benthic invertebrates were of concern with respect to a decreased food supply for fish, especially young fish, during the recovery period between August and November—a critical period leading up to over-wintering (see discussion below).

8.6.5 *Fish*

Chemical analysis of sportfish sampled above and below the spill site did not indicate any trends in concentrations of total extractable hydrocarbons or PAH in liver and muscle tissue (Amec 2001c). Amec concluded that consumption of the Pine River fish caused no significant unacceptable risk to humans.

The initial spill of crude oil into the Pine River produced sufficient toxic material (especially that which dissolved to produce a water-soluble fraction likely a concentration of higher than 3 mg/L, Chapter 4) in the river that killed fish over a relatively short period of time (hours) (Birtwell 2003). Unfortunately, the actual concentrations in river water were not determined as samples were not collected at the time when the fresh crude oil was entering the river (Birtwell 2003).

Results of analysis of fish tissue and stomach contents indicated that longer-term risks to fish can be driven by feeding behaviour combined with oil dispersion and stranding on large woody debris. Analysis of fish bile showed no benzo(a)pyrene metabolites but some phenanthrene metabolites, indicating at least some PAH exposure (Alpine Environmental and EBA Engineering 2001). Although concentrations in whole fish were at levels of detection for total PAHs in surface feeders, predators and bottom feeders, the stomach contents of rainbow trout showed large quantities of unmetabolized PAHs. These fish were sampled at a logjam where a considerable amount of free oil was collected, suggesting that the fish were feeding within the pooled oil on drifting invertebrates. The hydrocarbons in the stomach contents mirrored the oil characterization results (Alpine Environmental and EBA Engineering 2001).

Exposure of fish to hydrocarbons can also be driven by temperature-related behaviour. Fish often conceal themselves in the substrate at temperatures less than 9 °C, particularly bull trout (Alpine Environmental and EBA Engineering 2001). If the concealment areas coincide with areas of oil deposition, the fish will be exposed. No consideration of hyporheic flows and effects on spawning gravels was apparent in the published reports about the spill.

The annual fidelity of fish to feeding areas could result in reduced food intake if prey species were less abundant or unavailable due to the impact of spilled oil (Birtwell 2003). Fish must obtain enough food prior to ice cover to survive the cold northern winter. However, if this is not accomplished and/or the metabolism of the fish is elevated due to exposure to contaminants and/or other stressful circumstances, survival is jeopardized (Lemly 1993 cited by Birtwell 2003). Because exposure to oil can elevate metabolism in fish, their survival under the colder winter conditions was a concern, especially at a time when metabolic activity and food intake usually decreases (Birtwell 2003).

The concerns about sublethal effects on fish led to an assessment of snorkel surveys conducted in the Pine River in 1993 (pre-spill), 1994 (after the 1994 spill), 2000 (about two months after the pipeline rupture), 2005, 2006 and 2007 (Goldberg 2011). The results suggested that the sportfish species composition (mountain whitefish, Arctic grayling, bull trout and rainbow trout) and abundance observed in 2005, 2006 and 2007 were similar to pre-spill observations (1993) in the river sections surveyed.

In summary, the 2000 spill caused mortality of several thousand fish, but there were insufficient studies to establish, with confidence, the nature and extent of sublethal effects on reproduction and recruitment. The concentrations of PAH compounds in fish stomach contents confirmed PAH exposure via the food chain. There was a potential for concentrations of PAH in spawning habitat to have exceeded thresholds for sublethal effects, particularly for fall spawning species such as bull trout in 2000. However, there were no coordinated efforts to measure PAH concentrations and fish egg/embryo survival in spawning areas downstream of the spill.

8.6.6 Important factors affecting the consequences of the Pine River spill

8.6.6.1 Oil properties and behaviour

- Evaporation of light oil plus dissolution and natural dispersion were important factors leading to hydrocarbon concentrations within the water column of the river declining to detection limits within one month.
- Physical interactions with shorelines, sediments and woody debris led to substantial stranding of oil.

8.6.6.2 Effect of the environment on fate and behaviour

- Water flow led to rapid dispersion of acutely lethal concentrations of the residual oil up to 80 km downstream.
- Temperature declines in the fall triggered fish behaviour that increased exposure to oil in sediments.
- Substrate particle size was an important factor leading to retention of oil in fine sediments in slow-water areas.
- River channel and shoreline characteristics were also important with respect to creating conditions that allowed oil to become associated with the river bottom (backwater and side channel areas).

8.6.6.3 Oil toxicity

- Substantial acute lethality to fish and benthic invertebrates occurred immediately after the spill.
    - Most fish deaths were of bottom-feeding species. Exposure may have been via both water and food organisms based on stomach content analysis, and
    - Mortality of benthic invertebrates was observed in the first month but rapid recovery was observed.
- There was possible increased overwintering mortality or increased susceptibility to predation (because of decreased fitness) caused by exposure to PAHs in overwintering habitats and possible effects on embryo survival and recruitment due to oil deposition in spawning areas.
    - There was no demonstrated avoidance of oiled areas by fish (anecdotal evidence only);
    - Fidelity to feeding and overwintering areas may have exposed the fish to oil in sediments and food organisms, or reduction in food abundance may have reduced fitness going into the winter season; and
    - Metabolizing the PAHs may have created an energy cost that affected fitness.
- Population-level effects.
    - Similar abundance and species composition of fish in snorkel surveys conducted in 1993 and 2005, 2006 and 2007. However, the natural variability of abundance and the

influence of migration from un-surveyed areas is unknown, and there were no measures of reproduction or recruitment.
    - No definitive statements can be made regarding the presence or absence of population-level effects.

8.6.6.4 Spill response

- Active recovery of liquid oil and oil-plus-soil from the river and spill site removed about 84% of the total spilled oil; 91% of the oil was either removed or accounted for.
- Physical removal from the river channel, shorelines and woody debris.
    - Direct damage to habitat from heavy machinery within the river channel;
    - Changes in channel morphology caused by bank armouring cut off fish access to an important back-channel habitat area; and
    - Removal of logjams eliminated important fish habitat and altered flow dynamics, in some cases to such an extent that significant areas of side channel habitat were lost, and subsequent seasonal increases in flow restructured channels and degraded fish habitat.

8.6.7 Lessons learned from the Pine River spill

- Fish kills in moderate-sized rivers can extend far downstream if the spill is not contained immediately.
- The extent of impacts on fish can be obscured if there is a slow response to the spill (e.g., remote spill site) and dead fish are consumed by scavengers before being identified.
- Benthic invertebrate communities can recover quite quickly after spills that occur in summer months, provided the initial scale of the impact is sufficiently small.
- The effects of cleanup activities were substantial, decreasing or eliminating important fish habitats.
- Data were insufficient to support any definitive statements regarding long-term effects on fish abundance and species composition.
- Opportunities for more detailed and sophisticated investigation of the effects of the spill on were not pursued, perhaps due to logistic and financial constraints.

8.6.8 Research needs related to the Pine River spill

Recommendation: Standard guidance is required for measurement of oil contamination of sediments, pore water and biota within flowing waters of Canada. This guidance should consider the range of lotic receiving environments and logistic constraints common to remote locations. The guidance should include the *de minimis* level of investigation required for decision-making regarding cleanup requirements and techniques, as well as for determination of acceptable residual levels of oil.

Recommendation: The Pine River spill offered the opportunity to track longer-term response to cleanup activities, as well as to residual oil. Such opportunities should not be lost if such spills occur again, because the longer-term trade-offs involved in selection of cleanup methods remain uncertain.

Recommendation: Standard guidance for monitoring the fate of spilled oil in all major environmental compartments of lotic systems is required.

Recommendation: Research is needed on the relative role of hyporheic flows in contributing to exposure of fish to hydrocarbons after a spill. A range of experimental conditions using relevant concentrations and both weathered and unweathered oil should be tested on salmonid species (and

demersal spawners in general) under conditions that represent actual field conditions in terms of variables such as flow, temperature, substrate and dissolved oxygen.

<u>Recommendation:</u> The Pine River spill case study illustrates the importance of baseline information with which to compare post-spill monitoring data. The Panel strongly recommends the establishment of a national baseline database for freshwater systems adjacent to pipeline corridors (e.g., data collected for EIAs, environmental effects monitoring (EEM) programs, compliance monitoring [e.g. for municipal or industrial discharges], research programs, etc). The Panel is aware that some databases are already established (e.g. for EEM data); however, there is no readily accessible, national portal to metadata on freshwater systems.

<u>Recommendation:</u> The Pine River spill could have yielded highly valuable data regarding effects of spills in riverine systems in the short, medium and long-term. The Panel recommends that there should be national guidance regarding 'spills of opportunity', by implementing communication and coordination protocols among agencies and industry to optimize the collection of scientific knowledge and lessons learned from incidents.

8.7 Wabamun Lake, Alberta Train Derailment

On August 3rd, 2005, 43 Canadian National Railway Company (CN) rail cars derailed immediately adjacent to Wabamun Lake (**Figure 8.6**), approximately 65 km west of Edmonton, AB. The lake (area = 82 km^2; mean depth = 6.3 m; maximum depth = 11 m) is moderately to highly enriched with nutrients and is generally well mixed and thus generally well oxygenated throughout the water column during the open-water period (Prepas and Mitchell 1990; Hollebone 2008).

Of the 43 derailed train cars, 11 containing heavy fuel oil (HFO 7102, a type of Bunker C oil; Table 2.2) ruptured, spilling 712 m^3. A single car carrying Imperial Pole Treating Oil[6] (PTO) also ruptured spilling about 88 m^3 on to the ground at the derailment site. A total of about 149 m^3 of heavy fuel oil entered the lake (Birtwell 2008). The oils ran onto the lawns of cottages about 100 m from the lakeshore. HFO entered the lake less than 1.5 hours after the derailment along a broad front of about 0.5 km (**Figure 8.8**). The flow was aided by the fact that the HFO 7102 had been loaded a few hours before and was still warm and relatively less viscous than it would be at ambient temperature (Hollebone 2008).

Figure 8.8 Wabamun Lake Train Derailment. Source: Dangerous Goods Newsletter, Spring 2006. *Image from Transport Dangerous Goods Directorate, Transport Canada (https://www.tc.gc.ca/eng/tdg/newsletter-spring2006-323.htm)*

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[6] *A hydrocarbon-rich liquid used for preserving wooden poles, containing naphthalene and other PAHs (http://www.enr.gov.nt.ca/sites/default/files/pahs.pdf)*

8.7.1 Early behaviour and effects of the spill

Initially, all of the oil appeared to be floating on the surface, rapidly spreading in warm, calm weather conditions, and escaping boomed areas once the wind increased. Over 1.1 million m^2 of lake surface was visibly oiled, of which 63% was heavily coated (Birtwell 2008). A few days later, strong westerly winds and waves concentrated the oil along the north, east and south shorelines (Anderson 2005). Langmuir circulation patterns during the windy conditions contributed to the rapid horizontal movement of the oil, as well as vertical movement of oil droplets into the water column. Much of the shoreline was boomed off and oil was trapped with varying degrees of efficiency in the littoral zone (Anderson 2005; Hollebone et al. 2011). Measurement of hydrocarbon concentrations within the boomed area showed concentrations well in excess of guidelines for the protection of aquatic life. Concentrations of BTEX and PAHs in open-water areas of the lake outside of the boomed areas were well below water quality guidelines (Anderson 2005).

Tar balls quickly formed (from <1 to 10 cm in diameter) in near-shore areas. The rapid formation of tar balls was attributed to the loss of volatile components from the spilled oil which also picked up fine mineral and organic particles along its overland flow-path to alter its density (Parker-Hall and Owens 2006). Within hours, some of the tar balls were showing neutrally-buoyant behaviour, and were seen riding up and down in the water column. Some would rise to the surface, others would be seen sinking to the bottom. In addition to tar balls, tar logs were observed, up to 30 cm in diameter and 5 m in length, consisting of a mixture of organic debris and oil (Hollebone 2008). Some near-shore areas had extensive tar mats.

Dead fish were observed in oiled areas immediately following the spill and for about two months afterward. A total of about 100 dead fish were observed by cleanup crews. Live fish captured two weeks after the spill showed biochemical evidence of exposure and had elevated levels of hydrocarbons in tissues (Hodson et al. 2007; Birtwell 2008).

People in the Whitewood Sands cottage community (where the derailment took place) were evacuated within 15-20 minutes of the derailment and allowed back to their properties later that evening (Lake Wabamun Residents Committee 2007). The health authority advised residents on the day of the spill to avoid using the lake until further notice. In August, 2008, three years later, advisories were still being issued against eating certain wildfowl and the fishery was catch-and-release only.

8.7.2 Shorelines

During the Shoreline Cleanup and Assessment Technique (SCAT) survey in 2005, the majority of tar balls or tar mats were observed near the shores in water depths from 0.1 to 1.5 m, with their frequency decreasing with increasing depth (Hollebone 2008). After shoreline treatment a high proportion of oil remained. The coverage of oil varied but was highest in treated reed beds (**Figure 8.9)**. In the reed bed areas on warm days, tar balls would rise to the surface, shed oil from several points around their circumference and create a sheen (Hollebone 2008). Beach re-oiling continued until freeze-up during the first winter.

Figure 8.9. Near-shore reed bed with tar balls in Wabamun Lake. *Image from Hollebone (2008).*

By the spring of 2007, a SCAT survey showed almost all oiling to be in the Very Light or Trace categories found in marsh, peat-soil or vegetated bank shoreline types.

8.7.3 Weathering

Four months after the spill, about 79% of the HFO 7102 and 47% of the PTO had been recovered from the lake spill site, and flow path to the lake and water concentrations had decreased to below detection limits (Birtwell 2008). According to Birtwell (2008), acutely toxic PAH concentrations were likely limited to the reed beds, where high concentrations of PAHs in the water would be promoted because the water circulation would be poor and the surface area of the oil large.

While on the surface of the lake, the oil weathered considerably with a loss of most of the lighter components. Oil coating the reeds was heavily weathered 40 days after the derailment. The weathering of tar balls varied, with some tar ball samples collected about 80 days after release showing only moderate weathering. Some free-floating oil was able to survive until near freeze-up in a largely fresh, lightly-weathered state (Hollebone 2008).

A year and a half after the derailment in February 2007, oil was found in the lake in primarily two forms:

- Large (>5 cm) flat conglomerations on the lake bottom, often tangled into vegetation and highly weathered, with high sediment loading, water content and viscosity; and
- Small (<5 cm), less chemically-weathered spherical balls of soft, fluid oil containing a significant fraction of the original aromatic content of the fuel oil, surrounded by a tough, more weathered layer of oil, which were easily stirred up from the bottom and readily moved with currents and wind due to lower density and viscosity (Hollebone 2008).

Virtually all of the alkanes and 'Priority Pollutant' PAHs had attenuated by the spring of 2007 (Parker-Hall and Owens 2007). Tar balls, particulates and the oil coating the vegetation contained primarily asphaltenes (which are unregulated chemicals) and low concentrations of non-'Priority Pollutant' PAHs (Parker-Hall and Owens 2007). Foght (2006) stated that while competent hydrocarbon-degrading microbes existed in lake sediment, the mass of oil they were likely to be able to degrade was small due to the recalcitrant nature of the oil in tar balls and coating the vegetation. Foght also pointed out that the tar balls would limit microbial access to the biodegradable components of the spilled oil and concluded that the prognosis for extensive natural biodegradation over 5-10 years was poor.

Given the amount and chemical nature of residual oil in the spring of 2007, Parker-Hall and Owens (2007) concluded that further treatment or recovery of sunken oil beyond that planned for May and June of that year was not practical or feasible and would pose a risk of further damage to lake bottom and near-shore communities. Short (2008) estimated that cleanup activities recovered more than 95% of the oil components that were not lost through natural weathering.

8.7.4 Observed effects on aquatic biota

The chemistry of the heavy fuel oil spilled in Wabamun Lake differed in specific ways from typical Bunker C fuel oil and may have contributed to the observed toxicity, especially to fish embryos. The HFO 7102 product was primarily composed of saturated hydrocarbons and also contained a high content of aromatic hydrocarbons (48%) and high concentrations of PAHs (60,400 µg/g oil) (Hollebone 2008). In comparison, a typical Bunker C fuel has a total aromatic content of 29% and a total PAH content of 29,000 µg/g oil (Hollebone 2008). The PAHs of the HFO 7102 were predominantly alkylated naphthalenes (Table 2.1) with smaller amounts of alkylated 3-ring phenanthrene and members of the fluorene homologous series (Hollebone 2008). No BTEX compounds were detected except in the PTO.

8.7.4.1 Algae and macrophytes

Field observations of phytoplankton community characteristics and macrophyte survival and growth did not indicate any effects of oil exposure overall (Golder Associates 2007 cited by Birtwell 2008). The spill had little direct effect on the abundance and productivity of softstem bulrush (*Schoenoplectus tabernaemontani)* (Thormann and Bayley 2008; Wernick et al. 2009) (see Chapter 4).

8.7.4.2 Zooplankton

Standard acute toxicity tests using the water flea species *Daphnia magna* and chronic tests using *Ceriodaphnia dubia* showed no acute lethality but reduced growth near the spill site. The reduced growth was considered to be a result of factors other than oil by Golder Associates (cited by Birtwell 2008b). However, Birtwell (2008) argued that the significant results of tests between reference and oiled locations in the lakes had validity even if background ambient conditions differed from those in the laboratory setting. The characteristics of the zooplankton community did not change when compared with pre-spill data (Golder Associates 2007 cited by Birtwell 2008).

8.7.4.3 Benthic invertebrates

No data existed on immediate effects of the spill on benthic invertebrates but physical smothering effects were considered likely (Birtwell 2008). Laboratory toxicity tests showed significant toxicity to two test species *Chironomus tentans* (a midge) and *Hyalella azteca* (an amphipod crustacean) from sediments collected near the spill site. However, the proportion of sand in the sediment was an important confounder, with higher mortality in high-sand substrates. Both test species showed significant reductions in growth in both high- and low-sand sediments. PAH concentration was correlated with toxicity to the nematode *Lumbriculus variegatus*, with significant reductions in growth in both high- and low-sand sediments.

8.7.4.4 Fish

Risk to fish was due to direct toxicity immediately after the spill, and longer-term direct and indirect risks associated with the near-shore areas, which were important for at least one life stage for the eight fish species inhabiting the lake. The near-shore areas were primary nursery, rearing and food supply areas, and fish did not avoid oiled areas. The summer timing of the spill increased the risk because it coincided with the presence of numerous life stages of each of the eight fish species present in the highly exposed areas (Birtwell 2008). Risk was also related to destruction of habitat during cleanup and survey activities.

Hodson (2008) noted that the exposure of adult fish to the spilled oil corresponded to the discovery of significant numbers of dead fish in the oiled part of the lake. However, Hodson (2008) commented that heavy oils with low concentrations of LMW compounds would be less likely to cause acute lethality. The area closest to the oil spill was also affected by non-spill stressors, including: a thermal plume from a power plant; physical removal of macrophytes (to address concerns of cottagers regarding access to the lake for swimming and boating); and high fishing pressure (Schindler et al. 2004). Thus, fish inhabiting the area nearest to the spill were already exposed to other stressors and may have been more susceptible to the additional stress of the spill.

Within two weeks of the spill, a survey of adult fish demonstrated that exposure to PAHs from the spilled oil was widespread; this exposure was relevant with respect to sublethal effects (Hodson 2008). A second survey, about 10 weeks after the spill, showed continuing exposure of adult fish, although at a lower level than in August (Hodson et al. 2007; Hodson 2008;). One year after the spill, detectable PAH concentrations were found in fish flesh. However, PAHs in fish decreased over time due to metabolic processes in the fish plus weathering of the hydrocarbons in water and sediment (Birtwell 2008).

Embryo-toxic levels of PAHs were found in August 2005 through to spring of 2007. Toxicity studies conducted *in situ* by Golder Associates (2007 cited by Birtwell 2008) showed embryo deformities in caged eggs of lake whitefish (*Coregonus clupeaformis*) at spawning shoals in the winter and spring following the spill and on northern pike (*Esox lucius*) eggs caged in the spring of 2007. Effects were most pronounced in whitefish embryos with significant moderate to severe deformities correlated with PAHs in lake water months after the spill. Pike suffered >50% increased frequency of moderate to severe deformities relative to reference areas but few deformities overall (Golder Associates 2007 cited by Birtwell 2008; deBruyn et al. 2007 ; Hodson 2008). Uptake of PAHs into semi-permeable membrane devices deployed at the egg incubation site confirmed a correlation between PAHs and egg deformities.

Although some embryos survived exposure, the marginal state of a once-thriving whitefish population in Wabamun Lake raises concerns for cumulative impacts of oil and other anthropogenic stressors (Schindler et al. 2004; Donahue et al. 2006) on recruitment and production of whitefish. The whitefish fishery and all other sport fish in Wabamun Lake are catch and release only (Government of Alberta 2015).

8.7.4.5 Effects of the cleanup

Effects on fish habitat occurred due to the requirement to remove oil from Wabamun Lake (Evans 2008). These actions resulted in loss of structural habitat and alteration and disruption of lake substrates. Additional impacts occurred due to increased suspended sediment and turbidity during habitat removal and cleaning, increased erosion along shorelines that became unprotected from wave action, the remobilization of oil, and physical disturbance by trampling and similar activities.

Although the oil spill in Lake Wabamun did not have direct toxic effects on the reed beds, the ’treatment’ impacts in the deeper reed beds reduced plant and rhizome density, and this may have had long-term consequences, remaining open or sparsely vegetated for several years and thereby providing lower quality habitat for fish.

Fish were killed when aquatic vegetation was cut. The presence of fish within harvested vegetation was probably less an issue of entrapment and an inability to escape than it was an example of their vulnerability due to habitat fidelity (the need for cover, etc.).

Benthic habitat and the associated communities were impacted due to the removal of oil by the use of numerous techniques, as well as the cutting of macrophytes and removal of whole plants. The techniques included low- pressure flushing, vacuuming and dragging over substrates. Trampling in shallow waters for survey work or for cleanup caused further damage. The impacts of the cleanup on the quality of habitat persisted for several years (Hollebone 2008) (see Chapter 4).

A survey of riparian habitat along the shoreline of Wabamun Lake in 2015 showed that approximately 57% of the lake's Riparian Management Area was in healthy condition, 9% was moderately impaired and 34% was highly impaired (North Saskatchewan Watershed Alliance 2015). Residential development was cited as the major cause of riparian disturbance.

8.7.5 Analysis of the response to the spill

In a review of the response to the spill, McCleneghan (2008) noted that containment of much of the oil within the first few hours of the spill would have been possible if the railway company had taken steps in the years preceding the event to prepare for an on-water spill from its operations.

CN estimated that it spent $28 million on cleanup and $7.5 million in compensation to property owners (Lilwal and Fitzpatrick 2015). The company was fined $1.4 million for its part in the disaster (Lilwal and Fitzpatrick 2015). The Wabamun spill spurred the establishment of a new agency in Alberta to coordinate disaster response. The Alberta Emergency Management Agency was created in 2006 (CBC 2006). According to the Agency website, it leads the coordination, collaboration and cooperation of all organizations involved in the prevention, preparedness and response to disasters and emergencies (http://www.aema.alberta.ca).

8.7.6 Public consultation and involvement

The spill generated outrage and protests, including a blockade over the CN tracks, with people accusing CN of being more concerned with restoring rail service than stopping the spread of the oil. The blockade ended after the company promised to meet with the public (Lilwal and Fitzpatrick 2015).

Ten years after the spill, some members of the public stated that the lake still suffered some lingering damage, with reports of tar balls and oil buried in the sand. However, a representative of the cottage community stated that CN had fairly compensated cottage owners and applauded the establishment of the Alberta Emergency Management Agency and stronger regulations for railways (Lilwal and Fitzpatrick 2015).

Public consultation was conducted by Alberta Environment, including workshops to discuss the establishment and operation of a Lake Wabamun Citizen's Panel that became the Wabamun Watershed Management Council, which provides input to watershed planning.

8.7.7 Aboriginal community concerns

Interaction between the Paul Band First Nation and provincial and/or federal government agencies was hampered due to the lack of notification, which resulted in challenges with respect to communication and collaboration. The First Nation filed a lawsuit over damage to the band's land and water. A settlement was reached with CN in 2008, resulting in a payment of $10 million (CBC 2008).

8.7.8 Important factors affecting the consequences of the Wabamun Lake spill

8.7.8.1 Oil properties and behaviour

- Wind dispersed the surface oil over a wide area and onto shorelines. Langmuir circulation may have increased horizontal and vertical dispersion.
- The unique circumstances of the spill (hot oil flowing over land and picking up sediment before entering the lake) meant that tar balls were formed with accumulated sediment and sank.

- The heavy fuel oil contained about six times more total PAHs than most crude oils and also contained a higher proportion of alkyl PAHs than most crude oils (alkyl PAHs pose greater risk of chronic toxicity).
- The tough, weathered coating on the tar balls sequestered the less weathered oil within the balls, greatly limiting access to biodegradation and creating a longer-term source for release of less weathered (and more toxic) oil in near-shore environments as the tar balls broke apart.

8.7.8.2 Effect of the environment on fate and behaviour

- Lake morphometry and mixing characteristics.
  - The lake is shallow, wind-swept and well-mixed, which created conditions conducive to rapid surface dispersion; and
  - Shoreline characteristics that include small bays, creek mouths and marshy areas increased the areas with a high potential for accumulation of oil.
- Seasonality.
  - Winter conditions extended the time required for biodegradation and interrupted cleanup activities;
  - Less mixing energy under winter ice may have contributed to oil-related effects on fish already stressed by natural ecological factors; and
  - The behaviour of the residual oil in its various forms (e.g., tar balls) was influenced by temperature.
- Presence of existing anthropogenic stressors.
  - The area closest to the oil spill was also affected by a thermal plume from a power plant, physical removal of macrophytes (for aesthetic reasons) and high fishing pressure (Schindler et al. 2004). Thus, fish inhabiting the area nearest to the spill were already exposed to other stressors and may have been more susceptible to the additional stress of the spill.

8.7.8.3 Oil toxicity

- Relatively few fish deaths were observed, commensurate with the temperature of the oil when it entered the lake which was at summer temperatures, leading to rapid loss of low molecular weight components.
- There were possible effects on benthic invertebrate community structure but confounding factors, such as water depth and substrate particle size, may have been at least partially responsible for observed results.
- Sublethal toxicity:
  - Embryo deformities were observed in whitefish and pike associated with exposure to PAHs (the heavy fuel oil had a higher relative concentration of alkylated PAHs than typical Bunker C);
  - There was no avoidance of near-shore oiled areas by fish. Fidelity to nursery, rearing and feeding areas may have exposed the fish to oil in sediments and food organisms or reduction in food abundance may have reduced fitness going into the winter season; and
  - Metabolizing the PAHs may have created an energy cost that affected fitness and sufficient concentrations of PAH metabolites and reactive oxygen species to have caused oxidative stress (see Chapter 4).

8.7.8.4 Spill response

- Physical removal of oil caused direct damage to habitat from trampling, low-pressure flushing, vacuuming and dragging over substrates and direct fish mortality due to being removed together with cut vegetation.
- Cleanup activities recovered more than 95% of the oil components that were not lost through natural weathering. The effects of physical removal were balanced against the degree of cleanup required to re-establish human uses of the lake.
- Delays in response were related to lack of preparedness and response capabilities.

8.7.9 Lessons learned from the Wabamun Lake spill

- The consequences of spills of oil adjacent to lakes can be greatly reduced if spill response is rapid and effective in preventing the oil from reaching the lake in the first place.
- Formal notification and involvement of Indigenous communities directly affected by oil spills is necessary for provision of ground support and to avoid adversarial relationships during the response.
- The exposure of spilled oil to soils and organic matter along the spill path increase the potential for production of tar balls.
- Deposition of tar balls and tar mats into heavily vegetated shorelines greatly increases the difficulty of cleanup and prolongs exposure of aquatic biota to physical smothering effects of oil, as well as to toxic effects of the oil.
- Cleanup of shoreline areas resulted in reduced density of vegetation and a decrease in habitat quality for several years.
- An advance plan should be developed for decisions regarding when the effects of cleanup activities outweigh the benefits.
- Wabamun Lake was one of the most well-studied lakes in Alberta, allowing a more confident assessment of the effects of the spill relative to baseline conditions (including effects of existing anthropogenic stressors).
- Crude oil spills into freshwater lakes can cause sublethal effects on fish which are observable in the field.
- There was a significant impediment to an assessment of impacts following the spill due to the priority given to enforcement activities and the control on collection and analysis of samples.

8.7.10 Research needs related to the Wabamun Lake spill

<u>Recommendation:</u> The Panel recommends a follow-up study of residual oils in reed beds and along sandy shorelines of Wabamun Lake. Anecdotal reports in 2015 of tar balls and buried oil in sandy beaches indicate the need for a study. This study would generate useful information, with respect to the chemistry and persistence of the residual oil, the impact of cleanup operations and the longer-term effects on ecosystem services, such as recreational use.

<u>Recommendation:</u> This spill represented a lost opportunity to learn about oil fate and effects in a small ecosystem where there was a high potential to discriminate oil effects from other natural and anthropogenic stressors. The Panel reiterates its earlier recommendation regarding identification of 'spills of opportunity'.

8.8 Spill from a Ruptured Pipeline into Talmadge Creek and the Kalamazoo River, Michigan

On July 25, 2010, a rupture in a pipeline carrying diluted bitumen (dilbit) resulted in the release of ~3,200 m^3 into Talmadge Creek and from there into the Kalamazoo River. It took over 17 hours for the rupture to be confirmed and the flow of dilbit to be stopped. The spill consisted of 23% Western Canadian Select and 77% Cold Lake Blend dilbit (Table 2.2). Western Canadian Select is a heavy blended unconventional sour crude (*CrudeMonitor.ca*) composed of bitumen blended with sweet synthetic and condensate diluents and 25 streams of conventional and unconventional Alberta heavy crude oils blended at the Husky Terminal in Hardisty, AB. Cold Lake Blend is an asphaltic heavy crude blend of bitumen and condensate.

The spill occurred during a period of high rainfall. Water-soaked soils allowed the dilbit to easily run overland to Talmadge Creek and from there downstream to the Kalamazoo River. The flood flows caused significant contamination of riparian lands. The flow conditions had an exceedance probability of 4% with a mean velocity of about 1.1 m/s and a mean depth of 1.2 m (Fitzpatrick et al. 2015). About 3.2 km of Talmadge Creek, 60 km of the Kalamazoo River and three impoundments involving medium to high quality wetlands were affected (Noble 2012). The spilled dilbit ultimately reached a reservoir called Morrow Lake about 65 km downstream. At that point, the high flows dropped, stranding oil on the floodplain.

Local residents self-evacuated from 60 residences and about 320 people reported symptoms consistent with crude oil exposure, including headache, nausea and respiratory symptoms (Stanbury et al. 2010; EPA 2012; Fitzpatrick et al. 2015). Benzene (Table 2.1) was the primary public health concern for residents and workers during the first 30 days.

About 2,900 m^3 of the spilled oil was recovered during the first year and about 10% submerged (about 300 m^3) (Fitzpatrick et al. 2015). The diluent of natural gas condensate volatilized. The weathered bitumen was positively buoyant at room temperature but submerged when mixed with river sediment under natural turbulent river conditions where it caused persistent globule and sheen releases (Fitzpatrick 2014).

8.8.1 Oil-particle interactions and submergence

The spill illustrated the importance of understanding the factors contributing to the formation and submergence of oil particle aggregates (OPAs; Figure 2.7). Flood conditions at the time of the spill increased turbulence and the presence of suspended particulate matter that, in turn, associated with oil particles to form OPAs (Fitzpatrick et al. 2015). Additional mixing from flows over two dams may also have played a role, although OPA and submerged oil accumulated in the first 5 km of river length, between the spill source and the first dam.

Some additional features of the Kalamazoo River may have been important factors in OPA formation, transport and deposition (Fitzpatrick et al. 2015). These features included:

- Abundant wetlands in the floodplain and flooding of riparian lands at the time of the spill. Thus, suspended and bottom sediments had relatively high organic matter content;
- The river is wide and has an average gradient of 0.06% in the spill-affected reach;
- Channel margins, backwaters, side channels, oxbows and impoundments all provided depositional areas; and
- Post-spill high-flow events caused re-suspension and resettling of OPA in downstream areas.

The USGS (Fitzpatrick et al. 2015) suggested that for impoundments with accumulations of thick fine-grained sediment, the process of gas bubble formation (e.g., from microbial methane production in anaerobic sediments) and release from sediments (ebullition) is likely to be an important mechanism for re-suspending OPAs in the water column and releasing oil as sheen on the water surface. Spontaneous releases of oil globules and floating OPAs have been observed regularly in the impounded sections of the Kalamazoo River during 2011–14, resulting in oil sheens at the water surface.

Fitzpatrick et al (2015) noted that OPA formation is a natural process that enhances the physical dispersion of oil and might result in enhanced biodegradation (Figure 2.3). The authors noted that the formation of OPAs would reduce the bioavailability and toxicity of the residual oil to aquatic organisms. They suggested that active enhancement of OPA production could be an alternative to the use of chemical dispersants. However, the prescribed sinking of spilled oil or the use of sinking agents is currently prohibited by the U.S. EPA because of the potential risks of acute and chronic toxic effects on benthic organisms and possibly decreased biodegradation once the oil is deposited and buried in anaerobic sediments (Fitzpatrick et al. 2015). These risks were illustrated in the case of the Wabamun Lake spill, where the tar balls or tar mats formed from interaction with soil particles were resistant to biodegradation and prone to releasing relatively unweathered oil from the interior of the tar balls. Tar balls and tar mats also continue to come ashore in the Gulf of Mexico subsequent to the DWH spill.

Fitzpatrick et al. (2015) concluded that a major factor in ecological risk of OPAs is whether they are physically diluted in suspension (less risk) or concentrated by deposition (more risk). The added context of water depth and the geographic extent are also important contributors to risk.

8.8.2 Environmental effects

Limited acute toxicity testing was performed on oiled sediments from the Kalamazoo River. As part of a NEBA, effects on aquatic organisms from weathered oil were assessed in laboratory acute toxicity studies of seven sediment samples collected from oil-affected backwater habitats along the Kalamazoo River in February 2012, about 19 months post-spill (Bejarano et al.2012 cited in Fitzpatrick et al. 2015). Ten-day whole sediment toxicity tests used *Chironomus dilutus* and *Hyalella azteca* and included survival, growth and biomass as the toxicity endpoints. Results from the toxicity tests indicated that *C. dilutus* were more sensitive to oiled sediment (and presumably OPAs) than *H. azteca* but that all samples exceeded the minimum survival (70%) and growth (0.48 mg ash-free dry weight at test termination) criteria for acceptable controls for the *C. dilutus* tests.

Fitzpatrick et al. (2015) concluded that on the basis of the weight-of-evidence approach and additional risk metrics, it is possible that residual oil at two heavily and one lightly oiled area may pose some risks to benthic receptors. However, chronic toxicity of residual oil to sensitive life stages of benthic invertebrate and fish species remained unknown at the time of writing (January 2015).

In the fall of 2010, all locations on Talmadge Creek and the Kalamazoo River showed signs of impact, but it was unclear whether the impacts were from the spilled dilbit or from physical disturbance caused by cleanup activities (see discussion of cleanup below). Benthic invertebrate abundance and diversity were reduced in Talmadge Creek, and habitat disturbance was severe (particularly overbank areas) (Noble 2012). Abundance and diversity in the Kalamazoo River were reduced due to severe habitat disturbance, sedimentation problems and bank erosion. By the summer of 2011 (13 months after the spill) benthic invertebrate diversity increased in areas of Talmadge Creek altered by the cleanup. Sheen and oil were present. The creek channel was more open, with more sunlight penetration due to extensive removal of oiled vegetation. Abundance and diversity of benthic invertebrates had also improved in the Kalamazoo River, but ongoing work continued to cause impacts. Increased sediment movement and deposition were problematic, and sheen and oil were noted during surveys. In August 2012, a second round of response work disturbed 3 km of the creek. However, according to Noble (2012) the restored creek provided much better habitat compared to 2011.

No fish kills were observed although the Talmadge Creek fish community was reduced and habitat greatly diminished in 2010 with some recovery in 2011 (Milsap et al. 2012). Some declines in fish community diversity and abundance were observed at some sites in the Kalamazoo River.

Crushed and freshly dead mussels were found in the spill area but not in a reference area. Over 3,000 turtles, 170 birds and 38 mammals were brought to rehabilitation centres with survival rates of 97%, 84% and 68%, respectively (Milsap et al. 2012). Turtles were affected the most because they burrow down into sediments. The affected sections of the Kalamazoo River were closed to public access for nearly two years.

8.8.3 Effects of cleanup activities

Talmadge Creek was reconstructed due to removal of bitumen deposits (**Figure 8.10)**. Significant areas of riparian vegetation were stripped from the banks of Talmadge Creek and riparian lands converted to dirt roads.

Figure 8.8 Response operations near the source of the spill on Talmadge Creek. *Image from US EPA.*

The persistent appearance of an oil sheen on the water was a cause for concern among the public, spurring efforts to locate, dislodge and disperse submerged oil (the source of the sheens) (**Figure 8.11**; Chapter 6). This activity employed long poles inserted into sediment to detect the submerged oil, followed by agitation to release buoyant oil, which continued until there was no sheen (S. Hamilton pers. comm.). Aggressive sediment agitation techniques (raking, flushing, aeration and skimming the river bottom physically or with water jets) was conducted in 2011 to liberate submerged oil as recoverable sheen, potentially contributing to further OPA formation and transport of OPAs to downstream reaches (Fitzpatrick et al. 2015). This was illustrated by results before and after agitation at the Ceresco Dam (Noble 2012).

Figure 8.11 Agitation of Kalamazoo River sediment with jets of water to flush submerged oil to the surface. *Image from US EPA.*

The persistent residual submerged oil and oiled sediment in the Kalamazoo River resulted in a protracted cleanup that ultimately required dredging and removal of several islands (because they had been over-washed by oil) and has accounted for a major share of the cleanup costs, which to date have surpassed $1.2 billion (Fitzpatrick et al. 2015).

An advisory group established to evaluate the risks and benefits of cleanup concluded that natural biodegradation could not be relied upon in this case, primarily because heavy oil is chemically recalcitrant to biodegradation and furthermore became buried in anaerobic sediment. The group noted that the weathered submerged oil had low acute toxicity and suggested that the majority of the submerged oil should be left alone. However, there were specific reservoir areas that were identified for further dredging. The group noted that agitation should no longer be considered an option since less than 1% of the oil was released and potentially further degraded the habitat (S. Hamilton, pers. comm.).

8.8.4 Evaluation of the spill response

The National Transportation Safety Board (NTSB) (2012) noted "pervasive organizational failures" in the pipeline company that included:

- Deficient pipeline integrity management procedures, which allowed well-documented crack defects in corroded areas to propagate until the pipeline experienced catastrophic failure;
- Inadequate training of control centre personnel, which allowed the rupture to remain undetected for 17 hours and through two start-ups of the pipeline that increased pressures and the amount of oil lost; and
- Insufficient public and agency awareness and education, which allowed the release to continue for nearly 14 hours after the first notification of an odour to local emergency response agencies.

The NTSB (2012) stated that the following contributed to the severity of environmental consequences:

- The pipeline company's failure to identify and ensure the availability of well-trained emergency responders with sufficient response resources;
- The lack of regulatory guidance for pipeline facility response planning by the Pipeline and Hazardous Materials Safety Administration (PHMSA); and
- PHMSA's limited oversight of pipeline emergency preparedness that led to the approval of a deficient facility response plan.

8.8.5 Important factors affecting the consequences of the Kalamazoo River spill

8.8.5.1 Oil properties and behaviour

- Rapid evaporation of the diluent occurred, creating a respiratory and combustion hazard.
- There was a consequent increase in density of the weathered dilbit.
- Biodegradation potential was limited due to the high proportions of HMW compounds, such as resins and asphaltenes.
- Abundant wetlands with high organic matter contributed to OPA formation, followed by submergence.

8.8.5.2 Effect of the environment on fate and behaviour

- River flow.
    - Flood conditions at the time of the spill increased turbulence and the presence of suspended particulate matter that, in turn, associated with oil particles to form OPAs, and caused oiling of riparian lands and vegetation; and
    - Post-spill high-flow events caused re-suspension and resettling of OPA in downstream areas.
- River channel characteristics.
    - Channel margins, backwaters, side channels, oxbows and impoundments provided depositional areas.
- Sediment characteristics and processes.
    - Gas bubble formation and release from fine-grained sediments in reservoirs (ebullition) re-suspended OPAs, resulting in a sheen on the water surface; and
    - Fine-grained sediment reduced oxygen replenishment and led to anaerobic conditions.

8.8.5.3 Oil toxicity

- There were few apparent acute toxicity effects—no fish kills were noted immediately after the spill and there was high survival among oiled turtles and birds.
- There were possible effects on benthic invertebrate community structure but effects of cleanup activities may have played a greater role than oil toxicity; e.g. crushed and dead mussels.
- OPAs appeared to be low in toxicity (at least to two benthic invertebrates in laboratory toxicity tests).
- There was no publicly available information on sublethal toxicity to fish.

8.8.5.4 Spill response

- Delays in response were related to lack of preparedness and response capabilities, as well as to deficiencies in regulatory oversight.
- Physical removal of oil caused:
    - Direct and major damage to habitat along Talmadge Creek. However, reclamation appeared to have successfully produced viable habitat;
    - Apparent direct mortality to mussels (via crushing) from cleanup activities; and
    - Agitation to dislodge submerged oil and create recoverable sheen appeared to cause greater impacts as it resulted in negligible oil recovery and most likely dispersed the oil into deeper anaerobic layers of the sediment where it would become more persistent.

8.8.6 Lessons learned from the Kalamazoo Spill

- Spilled dilbit can form OPAs under conditions of turbulent flow with elevated suspended sediments and abundant organic matter along the spill flow-path.
- Acute effects from spills of dilbit can be minimal given rapid evaporation of diluents.
- Chronic effects of residual bitumen can be difficult to distinguish from the effects of cleanup activities; therefore, a careful evaluation of net environmental benefit is required.
- It may be best to rely on (slow) natural cleanup processes for submerged oil since the negative effects of cleanup may be significant. However, the NEBA may also have to include net sociological benefit because of concerns of the public.
- The costs of cleanup can be huge relative to demonstrated effects. Cleanup appeared to be driven by concerns over submerged oil even though effects from the submerged oil were not particularly apparent (apart from the aesthetic concerns raised by sheens).

8.8.7 Research needs related to the Kalamazoo spill

Recommendation: Investigation of OPA behaviour and effects on habitat quality and on benthic invertebrates and fish would contribute valuable information to the overall evaluation of risks of spills of dilbit. Various approaches could be used to represent Canadian receiving environments, including a combination of laboratory and mesocosm experiments. Experimental conditions which include ice are required for the Canadian context.

8.9 Other Recent Spills

8.9.1 Westridge 2007 Spill, Burnaby, British Columbia

On July 24, 2007, a backhoe operated by a third-party contractor accidentally ruptured the Trans Mountain pipeline carrying crude oil to the Westridge Martine Terminal. Crude oil from the punctured pipeline sprayed about 12 to 15 m into the air for about 25 minutes. Fifty homes and properties, as well as a section of the Barnett Highway, were affected (TSB 2007). Approximately 234 m^3 of heavy synthetic crude oil blend was spilled. Approximately 40% of the oil entered the storm drain system and reached Burrard Inlet through shoreline storm outfalls, a submerged storm outfall and Kask Creek. Once in Burrard Inlet, the oil began to spread further into the inlet through wind and tide action (TSB 2007).

Western Canada Marine Response Corporation (WCMRC) responded to the spill within an hour and began booming marine areas within 45 minutes of oil being discharged through the shoreline storm water outfall (Stantec 2012).

Emergency phase cleanup techniques included:

- Booming to contain oil around the release points and also exclusion booming to protect sensitive shorelines; and
- Skimmers and absorbent pads to remove oil.

According to Kinder Morgan (2014), approximately 95% (210 m^3) of the released oil was recovered. An estimated 5.5 m^3 was not recovered and was considered to be released to the marine environment (Kinder Morgan 2014).

SCAT was used to identify oiled shorelines, establish cleanup methods and set priorities. Approximately 1,200 m of shoreline were affected by the spill (TSB 2007). Recovery and rehabilitation of affected wildlife was performed through daily surveys for six weeks following the spill (Stantec 2012). By 2011, most of the recovery endpoints established for the spill had been met (water quality in 2007; intertidal sediment quality, PAH levels in crab and intertidal community structure in 2011) (Stantec 2012). In 2012, PAH levels in mussels had not yet met the endpoint. However, results were considered to be confounded due to other sources of PAH in the area (e.g., urban runoff and vessel traffic) (Stantec 2012).

Favourable environmental factors at the time of the spill included:

- Sunny weather (no rainfall runoff to increase movement of oil in storm drains, good evaporation conditions);
- Slack tide conditions which helped keep the oil near the shore while booms were placed;
- Timing which was of primary migration and overwintering period for birds and after the breeding bird season; and
- Timing was prior to the main salmon migration period (Stantec 2012).

8.9.1.1 Lessons learned

The Westridge Pipeline spill was a case where spill response was appropriate and successful.

The TSB (2007) determined the factors contributing to the third-party pipeline breach. These factors are listed below:

- The field location of the Westridge Pipeline was not accurately indicated on design drawings, and the location was not verified, as required under the NEB *Pipeline Crossing Regulations, Part I.* Therefore, the actual field location was not discovered before the start of construction;
- Inadequate communication within Kinder Morgan Canada, Inc., and between Kinder Morgan, the consultant and the contractor;
- The conditions of the crossing agreement and the NEB *Pipeline Crossing Regulations Parts I and II* respecting an onsite pre-construction meeting, locating the pipeline and supervision of construction activities were not adhered to, thus compromising the safe operation of the pipeline; and
- The initial decision by Kinder Morgan to shut down delivery pumps without isolating the gravity feed from the terminal instead of continuing with drain-down of the Westridge Dock Transfer Line increased the volume of crude oil released and was not in conformity with standard emergency shutdown procedures (TSB 2007).

A review of the incident by Kinder Morgan led to the implementation of a Pipeline Protection Department with responsibility for:

- Public awareness;
- Pipeline and associated facilities markings;
- Permits for safe work around pipeline and associated facilities;
- Aerial and ground patrols; and
- Response to emergency calls (Kinder Morgan 2014).

The WCMRC noted that there would be a clear benefit of having an on-water facility linked closely to personnel access and stated that it is reviewing different options within Burrard Inlet to achieve that end (Kinder Morgan 2014).

8.10 Release of Fuel Oil from the *Marathassa* Grain Carrier into English Bay, British Columbia

On April 8, 2015, about 2.7 m^3 of intermediate fuel oil (suspected to be IFO 380) was leaked from the *Marathassa* bulk grain carrier into English Bay, Vancouver (**Figure 8.12**) (CCG 2015a). This resulted in highly visible consequences due to the multi-use nature of the English Bay area (anchorage for Port Metro Vancouver tanker traffic, tourism, recreation). For example, the spill formed a visible sheen and fouled beaches around English Bay, the North Shore, Stanley Park and up into Burrard Inlet, resulting in closing of beaches by Vancouver Coastal Health. One week after the spill, the DFO closed recreational fisheries in a section of the affected area after advice from Vancouver Coastal Health. The Musqueam First Nation issued its own urgent notice one day after the spill, warning those who harvest crab and prawn in the area to stop fishing. However, subsequent chemical analyses of water samples showed hydrocarbon levels below laboratory detection limits, including in waters surrounding the ship, in line with this very small and localized spill.

Figure 8.12 Booms placed around the Marathassa. *Image from CCG (2015a) (http://www.ccg-gcc.gc.ca/independent-review-Marathassa-oil-spill-ER-operation)*

An operational update by the Canadian Coast Guard on April 23, 2015 (CCG 2015b) reported that shoreline cleanup and assessment teams had completed work, with no observed oil reported. Beaches were re-opened at all affected beaches, in conjunction with Vancouver Coastal Health. Sediment and mussel sampling was reported to be ongoing and the precautionary recreational fisheries closure remained in effect. An independent review of the spill response provided to the Canadian Coast Guard in July, 2015, noted that impact on the public was minimal from a health and safety perspective. However, Environment Canada estimated that approximately 20 birds were affected. As of the date of this writing, monitoring continues.

8.10.1 Lessons learned

An independent review of the spill response (CCG 2015a) noted a number of areas for improvement in spill response:

- A need for improved communication with partners to ensure accuracy of communications;
- The Canadian Coast Guard did not have sufficient nearby initial capacity to respond due to demobilizing from another pollution response. Therefore, the Canadian Coast Guard contracted the WCMRC to initiate the on-water response and provide support to the Incident Command Post;
- Information sharing on a common network was not optimal due to federal government electronic policies and protocols;
- Canadian Coast Guard had not yet reached full operational capacity for its Incident Command system. Therefore, it took several days for Unified Command to achieve an operational rhythm;
- Early alerting of municipalities, First Nations and stakeholders was delayed due to the low classification of the incident in the provincial alerting system;
- Vancouver Area Emergency Response Planning timelines did not align with the immediate need to engage partners in the development of an efficient and effective plan in Vancouver harbour;
- The lack of a physical presence of Environment Canada impacted the effectiveness and efficiency of the Environmental Unit; and

- Public communications from Unified Command were challenging because energy was focused on supporting government officials in media briefings, rather than ensuring key facts were being shared with citizens and Unified Command partners.

The independent review presented 25 recommendations for consideration by the Canadian Coast Guard and partners. The recommendations covered communication, training, standards, adequacy of staffing, systems, protocols, tools, approval processes and need for involvement of other federal agencies, notably Environment Canada (CCG 2015a).

In addition to the findings of the independent review, a representative of the Vancouver Aquarium (one of the groups that assisted in the response) pointed out that:

- Gaps exist in research and preparedness because of the lack of cohesive long-term monitoring of coastal ecosystems, creating a lack of baseline data which, in turn, makes it difficult to assess spill impacts;
- There is no official clarity around who is to monitor the effects of a spill; and
- Coordination among agencies and organizations was lacking, resulting in duplication of effort (e.g. at least three agencies collected water samples for testing) and/or gaps in information (Kane 2015).

Recommendation: The Panel trusts that the recommendations made to the Canadian Coast Guard by the independent reviewer arising out of the *Marathassa* spill will be fully implemented. The Panel notes that deficiencies in communication and coordination are common themes among the Canadian case studies reviewed in this chapter.

Recommendation: The Panel reiterates its recommendation for standard guidance regarding monitoring after oil spill events, as well as a targeted program of baseline data collection focussed on areas identified as high-risk.

8.11 Release of Bitumen Emulsion from a Pipeline in Alberta

On July 15, 2015, Nexen Energy reported a pipeline failure at its Long Lake facility near Fort McMurray, AB, that released an estimated 5,000 m^3 of an oil emulsion consisting of bitumen, process water and sand. The release affected an area approximately 40 m by 400 m and was confined primarily to the pipeline right of way, which includes muskeg (AER 2015a). A water body near the release site had apparently not been impacted. The spill created concern because of its size, and the fact that it involved the rupture of a new, double-walled pipeline that had recently been inspected. There were also reports of at least one waterfowl death.

Subsequent to the release and investigation by the Alberta Energy Regulator (AER), it issued a Suspension Order to Nexen due to what was referred to as “noncompliant activities at Long Lake oil sands operations pertaining to pipeline maintenance and monitoring” (AER 2015b). The order directed the company to: immediately suspend 15 pipeline licenses, which required shutdown of 95 pipelines carrying natural gas, crude oil, salt water, fresh water and emulsion; and provide sufficient documentation to assure the AER that the pipelines can be operated safely. As of this writing (September 2015), the suspension has been partially lifted. The cause of the failure is under investigation.

8.11.1 Lessons learned

This spill illustrates that the technology incorporated into newer pipelines is not sufficient to eliminate failures, even of monitored double-walled pipelines. New pipelines must be managed, maintained and monitored, and their performance must be reported rigorously and transparently.

This case also illustrates that the AER apparently was not aware of Nexen's lack of compliance regarding maintenance and monitoring until after the spill occurred. Regulatory oversight is required at all times, not just after a spill event**.**

<u>Recommendation:</u> Systematic and efficient regulatory oversight of industry inspection, testing and maintenance is required for all pipelines, old and new.

8.12 Overall Conclusions Arising from the Case Studies

Delayed response was a critical factor affecting the consequences of all of the oil spill case studies. In some cases, adverse weather was a factor, which delayed initial response. Remote locations made quick response difficult. Ineffective well-capping technology resulted in a flow of oil from the DWH blowout, which lasted three months (although flow was greatly reduced two months after the blowout). However, notwithstanding the importance of weather, remote locations and technological challenges, human error (at an individual and organizational level) was a dominant factor across all case studies. Absent or inadequate planning, insufficient integration, inadequate training, poor communication, insufficient capacity (personnel and equipment), poor or no information sharing and lapses in regulatory oversight were noted for most, if not all, spill case studies. Despite the improvement in engineering design and monitoring technology, spills continue to go unnoticed and unreported for unacceptable lengths of time (e.g., the recent Nexen pipeline spill).

The case studies illustrate that the **consequences of oil spills cannot be predicted simply on the basis of the type of crude oil.** As discussed in Chapters 2, 3 and 4, the interactions among oil chemistry and the receiving environment produce a wide range of potential exposures to aquatic organisms, with an associated wide range of toxicity to individuals and effects on populations. Thus, the effects of diluted bitumen spills will not always be more severe than spills of conventional crude oil. For example, the spill of light crude oil into the Pine River, BC, had more severe consequences (particularly with respect to acute mortality) than the spill of diluted bitumen into the Kalamazoo River.

Studies of the medium and long-term effects of spills into fresh water are rare to non-existent. The consequences of crude oil spills to freshwater systems in Canada can be substantial because of less dilution potential and because of the tendency for oil to quickly become stranded along shorelines where it can remain for long periods of time. It cannot be assumed that spills in fresh water cause fewer adverse effects than spills in marine systems.

Relevant baseline data are often limited or completely lacking, thus hampering rapid decision-making regarding the most appropriate spill response and cleanup measures and limiting the ability to design an appropriate monitoring program with sufficient statistical rigour to reliably indicate effects. Data should include key species at risk by region and type of watercourse (marine offshore, marine inshore, estuaries, rivers, lakes, wetlands). Studies should include analysis oil biodegradation potential to assist in the prediction of environmental persistence as well as the development of remedial technologies.

There is often inadequate knowledge of the natural variability of indicators used in post-spill monitoring. Therefore, achieving a rigorous statistical sampling design capable of establishing whether there are significant effects from an oil spill is challenging. The effects of confounding anthropogenic factors are also often not well understood (e.g., other point and non-point hydrocarbon sources, the presence of other physical and chemical stressors, invasive species, commercial or recreational fisheries and habitat degradation caused by human activities). The influences of large-scale phenomena, such as the Pacific Decadal Oscillation and climate change, on biological indicators must also be considered.

SL Ross (2014) provided the following suggested requirements for baseline information in support of monitoring effects on fish:

- Species of potential interest in the area threatened by the spill (e.g., sentinel species, most abundant species, protected species, exploited species, i.e., subsistence, commercial, recreational);
- Abundance and spatial distribution of key species within and beyond the areas threatened by oil;
- Location of nearby areas that could serve as uncontaminated control areas for comparative purposes (e.g., similar habitat, same species, age distribution, conditions, physical conditions); and
- Information concerning baseline levels of biomarkers in key species prior to the spill (e.g., tissue levels of PAHs, EROD levels, information on spatial or seasonal variation in biomarker parameters).

In addition to the above list, there is a need for baseline information on measurements that allow assessment of effects on productivity in aquatic systems, particularly fish productivity. For example, data on fish age and size distribution and recruitment of young would provide the basis for evaluating whether a spill had the potential to alter the population via partial elimination of a year class.

Priorities for the acquisition of baseline data can be based upon the identification of locations that are under the greatest risk of contamination from oil spills. The results of existing national relative risk assessments (such as those reviewed in the following section) can be used for prioritization. A review of locations with a combination of characteristics that increase risk should be conducted. These characteristics could include increased likelihood of exposure to oil spills due to proximity to multiple modes of transport of crude oil (e.g. rivers with pipeline crossings, railways and/or roads running parallel to the river, and oil tanker traffic in estuarine areas). Other characteristics could include relative sensitivity of the receiving environment determined by the presence of critical habitat and/or sensitive species, and the presence of culturally important species. Professional judgement will also be needed for this prioritization. Furthermore, it may be more appropriate to focus on indicators, such as benthic invertebrates, for standard monitoring purposes.

Aquatic ecosystem resilience to shocks from oil spills is key to the maintenance of ecosystem services. The presence of long-term stresses may tax the capacity of ecosystems to be resilient to shorter-term shocks. In some cases, ecosystems will undergo fundamental shifts in structure and function following disturbances (e.g., changes in trophic structure caused by invasive species). If policies and decisions are to be based upon resilience and the preservation of ecosystem services, multi-disciplinary research effort on the resilience of key marine and freshwater ecosystems will be required.

Effects of oil spill cleanup on aquatic ecosystems can be significant. This is particularly true for cleanup of stranded oil in both marine and freshwater environments, whether it is in the inter-tidal zone, the shorelines of lakes and rivers, or on woody debris and man-made structures in river channels. A careful, but rapid, NEBA is required tailored to each unique spill situation. Unfortunately, there is insufficient knowledge of the long-term consequences of residual stranded oil to allow for confident NEBA in many environments, including Arctic and sub-Arctic systems.

The potential for long-term effects on animal populations continues to generate much debate and controversy. The Panel recommends that there be support for long-term research into effects of different oil types on populations of aquatic biota, especially fish, marine mammals and waterfowl. This research could be part of the suite of studies associated with significant oil spills.

There is an urgent need for the development and production of innovative, cost-effective and readily available spill prevention and response measures for use in Canada, including the Arctic. As already stated in this report, if spills do occur, maximum advantage should be derived from the opportunity to study the fate, behaviour and effects of the spill in the short, medium and long-term. Studies of the relative effectiveness of response measures should also be part of a suite of investigations associated with all significant oil spills in Canada. Pre-approved funding should be put aside for 'spills of opportunity' that would incorporate a combination of research and monitoring. Responsibility for each component of spill studies must be clear and research and monitoring efforts must be well coordinated to eliminate redundancy and to ensure that all required study components are implemented.

The consensus of scientists in oil spill countermeasure research is that major advances in the development and validation of spill response technologies are being hampered by our inability to conduct controlled field experiments with oil. In addition, validation is hampered by crude or no methods for measuring the efficacy of response measures. While 'spill of opportunity' case studies will provide lessons learned, they do not provide an optimal platform for the delivery of science due to logistical constraints (e.g., lack of experimental replication due to site heterogeneity, etc.). To support predictive numerical models and operational guidelines for spill response, there is a need for a rigorous database for the fate, behaviour and effects of various types of oil spilled and the efficacy of current and emerging oil spill countermeasures over a range of environmental conditions. This will require support for the conduct of field trials designed with statistical rigour that incorporate controlled releases of oil.

National guidance for monitoring of oil spills is urgently required to ensure that information gathered is reliable, adequate, credible and consistent. The guidance should include provisions for adjustment in response to specific characteristics of the receiving environment. The guidance should also include requirements for standard baseline datasets (tailored to specific receiving environments). The guidance could be divided into two parts: 1) which information to collect without exception; and 2) which information gathering can be deferred until the full scope of the spill and its potential effects are better understood. The guidance should include information on data quality requirements, including determination of minimum sample sizes, standard sampling protocols and laboratory quality assurance/quality control.

SL Ross (2014) also provided a list of recommendations for specific areas of research and development that can improve the ability to mount monitoring efforts efficiently for spills in Canada. The list is as follows:

- For potential Canadian biomonitoring species (cod, Arctic cod, snow crab, salmon, flatfish, mussels, oysters) prepare an annotated bibliography of studies on effects and relationships among exposure, bioaccumulation of and effects of PAHs (e.g., physiological biomarkers). *The Panel adds specific mention of freshwater species, such as whitefish, pike or small-bodied fish species, used in programs such as the national Environmental Effects Monitoring program.*
- For representative species used for monitoring, determine the exposure-response-recovery relationships for biomarker activity and occurrence of histopathological changes. *The Panel suggests that the relevance of physiological biomarkers to exposure versus effects should be examined (see Chapter 4).*
- Identify and acquire or develop a model for estimating fate, behaviour and persistence of spills into rivers. *The Panel notes that several hydrodynamic models are already available that are in common use in Canada. However, very few are three-dimensional and there appear to be no widely accepted models to describe surface water-groundwater interactions across a wide array of river types.*

8.13 Prediction of Risk of Crude Oil Spills in Canada

8.13.1 Risk assessment for marine spills in Canadian waters south of 60th parallel

A risk assessment of marine spills along four sectors of the Canadian coastline - the Atlantic and Pacific Coasts, the Estuary/Gulf of St. Lawrence and the Great Lakes/St. Lawrence Seaway System - was conducted for Transport Canada and reported in 2014 (WSP and SL Ross 2014a), hereafter referred to as the TCRA (Transport Canada Risk Assessment). A brief description of the approach and key findings of this assessment is provided in Chapter 7. In this chapter, uncertainties associated with that risk assessment are identified and discussed in detail because of its potential influence on future policy, spill preparedness and response activities.

8.13.2 Risk assessment methods

8.13.2.1 Spill frequency

The TCRA considered production (offshore wells) and transportation sources and divided spills into four sizes: 10-99.9 m^3; 100-999.99 m^3; 1000-9999.9 m^3 and >10,000 m^3.

Each of the four sectors was divided into subsectors that were further subdivided into three zones representative of near-shore, intermediate and deep sea environments. A total of 77 zones were allocated a frequency of spill and an environmental sensitivity, which were then applied to generate a risk estimate (WSP and SL Ross 2014a).

Estimated spill frequency was based on the past 10 years of spill data from Canadian and international data sources. Spill frequency was estimated for crude, refined cargo and fuel according to the relative volumes transported across each subsector. The Panel focused on the results for crude oil.

Uncertainty Regarding Spill Frequency

- The TCRA noted that while the variability in spill rates is not wide among different governance structures around the world except perhaps at the highest end of spill size ranges, the use of worldwide incident data may have overestimated the likelihood of spills in Canada given the robust marine governance regime and the actual spill record. This assumption is subject to debate based on evidence such as the global review of environmental damage liability regimes by Goldsmith et al. (2014). Furthermore, despite advances in technology and improved safety protocols, accidental releases, such as the recent *Marathassa* spill, will continue to occur (Section 8.12). The effects of increases in the volume of tanker traffic on spill rates in the various sectors and subsectors were not discussed in the report.
- Probability estimates by the TCRA for the St. Lawrence Seaway were identified to be conservative as they were not corrected to account for closure of the Seaway about 30% of the year due to ice cover. However, their analysis did not include US traffic in the Great Lakes, which would have provided a similar precautionary approach for evaluating the risk of spills in the Great Lakes.

8.13.2.2 Environmental sensitivity

The TCRA estimated environmental sensitivity of each zone using three indicators: physical sensitivity (PSI), biological resource (BRI), and human-use resource (HRI). The environmental sensitivity index (ESI) was calculated as follows: ESI = 0.3(PSI) + 0.5(BRI) + 0.2(HRI). The weights applied to each indicator were from a review of costs, such as the influence of physical factors in determining cleanup costs.

The PSI rank was related to zone sensitivity, natural oil persistence and ease of cleanup.

- Exposed rocky shores were ranked least sensitive;
- Most sensitive were sheltered rocky shores, tidal flats, marshes, wetlands, eelgrass and ice infested waters; and
- Gravel was ranked in the middle.

A 0.3 PSI for open sea was based on average cost of cleanup per tonne compared to near-shore environments The BRI and HRI were based on a method developed for Australia (DNV 2011 cited in WSP and SL Ross 2014a). It was assumed that the BRI of intermediate and deep sea zones that did not include any of the identified biological components (e.g., species at risk, birds, mammals, reptiles, fish, meroplankton and invertebrates) would be related to that of the nearest near-shore zone times a weighting factor of 0.4x for intermediate and 0.1x for deep sea. Weights attributed to each biological component included data from the Strategic Environmental Assessment for the Gulf of St Lawrence study (GENIVAR 2013 cited in WSP and SL Ross 2014a) and from other marine environmental studies (dredging, harbour, etc.).

The HRI was based on a combination of commercial fishing intensity, tourism employment intensity, freshwater use intensity and freight tonnage index. Weights applied to each component were: 0.55 for commercial fishing, 0.2 for tourism, 0.15 for water usage and 0.1 for port industry. Commercial fishing intensity scores did not include recreational or traditional fishing due to absence of comparable data, but the authors maintained that the index would provide a sufficient indicator of overall vulnerability. Tourism Employment Intensity was based on the ratio of tourism industry employment versus total employment. The Freight Tonnage Index was based upon total tonnage in each port. The use of fresh water by humans (Freshwater Use Intensity) was based upon coastal population as a proxy because data on water intakes were not available.

Recommendation: Future relative risk assessments should include explicit consideration of intermediate and deep sea zones with greater sensitivity, particularly in zones with current or projected offshore oil production.

The TCRA report noted that the environmental sensitivity values were generally lower for intermediate and deep sea zones. They noted exceptions due to the availability of data for some particular, sensitive intermediate and deep sea zones. However, there was no attempt to include these areas in the analysis (for example, as exception layers). A discounting term may be appropriate in order to account for increased capacity for dilution, dispersion and biodegradation in some of the zones or subzones.

Recommendation: Future relative risk assessments should build upon the TCRA results by focussing on high-sensitivity areas within each of the assessment zones in order that preparedness and response plans can include explicit plans for the areas with the highest potential consequences.

The TCRA report presented ESIs as average values for an entire zone. The authors noted the shortcomings of this approach as the use of averaged numbers results in loss of detail—high sensitivity areas within a zone might be concealed if surrounded by relatively low-sensitivity areas due to the subsectors being so large.

Recommendation: Consideration should be given to the refinement of the PSI values based on recent shoreline mapping data (an ongoing initiative of Environment Canada) and site-specific data from past spills.

Recommendation: The methods for development of BRIs require review and refinement in order to increase the reliability of the relative risk indices at the subzone level. These refinements should

reflect the nature of the receiving environment within subzones and the specific valued components within the subzones.

__Recommendation:__ **The TCRA should be updated to include a fresh water-specific set of ESIs. Such an assessment would be relevant not only to ship-source spills, but to spills from pipelines, crude-by-rail and truck transport.**

The reliability of the BRIs depended on the quantity and quality of data on the components (e.g., birds, mammals, fish, etc.) in terms of where they are located within the zones plus the weighting for sensitivity. Data for some components in some of the subzones were limited or non-existent. The information presented in the TCRA on chronic effects provides evidence that raises questions about the weighting of sensitivity; e.g., Table 4.1 in the TCRA. For example, fish are given a medium-low sensitivity despite the sensitivity of early life stages to PAHs, as demonstrated in laboratory as well as field studies (Chapter 4). However, evidence from spills around the world seems to indicate that fish populations are not as sensitive as other marine biota. The cumulative impacts of stressors that can exacerbate the effects of spills (e.g. increasing water temperature and/or nutrient loads) were not considered under the BRI. Within the TCRA report there seems to be marine bias in the weighting approach used for sensitivity (probably due to the larger database available); thus, the applicability to fresh water (i.e., the St. Lawrence River and Great Lakes) is questionable.

__Recommendation:__ **Future relative risk assessments should include refined human use resource indices, which include the uses of waterbodies for traditional purposes by Indigenous peoples, and which include the presence of critical municipal, agricultural and industrial uses that may be adversely affected by a spill. The Panel notes that the TCRA report includes a similar recommendation.**

The appropriateness and completeness of the HRI is subject to criticism since the inputs to the index, and the weightings applied to those inputs, would be expected to vary significantly within zones and subzones. For example, the presence of critical water intakes for agriculture in areas with lower human population size along the St. Lawrence River might justify an increased weight for water use intensity in those areas. In addition, the HRI did not incorporate the significance of traditional resource uses by Indigenous peoples.

8.13.3 Results of the risk assessment

The results of the TCRA are described in Chapter 7, whereas this chapter focuses on key parameters determining the outcome of the risk assessment, followed by a review and discussion of uncertainties associated with the TCRA results.

WSP and SL Ross (2014a) identified the key parameters influencing the relative risk outcomes as:

- Oil persistence, a consequence of chemical composition and microbiological sensitivity or recalcitrance.
- Extent of the spill over time.
- Potential movement of the spill.
- Characteristics of the receiving environment.
    - Shoreline habitat, sediment type, topography, currents, hydrology;
    - Presence and concentrations of factors that would enhance natural attenuation or biodegradation, such as nutrients, electron acceptors, etc.;
    - Coastal resources in area of influence of spill;
    - Physiological and behavioural characteristics of coastal resources; and
    - Type and intensity of human activities.

- Type and volume of the spill.
  - Toxicity, bioaccumulation rates;
  - Volume and exposure concentrations in various media (water, sediments, soil, food, air);
  - Direct versus indirect exposure via food;
  - Exposure duration; and
  - Time of year—organism life cycles plus weathering.
- Type and effectiveness of the cleanup response.
  - Possibility of damage from cleanup activities.

The TCRA authors stated that effects on natural habitats in fresh water will resemble those of marine spills. However, they also stated that spills in fresh water have a much greater potential for contaminating potable water supplies, affecting areas of concentrated populations, damaging manmade structures and disrupting other human activities such as recreation.

The TCRA authors also noted that, in most habitats, site recovery from an oil spill will occur within 2-10 years, and cautioned that perception of contamination can last longer than actual contamination, with economic effects on fisheries and tourism sectors. The perennial and thorny question "How clean is clean?" has been noted in Chapters 6 and 7.

It cannot be assumed that the TCRA risk assessments are uniformly precautionary. The TCRA assessment is conservative in that it did not assume any marine oil spill prevention measures or responses, such as mechanical recovery or dispersant application. However, the overall level of conservatism in the assessment is difficult to determine because components within the assessment, such as environmental sensitivity, may not have been uniformly conservative.

<u>Recommendation:</u> Preparedness planning should consider information from Indigenous, provincial, territorial and municipal sources in order that smaller-scale, higher-risk locations can be identified. For example, the Strait of Georgia and the Gulf of St. Lawrence have areas of concentrated seabird and migratory bird use that would be a high priority for specific response measures targeted at reducing impacts to birds. Many of these areas have already been mapped at a finer scale than presented in the TCRA. Provincial laws and regulations must be considered in preparedness to ensure harmonization and avoidance of redundancy.

Not including data from provincial, territorial, and municipal sources is understandable for such a high-level assessment; but it produced significant limitations in the risk analysis.

Except for the St Lawrence River, the assessment did not include rivers such as the Mackenzie River and Fraser River, which have barge traffic and could have increased traffic in the future.

<u>Recommendation:</u> First Nation, Inuit, and Métis jurisdictions must also be considered and included in preparedness planning and broad consultation with Indigenous peoples should be part of such planning.

Any and all future preparedness planning should explicitly include First Nations, Inuit, and Métis jurisdictions as well as broad consultation with all Indigenous peoples. Indigenous peoples are often the most knowledgeable groups regarding local and regional conditions which would affect preparedness planning. Indigenous peoples are also often the closest people to spills in remote locations; therefore, they can be well-placed to be among the first responders (if capacity exists in Indigenous communities).

<u>Recommendation:</u> Any future relative risk assessments should include weather as a factor within the risk scenarios.

It was logical that local or regional-scale weather data were not included in the TCRA high-level assessment. However, consideration of the relative frequency of extreme weather events among the zones used in the assessment would have added value since the weather can be an important determinant of consequences (e.g., due to delays in response, weather effects on efficacy of response measures and weather effects on dispersion of the oil).

Recommendation: The TCRA should be revised to include risks of spills from U.S.-bound tanker traffic in Canadian waters.

Risk in the Pacific sector was related largely to tankers going to refineries in Washington State, and the authors stated that, therefore, these spills would not be subject to Canada's spill response regime, despite close proximity to southern British Columbia's coastal areas. There is also concern that the risks of spills from U.S.-bound tanker traffic within Canadian waters was not considered.

Recommendation: The Panel has made several recommendations with respect to research on the fate and effects of diluted bitumens. Results of this research should be included in future risk assessments, particularly for scenarios where research indicates that the fate or toxicity of diluted bitumens would differ significantly from conventional crude oil.

The modeling of the behaviour of spills did not distinguish diluted bitumens from conventional crude, and it was not clear whether critical differences between marine and freshwater systems with respect to the processes were included in the model (drifting, spreading, evaporation, photooxidation, natural dispersion-dissolution of oil in water, water-in-oil emulsification, biodegradation and sedimentation; Chapter 2).

Recommendation: The current lack of inland shoreline sensitivity information in the open literature is a serious gap affecting the ability to apply risk-based preparedness and response planning. Prioritization of areas requiring mapping could be based upon evaluation of the intensity of human use, the current knowledge of the relative sensitivity of ecosystems, and the availability of information from various sources. For example, high-priority areas for mapping might include areas upstream and downstream of hydroelectric dams.

Shoreline mapping is still incomplete, particularly inland, including along the Great Lakes. The Panel is aware that industry is doing some mapping and that Environment Canada continues to work on mapping marine coastal areas. The Panel also understands that Environment Canada has been working with Alberta, British Columbia, and CN Railway on mapping of rail corridors and that similar work was done in Quebec (S. LeBlanc, pers. comm). Environment Canada has been approached by Canadian Pacific regarding conducting similar work along their railway corridors (S. LeBlanc, pers. comm.).

Recommendation: National-scale relative risk assessments used for preparedness and response planning must be based upon reliable and consistent data and analysis. Therefore, standardized methodology for environmental sensitivity mapping is an urgent requirement.

Apparently, even when environmental sensitivity data are available, they are obtained using different methods. For example, according to the TCRA, survey methods used by each regional department of the DFO may differ, and bird data are obtained using different types of datasets, resulting in regional disparities**.**

Recommendation: Future refinements to relative risk assessment must include explicit modeling of freshwater systems, taking into account the unique features of freshwater environments that affect exposure and effects.

The TCRA assumption that effects in fresh water will resemble marine spills is problematic, as illustrated by the case studies reviewed earlier in this chapter and the review in Chapter 4.

<u>Recommendation:</u> The Panel recommends that the relative risk assessment method could be applied at a smaller scale for the purposes of identifying the critical areas for protection and preparedness, and could be used to identify critical data gaps.

As the authors state, rare events are difficult to predict—especially the really large spills. Therefore, preparedness planning should focus on events where consequences would be highest.

<u>Recommendation:</u> The Panel strongly recommends the development of a national, consensus-based set of indicator species for each of Canada's high-risk major marine offshore and inshore zones. Once these indicator species have been selected, coordinated research programs among academia, industry and government should be developed that: a) compile existing information; b) identify and prioritize critical data gaps; and c) conduct research to fill the priority data gaps. (See recommendations in the Section 8.15 for additional details.)

<u>Recommendation:</u> The Panel recommends that future national or regional-scale relative risk assessments should include indices of current status of receiving environments, with emphasis on existing levels of anthropogenic stressors. Future risk assessment could also combine risks of tanker spills with risks of pipeline, rail and road spills for a cumulative oil spill risk in the most sensitive receiving environments.

The overall TCRA environmental risk index appeared not to address cumulative risks or the existing state of the environment (which may already be degraded and at increased risk; reviewed in Chapter 4).

8.13.4 Major Conclusions and Recommendations from the Transport Canada Risk Assessment Report

Some of the key conclusions and recommendations presented in the TCRA report were:

- Spills in the 10 to 1000 m^3 range generate higher overall risks both respect to frequency and consequence;
- Eight of 10 highest risk areas are near-shore and two of the 10 are intermediate—this conclusion has implications for response capabilities and preparedness;
- The Marine Pollution Incident Reporting System database on pollution incidents maintained by the Canadian Coast Guard should be examined for improvements regarding comprehensiveness and quality of data;
- In future risk assessments, consideration could be given to effects of spill response according to oil type and spill size, as well as remoteness, weather and other factors;
- All regions should attain the same level of detail regarding environmental data, and these data should be in GIS (geographic information system) format;
- Regarding physical sensitivity, more information on evolution of coastal areas facing climate change impacts, in particular for sensitive components such as coastal wetlands, is urgently required. Integrating data on littoral geomorphology to capture erosion impacts would be a valuable refinement– these data are often available at the provincial level;
- Regarding biological resources, data should be incorporated for all protected marine areas under various jurisdictions and Ecologically and Biologically Significant Area (EBSA) or equivalent layers, and risk analysis for fresh water should be considered separately from marine analyses due to differences in the type of data available; and
- Regarding human resource use, information should be incorporated for provincial and municipal conservation/protected areas, for freshwater intake and utilization (drinking water, agricultural

and industrial) and for archeological and cultural heritage sites. The current risk estimates should be overlaid with information on Aboriginal communities.

The Panel supports the recommendations of the TCRA report.

8.14 Risk Assessment for Marine Spills in Canadian Waters North of 60th Parallel

A relative risk assessment for oil spills in Arctic waters was conducted, but only refined products were considered because crude oil is not currently transported in the Arctic (WSP and SL Ross 2014b). Therefore, the Panel reviewed this Arctic Marine Risk Assessment (AMRA) report as a general indicator of risk of oil spills in the Arctic, with emphasis on drivers of risk and uncertainties within the risk calculations.

The Panel's review focuses on the environmental risk index component of the AMRA since calculation of spill frequencies appeared to be the best possible given the available data. The authors discussed the overall poor coverage of Arctic navigational charts (except for the Beaufort Sea and Foxe Basin) but decided not to apply increased weight to spill frequency due to poor navigational information in specific subsectors. The reason is that there had not been a significant number of reported spill incidents related to navigational issues and, for the most part, marine traffic in the Arctic is performed by long-time operators who use up-to-date charts and are familiar with their routes.

The logic behind the use of the same basic methods for calculating risk for North of 60 as for South of 60 is debatable. The PSI represents the degree of difficulty involved in coastal cleanup due to factors such as remoteness and/or distance from first-response centres. Therefore, the weighting attached to the PSI for Arctic conditions arguably should have been higher than for the south. Furthermore, the HRI might need upward adjustment due to use by Indigenous peoples.

Recommendation: Shoreline mapping should be conducted in areas where oil and gas exploration and development is already occurring or is expected, e.g., Beaufort Sea and the Mackenzie Delta. The mapping should also consider other human activities that would affect relative risk, such as mining, where large port facilities have been proposed involving not only transport of the minerals out but fuel in, and increased commercial shipping traffic through the Northwest Passage, which brings greater risk of fuel oil spills. The current rapid rates of coastal erosion should also be noted and mapped for the purposes of continued monitoring.

The AMRA authors assumed that ice-free shorelines are the most sensitive because the presence of ice prevents the oil from reaching the shoreline. This was a simplistic assumption as there could be times when the shoreline is partially ice-covered and the situation will be very dynamic. The highest risk would probably be during the seasonal changes when multiple processes might control fate and effects (e.g. erosion, scouring, slumping that would take oil and mix it in with shoreline materials or near-shore sediment materials).

The AMRA authors noted the lack of information regarding Arctic shoreline types.

Recommendation: The Panel acknowledges that shipping traffic volume is low in the Arctic. However, shipments of fuel oil to Arctic coastal communities do occur, and the risks of spills of fuel oil should be assessed. Furthermore, in preparation for increases in Arctic traffic the AMRA methodology needs to be revised and tailored for the Arctic.

Risks of spills during shipment of fuel oil by ship and barge as well as transfer of fuel from barges to storage facilities require assessment in order to inform preparedness planning. The methods used for the AMRA biological resources index were basically the same as for the South of 60° TCRA study. The Panel questions the use of the same methods for the Arctic as for more southerly zones, particularly sensitivity weights. Sensitivity in the Arctic should consider more than marine species and habitats, as river deltas and the rivers themselves are important for anadromous fish[7] and other sensitive uses (including human uses).

The calculation of the HRI involved the following:

- Coastal population index (CPI);
- Tourism index (TI);
- International freight tonnage index (IFTI);
- National freight tonnage index (NFTI); with
- HRI = 0.7(CPI) +0.2(TI)+0.05(IFTI)+ 0.05(NFTI)

The AMRA authors state that, "since the majority of the population in the area of study is Inuit, the coastal population indicator captures explicitly the human use for these communities."

This assumption that the coastal population captures human use of the coastline is an over-simplification because many coastline areas with zero population can have high traditional use value. The Panel questions whether the CPI would be found to be sufficient by Inuit people.

Recommendation: Additional research should be conducted in the near future to capture both increases in marine traffic and the activities of commercial fisheries in the regional risk assessment.

The AMRA report acknowledged the value of royalties paid to Nunavut by offshore turbot and shrimp fishing companies and also acknowledged the value of Arctic char and sealing to communities and state that these activities are vulnerable to marine spills. It was felt that the large scale of the assessment limited the incorporation of commercial fisheries as their activities may not be associated with coastal environments.

Recommendation: Current environmental risk index (ERI) values are low or very low because of projected low spill frequency. Therefore, the Panel is uncertain whether ERIs, in their present form, are useful for planning. The Panel suggests using the ESI component of the ERI equation as a means of identifying priorities. However, the way that the ESIs are calculated would have to be revisited using input from communities and scientists because the Panel is not convinced that the current ESI methods are relevant and representative of Arctic conditions.

The authors state that, from an emergency planning point of view, the ERI can be interpreted as a relative measure of the importance of risks associated with oil spills. A large ERI value implies a relatively higher risk of economic and environmental damage. Therefore, the index could be applied to damage reduction in Arctic waters if combined with emergency planning by authorities. However, the results of the ARMA did not provide a particularly useful level of resolution, given the scale of the Arctic and the location of population centres that may serve as the location for Arctic preparedness.

The AMRA report gave little consideration to risks in the Mackenzie River and Great Slave Lake (and other freshwater areas), except with respect to the Mackenzie River delta where it enters the Beaufort Sea. Traffic is low in these areas; however, the same can be said for the Beaufort Sea and the southern part of Hudson Bay, including James Bay and the Foxe Basin, where ERIs were high in some cases. Given the description of the ecology of the Mackenzie River and Great Slave Lake in Section 4 of the AMRA report, and the presence of EBSAs, it is puzzling that the calculated risks for these two areas did not exceed the "relatively low" category. There were no comments about the future risks for the River or the Lake in Appendix 2 of the AMRA report.

[7] *Anadromous fish hatch in fresh water, spend most of their life in the sea, and return to fresh water to spawn; e.g., salmon.*

8.14.1 Recommendations from the Arctic Marine Risk Assessment Report

The Panel concurs with the following recommendations made in the AMRA report:

- Matching vessel codes from the Automatic Identification System database and Transport Canada commodity database would allow consideration of the exact trajectory of specific cargo—this should be considered for the Arctic as well as other regions;
- The current analysis is based on yearly estimates of spill frequencies. The estimate could be refined by taking into account the length of the shipping season within each subsector and thereby considering seasonal variations that influence risk estimates;
- Evaluation of coastal areas facing climate change impacts is required;
- A separate analysis for fresh water (Mackenzie River and Great Slave Lake) is necessary to account for differences in critical processes affecting fate and transport of oil as well as effects; and
- Commercial fisheries information should be incorporated into the HRI.

Recommendation: The Panel also recommends that future relative risk assessments for the Canadian Arctic include spills from exploration and production in adjacent U.S. waters of the Beaufort Sea as well as future drilling in Canadian waters.

8.15 Assessment of Marine Oil Spill Risk and Environmental Vulnerability for the State of Alaska

The Panel reviewed an assessment of oil spill risk for Alaska (Reich et al. 2014) to compare and contrast the methods used with those used for the two Canadian risk assessments reviewed above. The results of the Alaska risk assessment are briefly described in Chapter 7.

The Alaska assessment was at a smaller spatial scale than the Canadian AMRA assessment, but still covered a large area. This scale required the use of similar generalizations regarding spill behaviour and effects as those used in the AMRA.

Recommendations based on the differences between the Alaska and Canadian (AMRA) assessments that should be considered for future risk assessments in Canada are presented below.

Recommendation: Future relative risk assessments conducted for the Canadian Arctic include season-specific influences on sensitivity.

The Alaska assessment included season-specific vulnerability, which is very important in Arctic regions.

Recommendation: Future risk assessments for the Canadian Arctic should include consideration of crude oils, including exploration and oil production facilities.

The Alaska assessment considered crude oils, heavy oils, light oils and distillates, whereas the Canadian assessment focused on refined products only.

Recommendation: The Panel considers the inclusion of dispersion modeling to be an essential component of risk assessments of oil spills, particularly at the regional scale. However, the Panel notes that the dispersion modeling done in support of the Canadian assessment was basic and would require refinement for application to finer scales (with the accompanying requirement for additional data including oil interactions with ice, and biodegradation potential as bioremediation may be the most feasible cleanup strategy in remote Arctic areas).

Weathering processes and the amount of oil reaching shore were not modeled in the Alaska assessment. However, the report recommended that for regions with high relative risk, trajectory and fate modeling should be conducted.

Recommendation: **The Panel notes that the vulnerability method used in the Alaska assessment is applied at a finer-scale and does not rely on broad sensitivity categories applied to entire groups; therefore, this approach may be more appropriate if finer-scaled relative risk assessments are conducted in Canada.**

Vulnerability was assessed for Alaska receiving environments using habitat (shoreline, bottom marine and sea ice) and species sensitivity and recovery information compared with "sensitivity" in the Canadian assessments, which combined physical, biological and human-use indices.

Recommendation: **The Panel suggests that an assessment of future risks in the Canadian Arctic include a critical review of the preparedness and response/mitigation options applicable to Arctic conditions and the likelihood of these measures being effective in reducing both the probability and consequences of oil spills, with special consideration of spill site remoteness and distance from first-responder centres.**

The Alaska assessment assumed that risk mitigation would reduce the probability of an incident becoming a spill event and also assumed increased effectiveness of spill prevention and risk mitigation measures to reduce spillage.

Recommendation: **The Panel suggests that a Spill Risk Calculator tool for Canada would be beneficial to preparedness planners and responders.**

The authors of the Alaska study provided a Spill Risk Calculator Tool and noted that the transparency of the method allows for quick updates of results as more data become available.

The Alaska assessment method was very data-intensive. A similar quantity of relevant data would not be available for the Canadian Arctic except for a few relatively small areas.

Recommendation: **The Panel strongly recommends a national database of information required for relative risk assessment in the Arctic. This database would include government, academic and industry sources, as well as traditional knowledge sources.**

Recommendation: **The Panel suggests that a more detailed assessment of the Beaufort Sea be a priority for the next round of relative risk assessments. The assessment could be used to identify critical data gaps for parameters that drive risk in the Beaufort Sea.**

Both the Alaska and Canadian assessments identified the Beaufort Sea as a high relative risk area for crude oil spills in the future.

Recommendation: **Although it would require some educated guesses (preferably in collaboration with industry), incorporation of cleanup costs would add value to the results of relative risk assessments for the Arctic.**

Neither the Alaska nor the Canadian assessments included cost of cleanup because information on such costs was lacking (due to the fortunate lack of major spills).

In summary, the Alaska analysis provided a conservative relative environmental risk map based on maximum most probable discharge or worst-case discharge. The assessment did not account for weathering and did not model amounts reaching shorelines, but it did include seasonal differences, a fairly large number of discrete habitat types, and a cross-section of species or species groups that are assessed for vulnerability using several parameters. The Alaska analysis did not provide socioeconomic analysis, which can be regarded as a significant weakness.

8.16 Assessment of Risks of Hypothetical Spills from the Proposed Northern Gateway Pipeline

Detailed ecological risk assessments were conducted to evaluate risks to freshwater and estuarine resources from hypothetical spills along the proposed Northern Gateway pipeline (NGP) route (Green et al. 2015). The risk assessments conducted for the NGP were quantitative and detailed, in contrast to the relative risk assessments reviewed above. The purpose of the NGP assessment was to evaluate the risks associated with a full bore pipeline rupture at discrete locations.

> Ecological risk assessment (Figure 8.13) is conducted using a standard framework that starts with Problem Formulation, proceeds through exposure and effects analysis and concludes with characterization of the risk. Problem formulation includes: development of risk management goals and objectives; identification of assessment and measurement endpoints; determination of the spatial and temporal context; screening for stressors of concern; and selection of valued ecosystem components (VECs). Engagement of interested parties in problem formulation can reduce the level of criticism and debate because the range of values can be represented via selection of goals, endpoints, receptors, etc. Exposure assessment is conducted via measurement and/or modeling. Effects assessment is usually conducted by comparing predicted or measured exposures with derived effects thresholds based on toxicity test results. Risk characterization estimates the level of effect, most commonly through the calculation of so-called hazard quotients (the ratio of the predicted exposure and the effects threshold).

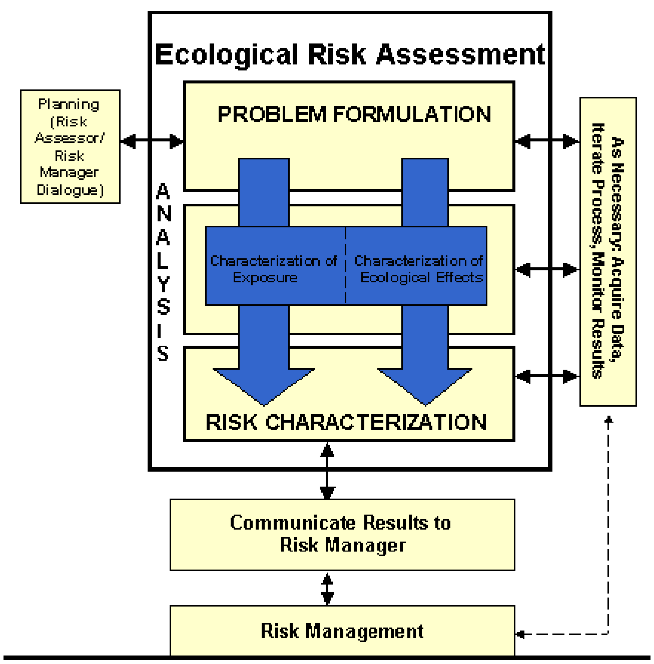

Figure 8.13 Framework for Ecological Risk Assessment. *Image from EPA (1998).*

These detailed assessments included modeling of dispersion and resulting concentrations of whole oil and oil components on the water surface, shorelines, in the water column and in sediments of four different receiving streams that were selected on the basis of environmental, socioeconomic, cultural and traditional values (Green et al. 2015). The receiving streams also reflected a range of watercourse types and had limited access, thus increasing response times. The predicted concentrations in and on water, in sediments and along river and estuary shorelines were then assessed against thresholds for acute and chronic effects for a range of species.

The four locations selected for the NGP assessment were:

- Chickadee Creek – low gradient interior river tributary discharging to the Athabasca system upstream of a populated centre in Alberta (Whitecourt);
- Crooked River – low gradient interior river with wetlands entering a lake system in the Interior Plateau, BC;
- Morice River – high gradient river along the western boundary of the Interior Plateau with sensitive fisheries resources and downstream human population; and
- Kitimat River near Hunter Creek – high gradient coastal tributary discharging to a large watercourse with sensitive fisheries resources, downstream human population and discharging to Kitimat River estuary (Green et al. 2015).

The Panel's review of the NGP assessment focuses on key findings of the dispersion modeling and toxicity assessment and compares these findings with the spill case studies presented earlier in this chapter. However, before presenting our comments on the detailed findings, we have some comments regarding important aspects of the spill scenario.

The spill scenario was a so-called 'full bore rupture' releasing a volume of between 974 to 3,321 m^3, which would place the releases into the "moderate" or "large" spill categories used in the relative risk assessments conducted for tanker spills by WSP and SL Ross (2014a,b). The hypothetical volumes released depended on the volume of oil that would be contained within the pipeline from the full-bore rupture point to the nearest shutoff valves in the pipeline on either side of the rupture. It was assumed that 13 minutes would elapse before shutoff valves were activated. "While spill durations would likely be longer, as oil would drain from the pipeline, all oil was released in 13 minutes to represent conservatively high in-water concentrations" (Horn and French-McCay 2015).

The NGP risk assessment did not assume any efforts to prevent oil from entering the river or migrating downstream, nor did it assume any recovery of the oil. This 'worse-case scenario' for the conditions outlined maximized impacts for those conditions; however, the overall degree of conservatism in the assessment is subject to discussion and debate.

8.16.1 Review and Recommendations Based on the Key Findings of the Northern Gateway Pipeline Ecological Risk Assessments

Recommendation: Risk assessment scenarios that assume a more likely combination of factors (less than full-bore rupture with a longer elapsed time to response) would be more relevant and comparable to actual spill incidents.

In the Panel's view, the assumed time period to shutoff is not conservative, given recent experience; e.g. the 17-hour delay for stopping the Kalamazoo spill (Section 8.10) and an unknown period of time (but possibly several days) for the Nexen emulsion spill (Section 8.13). The assumed 13-minute elapsed time before shutoff of oil flow significantly constrains the spill volume, thus fundamentally affecting all subsequent outputs from the risk assessment.

Recommendation: Detailed risk assessments conducted in support of applications for new projects, such as pipelines and production facilities, should include winter conditions, including full or partial ice cover and spring flood conditions with accompanying ice jams.

The NGP modeling did not consider the presence of ice on or in the receiving streams. It is likely that the presence of ice would be a 'risk driver'. Oil might flow on top of the ice to impact river shorelines above the normal flow height. Heated dilbit might locally melt ice and thereafter travel below the ice where it would be difficult to detect and intercept. The presence of snow and ice could decrease evaporation—alleviating explosion hazards but increasing toxicity risk at spring melt. Any assessment of ecological risks in Canada should consider seasonal differences in parameters contributing to fate and behaviour as well as to toxicity.

Recommendation: Future detailed risk assessments should consider the influence of animal behaviour on exposure to oil spills.

Animal behaviour was not considered in NGP exposure modeling. As illustrated by some of the case studies reviewed above, fidelity to particular habitats can be an important contributor to animal exposure, especially to oil deposited to sediments or stranded on vegetation or organic debris. It would have been interesting to compare risks to receptors such as salmonids with and without assumptions of fidelity to particular locations in the receiving streams (e.g., spawning sites). British Columbia coastal rivers attract grizzly bears during salmon spawning migrations, providing another example of a behaviour-related risk scenario.

Recommendation: Differences and similarities between modelled and observed fate and transport of dilbit, synthetic oil and condensate should be used to develop future research projects as well as guidance for standardized monitoring of oil spills.

Several results of modeling of the fate and transport of three products—dilbit, synthetic oil and condensate—were consistent with observations during actual spill events (Horn and French-McCay 2015). The dilbit selected was the dense and highly viscous MacKay Heavy Bitumen diluted with Synthetic Light Oil. The synthetic oil was an intermediate Syncrude Synthetic Light Oil. The condensate was a highly aromatic and low viscosity CRW Condensate Blend (Table 2.2). The following list presents the NGP predictions and the corresponding observations from case studies (in italics):

- Extensive shoreline oiling within confined reaches of small creeks and parts of the larger rivers was predicted, *as was observed in the Pine River (light crude) and Kalamazoo River (dilbit) spills. However, there was little consideration of the interaction between river stage, exposed shoreline length and amount of shoreline oiled on falling or rising flow stages;*
- The magnitude of river current during the spill event was of primary importance—higher flows resulted in more extensive oiling of shoreline and transport further downstream transport, *as was observed in the Pine River and Kalamazoo River spills;*
- Higher wind cases for a hypothetical dilbit spill resulted in oil deposition to sediments as a result of wind preventing entrained oil from resurfacing and allowing more time for interaction with suspended sediments and eventual sinking. *The Wabamun Lake spill case, although it was a lake rather than a river, also illustrated the importance of wind in dispersing and mixing heavy crude in the water column as well as stranding heavy crude along shorelines;*
- Hypothetical dilbit spill cases typically resulted in the most extensive oiling of shorelines compared to the other oils, *as was observed in the Kalamazoo spill; however, the Pine River spill of light crude also resulted in extensive oiling of backwaters and side channels; and*
- Condensate was predicted to stay buoyant with little or no deposition –slicks were maintained longer under low flow and low wind; and extensive evaporation was predicted. *These predictions mirror observations of the diluent in the Kalamazoo spill.*

Other predictions did not have analogous spill cases, either because of the type of oil or because of the type of receiving environment. These predictions included:

- Vertical turbulence would be induced by bottom roughness of the stream bed and, secondarily, winds would entrain oil into the water, modified by the oil viscosity. *This was not observed in the river case studies, although there were no explicit attempts to examine entrainment in the Pine River case;*
- Floating dilbit that was not entrained or stranded ashore was predicted to emulsify quickly to form highly viscous mousse, which prevented additional entrainment and sinking as it was carried farther downstream. *Dilbit mousse formation was not reported for the Kalamazoo spill, nor has it been observed in open-tank experimental spills (Chapter 2). Dilbit is not as amenable to emulsification or mousse formation as are conventional crude oils;*
- Dissolution of soluble and sparingly soluble aromatics into the water was predicted to be enhanced by entrainment as small droplets. *This particular mechanism was not studied in the Pine River case and there are no published data regarding this mechanism for the Kalamazoo spills. However, it was suggested that wind-induced formation of Langmuir troughs in Wabamun Lake might have contributed to vertical mixing of the spilled heavy fuel oil;*
- Under high flow and high wind conditions, bottom roughness and wind-induced mixing was predicted to keep large amounts of condensate entrained in the water column. *The predominant fate of diluent (Kalamazoo River) and lighter fractions of light crude (Pine River) was rapid surface dispersion and evaporation; however, temperature and current regimes in the NGP assessment were very different;*
- Above a certain site-specific threshold, dependent on streambed roughness and total suspended solids, higher winds were predicted to maintain the entrained oil in the water column allowing large amounts of deposition to the sediment. *The mechanisms producing deposition to the sediment were different in Pine River (where the primary drivers were slow current and fine-grained sediments) and the Kalamazoo River (where the primary drivers were factors leading to the production of OPAs); and*
- The predicted behaviour of synthetic oil was distinctive and contributed to higher risks being associated with this type of oil. The predicted behaviour of synthetic oil included:
  - A relatively large percentage that became entrained and potentially settled into sediments. Synthetic oil under both high flow and low flow conditions resulted in the largest amounts of oil deposited to sediments;
  - The entrained oil and high concentrations of dissolved aromatics were in many cases transported down the full length of the modeled river; and
  - As a result aquatic biota were exposed to acutely toxic concentrations along the modeled reaches.

<u>Recommendation:</u> The Panel recommends that post-spill monitoring guidance include protocols for examining hyporheic flow.

The Panel notes that the NGP assessment did not include a detailed consideration of entrainment of dissolved and particulate oil into coarse sediments by downward hyporheic flows. These flows characterize salmonid rivers and may explain the fate of much of the unaccounted for oil in spill case studies. The NGP risk assessment mentions hyporheic flows only in passing as an inflow of groundwater that would act as a diluent of any dissolved oil in gravel beds. To date, the Panel is not aware of any reports of post-spill systematic investigations of oil distribution in stream gravel, particularly as it relates to hyporheic flow down-welling zones. The same principles apply at the river's edge where lateral hyporheic flows generated by river bends transfer river water (and potentially oil) into ground water of riparian zones.

Recommendation: **Differences and similarities between modeled and observed acute and chronic toxicity of dilbit, synthetic oil and condensate should be used to develop future research projects as well as guidance for standardized monitoring of oil spills.**

Predicted acute toxicity to water column organisms was greater for synthetic oil and condensate than for dilbit because of the high viscosity of dilbit (which impeded entrainment), the lower concentrations of low molecular weight compounds and PAHs in dilbit, and because of the smaller water areas and river lengths affected by dilbit. However, acute injury to wildlife and emergent vegetation was usually highest in modeled dilbit cases due to higher viscosity that kept it floating on the surface or adhering to the shorelines.

These predictions are consistent with the spill case studies reviewed by the Panel. *Acute toxicity to aquatic life appeared to be minimal during the Kalamazoo spill, with no reported fish deaths. In contrast, thousands of fish were killed due to the spill of light crude into the Pine River. Acute injury to wildlife was low during the Kalamazoo River spill. Death of emergent vegetation was observed during the DWH spill, but not during any of the freshwater spill cases reviewed.*

Assessment of the potential for chronic toxicity extended for up to one or two years post-spill. The chronic NGP assessment addressed: weathering on shoreline soils and in stream sediments; partitioning of hydrocarbons from sediment back into pore water in streambed spawning gravels; potential effects to fish eggs and embryos present in spawning habitat; and chronic risk to receptors that are higher level consumers (Stephenson et al. 2015). Two models were used to evaluate chronic fate and bioavailability: these models predicted the fate as a mixture of 61 hydrocarbons, including the Canada-wide Standard aliphatic and aromatic TPH fractions, BTEX and other monoaromatic hydrocarbons, PAHs and other miscellaneous hydrocarbon compounds. Long-term exposure to a full suite of alkylated and non-alkylated PAHs that may be dissolved in the interstitial water of stream bed gravels was considered for potential effects on developing fish eggs and larvae. Chronic exposure point concentrations were calculated for water, sediment, oil, vegetation and fish tissue at time points of four weeks and one to two years (Stephenson et al. 2015).

Chronic effects benchmarks were developed from the Target Lipid Model (TLM) of Di Toro et al. (2000) and Di Toro and McGrath (2000). Canada-wide standards for PAHs in soils were used for the assessment of risks to soil invertebrates and plants and CCME guidelines were used to assess toxicity of fresh crude to livestock (Stephenson et al. 2015).

As discussed in Chapter 4, graphs of predicted toxicity using the TLM versus observed chronic toxicity indicate very large variances (10-fold or greater). The versions of the TLM used by Stephenson et al. (2015) have been superseded by newer publications; however the newer TLM predictions are still imprecise and are based on many untested assumptions.

Predicted total PAH concentrations in sediment pore water were less than 0.2 µg/L after four weeks and less than 0.05 µg/L after 1-2 years. Predicted river water TPH concentrations were mostly less than 0.01 mg/L. No significant risks were predicted for fish or benthic invertebrates, assuming additive toxicity of the various hydrocarbon compounds (Stephenson et al. 2015). The exception was in the Chickadee Creek scenario where fine-grained sediments were predicted to create conditions leading to higher concentrations in sediment pore water. The authors stated that in gravels most likely to be used by salmonid fish as spawning habitats, the expected average TPAH concentrations were below benchmarks established to identify potential for blue sac disease or mortality of developing eggs (Chapter 4).

Although the statement regarding spawning gravels is logical if oil droplets are not entrained in sediments by hyporheic flows, it does not acknowledge that some fish species (including salmonids such as mountain whitefish) may use finer-grained sediments for spawning. Observed toxicity to lake whitefish *and northern pike embryos from exposure to PAHs in near-shore sediments of Wabamun Lake four to seven months after the spill of heavy fuel oil illustrates this point.*

Stephenson et al. (2015) discussed the possibility that crude oil could become entrained into and trapped in river gravels as a result of hyporheic flows (Figure 2.3). They speculated that although this fate is possible it would depend upon:

- Exchange between river water and subsurface pore water. This can occur within river reaches at scales of hundreds of metres to kilometres, or locally at the scale of a single salmon redd. Depending upon the season and local topography, rivers may alternate locally and seasonally between 'gaining' and 'losing' water from or to groundwater of hyporheic system;
- Whether upwelling dominates - for rivers like the Kitimat it is likely that hyporheic flows will be dominated by inflowing groundwater and that such groundwater will be upwelling through the gravels, thus limiting the potential for ingress and retention of crude oil; and
- Whether crude oil becomes dispersed by turbulent river flow as fine droplets that would not rapidly resurface and would be available to become entrained into hyporheic flow should conditions allow—such dispersion could occur for condensate although it has low density and is likely to rapidly resurface and could occur for synthetic oil, but is less likely for dilbit, which is more viscous. Stephenson et al. (2015) noted that the magnitude of predicted oil spill effects at the population level would depend upon the timing and location of the spill with respect to fish and their key habitat, as well as the availability of unaffected habitats either upstream or in tributaries.

The Panel notes that fish demonstrate habitat fidelity so even if there were unaffected habitats, the fish might not use those habitats but rather remain in the contaminated areas. This was the concern in the Pine River spill (Birtwell 2003); however, follow-up monitoring of population-level indicators in the Pine River was insufficient to either confirm or reject this hypothesis.

The Panel understands the emphasis on sensitive salmonid species when conducting risk assessments since the standard practice is to select the lowest effects thresholds for the contaminants of concern (and these are usually for salmonids). However, other species, such as white sturgeon or eulachon, would be more vulnerable if the last few remaining spawning habitats were oiled or the food supply was reduced in critical rearing habitats. Furthermore, species at risk would be less resilient to the loss of a year class (or even a portion of a year class).

8.17 Assessment of Risks of Hypothetical Spills from the Proposed Trans Mountain Pipeline Expansion Project

8.17.1 Semi-quantitative assessment of spills at selected locations

Kinder Morgan (2013) conducted a semi-quantitative risk assessment of the Trans Mountain Pipeline Expansion Project (TMPEP). Quantitative estimates of failure frequency and qualitative estimates of consequences were combined and applied to hypothetical spills at selected locations along the pipeline route. Risk results were used to identify the need for additional pipeline design measures to reduce the probability and/or the consequences of failure (e.g. relocation of a valve site to reduce potential outflow in a high consequence area). A reliability approach was used to estimate failure rather than incident statistics. Areas with higher potential consequences were identified based on land use or location with respect to water bodies.

A worst case full-bore rupture was used for the TMPEP assessment; however, as for the NGP assessment, the elapsed time to achieve valve shut-down was short—in this case only 10 minutes. The TMPEP authors stated that 10 minutes for a readily identifiable catastrophic rupture is conservative because the Control Centre Operation would recognize the event immediately.

The Panel has the same comment as for the NGP assessment—the assumption of 10 minutes to valve shutdown significantly (and possibly unrealistically) constrains the spill volume, thus fundamentally affecting the results of the risk assessment.

Recommendation: The Panel suggests that risk assessment scenarios that assume a more likely combination of factors (less than full-bore rupture with a longer elapsed time to response) would be more relevant and comparable to actual spill cases. These scenarios would also be viewed as more credible by stakeholders sensitized by recent spills that experienced long delays before shutdown.

Eight case studies were assessed in the TMPEP report to provide relevant information for use in developing assumptions and inputs to the qualitative assessment of consequences. The cases included the Kalamazoo River, Wabamun Lake and Pine River spills. All of the case studies used are presented in Table 8.2.

Table 8.2 Case Studies Considered for the Trans Mountain Pipeline Expansion Project (TMPEP) Assessment of Environmental Effects of Oil Spills

Oil Spill	Location	Year	Spill Source	Oil Type	Volume (m^3)
Kalamazoo River	Michigan, US	2010	Pipeline Full- bore Rupture	Diluted Bitumen	3,200
Wabamun Lake	Alberta, Canada	2005	Rail Accident	Bunker “C”	712
East Walker River	California/Nevada, US	2000	Truck Accident	Bunker “C”	14
Pine River	BC, Canada	2000	Pipeline Full- bore Rupture	Light Crude	985
Yellowstone River	Montana, US	2011	Pipeline Full- bore Rupture	Light Crude	240
OSSA II	Bolivia, South America	2000	Pipeline Full- bore Rupture	Mixed Crude	4,611
DM932	Louisiana, US	2008	Barge Accident	Bunker “C”	1,070
Westridge	Burnaby, BC	2007	Pipeline Third Party Damage	Heavy Synthetic Crude	224

The spill scenarios involved releases into the Upper Athabasca, North Thompson and Lower Fraser Rivers. “Credible worst case spill volumes” ranged from 1,250 to 2,700 m^3. The crude spilled was Cold Lake Winter Blend dilbit (see Table 2.2).

Recommendation: Differences and similarities between the assessed consequences of a dilbit spill into various locations along the Athabasca, North Thompson and Lower Fraser Rivers and case study results should be used to develop future research projects as well as guidance for standardized monitoring of oil spills. Some suggested topics for further investigation are indicated in italics.

The qualitative assessment of consequences varied with season and spill location. For locations on the Athabasca River and Thompson River, consequences in winter were assessed as low (except for localized effects on aquatic invertebrates) because many of the receptor organisms would be dormant and overland flow would be slowed with some oil absorbed into the snowpack. Furthermore, it was assumed that environmental effects may be minimized because most of the oil is recoverable. The consequences in summer in the Athabasca and Thompson Rivers were predicted to be much greater because of rapid dispersion due to high flows, entrainment due to turbulence, and deposition along shorelines. In addition, the TMPEP assessment assumed that as the oil is transported downstream and weathers, it becomes more viscous and dense and interacts with shoreline sediments, e.g., forming OPAs and resulting in oil that submerges in low energy areas such as eddies and backwaters. The TMPEP authors stated that although water in the Athabasca and Thompson Rivers is somewhat turbid, the suspended sediment load is not particularly high, little oil would be entrained in the water column, and the water has no appreciable salinity. Thus, OPA formation would not be a dominant factor in the fate of the spilled oil. The extent of dispersion was assumed to be greatest in the summer, extending as far as 100 km downstream. The magnitude of effects on aquatic biota ranged from low to high depending upon the group and the proximity to the spill.

Consequences in spring or fall were considered to be intermediate in the Athabasca and Thompson Rivers due to lower and less turbulent flows than during the summer. Some submerged oil was assumed to be present in eddies and backwaters, as was predicted for summer conditions. The extent of downstream dispersion was assumed to be about 25 km.

Actual seasonal differences in the consequences of spills may differ from those predicted by the TMPEP assessment. For example, winter time spills involve much slower loss of volatiles and a longer time for dispersion to occur, and recoverability of a winter spill will depend upon the logistic challenges associated with the spill location.

The conclusion of the TMPEP authors that OPA formation would not be a dominant factor in the fate of the spilled dilbit is subject to debate. If a spill occurs during high flow when suspended sediment is elevated and/or if the flow-path involves interaction with riparian and floodplain materials (as was observed in the Kalamazoo spill), OPA formation could be much more significant.

The Fraser River has ice-free conditions during the winter; thus, predicted winter consequences in the Fraser River differed from those predicted for the Athabasca and Thompson Rivers. While some receptors would be dormant, birds such as bald eagles and some waterfowl could be present and potentially experience high magnitude consequences. High to medium magnitude consequences were predicted for aquatic receptors in side channels.

Summer consequences in the Fraser River location also differed because a side channel at this location would be heavily affected during high flows. Much of the oil was predicted to become stranded along shorelines and in riparian areas. The potential for OPA formation and submerged oil in the side channel may have been underestimated given the experience with the Pine River, Kalamazoo and Wabamun spills.

Spring and fall consequences were also predicted by the TMPEP assessment to be greater in the Fraser River location because flow conditions would disperse the oil as much as 60 km downstream during a time when many migratory birds would be present and semi-aquatic mammals would also be present and active. Effects were assumed to be insufficient to affect regional bird populations. *However, this conclusion may not apply to species-at-risk, to situations where a population has insufficient resiliency to withstand the loss of a substantial portion of breeding pairs, or if sublethal effects of residual oil on food supplies essential to migrating birds results in reduced fitness.*

In summary, the qualitative assessment of consequences of modeled dilbit spills in the TMPEP report was reasonably consistent with case study data, with appropriate conservatism added to account for uncertainty. The potential for OPA formation may have been underestimated given the experience with the dilbit spill into the Kalamazoo River, as well as the behaviour of heavy fuel oil in the Wabamun Lake spill. The recovery period was assumed to be from 12 months to five years post-spill for almost all of the spill scenarios. No evidence was presented in support of this assumption; however, the limited information on recovery from case studies suggests that this range is reasonable for most receptors; e.g. fish in the Pine River (Section 8.8).

8.17.1.1 Stochastic modeling of spills at locations near and at the mouth of the Fraser River

<u>Recommendation:</u> The results of the stochastic oil spill fate and transport modeling for a spill at the Fraser River and Delta location should be used as input for spill preparedness planning, as well as for identification of priority requirements for verification of the model.

The TMPEP assessment included stochastic oil spill fate and transport modeling in support of the risk assessment for a spill at the Fraser River and Delta location near the Port Mann Bridge. Stochastic modeling was performed due to the complexity of the situation at that particular hypothetical spill location. The modeling results by season provide valuable insights regarding the most probable consequences and implications for cleanup. The results are summarized below, accompanied by comments from the Panel, which are in *italics*.

Winter: >80% of oil is stranded within three days of spill; 11% evaporates; < 5% remains on the surface; < 1% is submerged, biodegrades or dissolves; < 0.1% forms OPAs.

- *The implications are that the spill response will be focused on stranded oil, with potential for substantial disturbance of habitat during the cleanup. Also, if most of the oil cannot be removed before higher spring flows, re-mobilization might occur.*
- *The assessment assumed that many of the receptors are absent or dormant in winter—this would be true for plants (dormant) and some (but not all) invertebrates, and perhaps for amphibians, but many birds overwinter at this location.*

Summer: < 60% of oil is stranded, about 10% evaporates; about 30% remains on the water surface; < 1% is submerged, biodegraded or dissolves; < 0.1% forms OPAs.

- *There is still a substantial amount of stranded oil, resulting in medium to high effects on riparian vegetation and in marsh areas; trade-offs between the effects of the stranded oil and the effects of the cleanup will require very careful evaluation.*
- *The oil remaining on the water surface is predicted to result in medium to high effects on ducks and geese and high effects on semi-aquatic mammals; which illustrates the importance of rapid and effective removal of floating oil.*
- *OPA formation may have been underestimated, given the sediment load of the Fraser River.*

Spring and Fall: 70% of oil is stranded; 10% evaporates; 20% remains on the surface; a small amount of oil (< 1%) is predicted to become submerged, undergo biodegradation or dissolve; OPA formation is not predicted (< 0.1% of oil volume).

- *There is an implied assumption that spring and fall represent one condition, which does not account for the highly stochastic weather, discharge, ice state and biological events that typify these seasons. One condition does not encompass the range of conditions, nor the change in conditions during or immediately after a spill. <u>Thus, a source of significant uncertainty does not</u>*

seem to be recognized. The same argument applies to winter and summer, although the size and frequency of changes are not as large.

- *The assessment once again focused on the effects of recovery of stranded oil. This common theme again highlights the importance of having a sufficient understanding of the receiving environment to enable confident evaluation of the trade-offs between the effects of residual oil and the effects of further cleanup.*
- *The TMPEP assessment assumed that riparian habitat along the mainstem of the Fraser River would be remediated with less intrusive methods and a greater emphasis would be placed on natural attenuation of low levels of residual oil. This is a debatable assumption given the potential effects of the modeled spill on socioeconomic and cultural values. The Panel suggests that the net environmental benefit calculations would be challenging and subject to considerable uncertainty.*
- *High effects on semi-aquatic mammals (due to oiling) were predicted and medium to high effects on ducks and geese were predicted (including reproductive effects caused by transfer of oil to eggs or effects on habitat quality caused by disturbance arising from oil spill response efforts).*
- *Particular attention was paid to the western sandpiper. Hundreds of thousands of these birds may congregate in the assessment area, feeding on biofilm and invertebrates—the fate modeling showed that the probability of oiling areas used by the birds is very low—therefore the sandpipers are unlikely to be significantly affected and any effects are likely reversible.*
- *The Panel notes that the reliability of the TMPEP fate model is paramount regarding risk to western sandpiper.*

Recommendation: The Panel recommends the use of stochastic fate modeling for complex, sensitive receiving environments because of the additional important information provided to decision-makers regarding the probability of the various levels of effect on specific VECs. This information can assist decision-makers in focusing preparedness and response plans. Stochastic modeling also provides a basis for prioritization of environmental data collection.

8.17.1.2 Comparative assessments of Unmitigated and Mitigated Spills at the Westridge Marine Terminal

Assessment of an unmitigated and a mitigated spill of heavy synthetic crude oil blend at the Westridge Marine Terminal produced a mass balance comparison, presented in **Table 8.3** (Kinder Morgan 2013).

Table 8.3 Mass Balance Comparison for a 160 m^3 Spill at the Westridge Marine Terminal

Amount (m^3)	Unmitigated Case	Mitigated Case
On shore after 1 day	16.6%	10.7%
Left on water after 1 day	0.4%	0.1%
Evaporated after 1 day	1.2%	0.9%
Dissolved after 1 day	1.8%	1.2%
Biodegraded after 1 day	< 0.1%	< 0.1%
Inside the containment area but not yet recovered	80%	0%
Recovered inside the containment boom	n/a	80%
Recovered at sea	n/a	7.1%

After one day, no oil was predicted to remain on the water with mitigation, compared to 80% if unmitigated (although oil inside the containment area would be recovered over subsequent days).

Mitigation reduced shoreline oiling but did not eliminate it (10.7% on the shoreline with mitigation versus 16.6% on the shoreline without mitigation).

Recommendation: The Panel urges incorporation of lessons learned from incidents as well as assessments conducted for proposed project into preparedness and response planning by responsible authorities and industry. The Panel notes that common themes among incidents and assessments include communication, coordination, adequate resourcing and training.

The authors noted that the evaluation of responses to a spill at the Westridge Marine Terminal contributed to the following 'lessons learned' (these lessons learned are in addition to those presented in Section 8.11).

- Proximity of ready response capability to a spill site together with site-specific response plans (which responders have exercised) help to greatly increase the effectiveness of response. In the case of the simulation study, the modeling runs helped WCMRC gain a good understanding of key requirements to effectively improve response. This is similar to the iterative learning achieved through oil spill exercises.
- There is no substitute for establishing an early line of defense by rapidly booming a release or damaged vessel, when possible. This knowledge is tempered by the reality that health and safety conditions, suitable nearby anchoring sites and operational constraints may not always make this outcome possible.
- Recovery assets should be located in relatively close proximity to the spill, as would be the case for Westridge Marine Terminal.
- Use of model-derived trajectory and slick thickness information to direct skimmers can help identify optimum recovery locations. While remote sensing offers considerable opportunities for spill detection, it also has limitations. The combination of numerical modeling and remote-sensing data provides the most powerful approach to both current and future predictions of slick positions.

The WCMRC has proposed a harbour base that would be continuously staffed if the TMPEP is approved (Kinder Morgan 2014).

The Panel notes that some of the above lessons learned would also apply to the *Marathassa* spill which occurred in English Bay in 2015 (Section 8.12).

8.18 Assessment of Accidents and Malfunctions for the Energy East Pipeline Project

The Panel reviewed the assessment of accidents and malfunctions for the proposed Energy East Pipeline project (EEPP), which included consideration of the fate, transport and effects of three representative crude oils: Bakken crude oil, Husky Synthetic and Western Canadian Select diluted bitumen (Table 2.2). Four categories of rivers and streams were assessed based on magnitude of flow and width.

EEPP assumptions included:

- The release of the entire volume of the spill directly into the water body;
- Complete, instantaneous mixing; and
- The entire volume of Constituents of Interest dissolved into the water column (Energy East 2014a).

These assumptions were referred to as 'conservative'. However, the spill case studies illustrated that release to a terrestrial flow path leading to a watercourse can have significant consequences in terms of fate and behaviour of spilled oil as well as consequences to receptors along the flow path (see also the

TMPEP assessment). Complete, instantaneous mixing and complete solubilisation are not conservative assumptions because there would be no floating oil to cause acute mortality of birds and semi-aquatic mammals. These assumptions do not consider acute effects of floating oils or other important fate mechanisms that have been shown to significantly affect consequences (e.g., the formation of sinking oil).

The EEPP assessment was based on simplistic estimates of hydrocarbon concentrations, reliance on low likelihood of a spill occurring at particular locations, and blanket assurances regarding mitigation, which is illustrated by the following quote:

> "The environmental effect of a crude oil spill would vary both temporally and spatially depending on the volume, timing and location of the spill. Localized effects could occur from virtually any size of crude oil spill. In general, the chance of a spill occurring at any discrete location along the pipeline or marine transportation of oil is low and if a spill were to occur, it likely would be relatively small (4 bbl or less). In the event of a spill, Energy East would respond according to applicable regulations and their Environmental Response Plan which will contain provisions for protecting and mitigating potential effects to environmental receptors. In addition, in the event of a spill, Energy East will consult with regulatory agencies to determine the appropriate and preferred approach to cleanup and monitoring" (Energy East 2014b).

The Panel was initially encouraged to see that the EEPP assessment considered locations along the pipeline route that are rarely evaluated in the context of oil spills; e.g. the South Saskatchewan River, the Red River, a lake in Ontario (Trout Lake), the Rideau River, and the Iroquois River, NB (Energy East 2014b). These locations represent a wide variety of receiving environments with important differences that can have substantial effects on oil fate, behaviour and toxicity. Unfortunately, the simplistic nature of the assessment did not address these characteristics in any meaningful way (e.g., sediment loads in the South Saskatchewan River, morphometry of Trout Lake). Instead, the same statement that is quoted above was repeated for each location, with slight (if any) variations.

Statements regarding the low probability of a spill were also very similar for all assessed locations. The rationale for low probability included such points as:

- The Project's pipeline materials and design, as well as the strategic placement of valves, are expected to minimize the likelihood of a spill and reduce the volume of oil released in the event of a spill;
- Rivers will be crossed by horizontal directional drilling, which will reduce the probability of a rupture by reducing threats to the pipeline given the depth of the pipe below the river. The depth and overlying materials also would help confine a release and reduce the possibility of the crude oil reaching the river;
- Valves are strategically located along the EEPP route to reduce the amount of crude oil that potentially could be spilled. The location of valves, spill containment measures and emergency response procedures would mitigate adverse effects to both surface water and groundwater; and
- The assessment used conservative assumptions to overestimate risk. Many assumptions, such as all benzene from the oil would be instantly dissolved into the water, are unrealistic but help to screen for the potential for effects.

The Panel found the EEPP assessment to be overly simplistic, with blanket assurances regarding mitigation, generalized assumptions that mitigation would always be effective, and a reliance on low probability to reduce risk. The claim that the assessment used conservative assumptions to overestimate risk is incorrect since assuming instantaneous mixing of a spill would be conservative with respect to fish but liberal with respect to birds and semi-aquatic mammals. The EEPP assessment did not add any value with respect to risk-based prioritization of mitigation measures along the pipeline route.

<u>Recommendation:</u> The Panel suggests that the sites of interest used in the EEPP assessment merit being re-analysed using analytical tools similar to those used for Trans Mountain or Northern Gateway pipelines—particularly with respect to fate and transport and the level of sophistication with respect to acute and chronic toxicity, shoreline effects and overland flow effects with season.

8.19 Summary Comments and Recommendations Regarding Risk Assessments of Oil Spills within Environmental Impact Assessments

The NGP and TMPEP risk assessments are impressive documents in their scope and detail and are among the best of their kind. The fate modeling in support of the NGP assessment and the use of stochastic fate modeling for particularly sensitive and complex receiving environments done for the TMPEP assessment provided valuable details with respect to the relative proportion and location of floating, dissolved, entrained, stranded and submerged oil. The use of case study information to develop a qualitative effects assessment for the TMPEP provided a useful alternative to the calculation of quantitative hazard indices using single point-estimates of effects thresholds.

Although the NGP and TMPEP risk assessments had several strengths, they were subject to the same uncertainties and challenges as any large-scale assessment. The results of the assessments can be used as valuable input in identifying priorities for preparedness and responses as well as for focusing on critical uncertainties associated with factors which drive the risk. However, the results of the assessments cannot be assumed to be reliable predictors of what will actually happen during a spill. The state-of-the-science of risk assessment has not yet achieved the required level of verification via comparison of predicted versus observed effects. Furthermore, uncertainty in risk assessment will always be substantial, and in some cases irreducible. "Personal judgment and expert opinion will necessarily be a part of such risk assessments because they handle rare events in complex systems" (Hague et al. 2014).

The development of the scenarios to be used is one of the most difficult challenges in risk assessment, and the NGP and TMPEP assessments illustrate this challenge. In both cases, a full bore pipeline rupture was assumed and described as "worst case". However, the legitimacy of the description of the risk scenarios as "worst case" is subject to question because of the assumed short time period between detection of a pipeline breach and shutting off of valves to stop the flow of oil. Other sources of uncertainty regarding the "worst case" nature of the risk scenarios include:

- Lack of assessment of winter spills for the NGP;
- Choices of spill sites which, in some cases, reduced the amount of oil reaching the most sensitive areas (e.g. reducing oil reaching the estuary at Kitimat) (Hodson and Martin 2012);
- Inclusion of receptor species that may be sensitive because of their habitat, conservation status or cultural value (e.g. eulachon) (Hodson and Martin 2012);
- The use of average physical and chemical characteristics of river receiving environments (Hodson and Martin 2012); and
- Missing or inadequate representation of potentially important processes, such as hyporheic flows.

The development of risk scenarios is a fundamental issue because they represent high stakes, uncertain facts and conflicting values (Hauge et al. 2014). As Hauge et al. point out, uncertainty makes different interpretations possible, and values may be embedded in knowledge production and interpretation (as discussed in Section 8.6 with respect to the EVOS). The 'appropriate' size, location, flow-path, time-scale, receiving environment and receptor species for each oil spill assessment is subject to debate, not only regarding which particular combination might best represent a worst case, but also whether a worst case is what is needed to support decisions.

In some contexts, worst case scenarios are so highly unlikely as to be of little value for decision-making. It may be more useful to choose more likely scenarios which occur more frequently.

Reduction of some of the uncertainties associated with risk assessment is possible. For example, including migration patterns and other behavioural characteristics (e.g. fidelity to feeding grounds and spawning sites) and combining these patterns with stochastic dispersion modeling would offer new insights into the potential exposure of aquatic receptors. Unfortunately, data required for more sophisticated spatially and temporally-explicit exposure modeling is often lacking. The use of chronic toxicity data from the most relevant test species, combined with field information from spill case studies would produce less uncertainty than using acute:chronic ratios. Careful attention to all exposure routes for each receptor helps ensure that exposure is not underestimated.

Several sources of uncertainty are very difficult to reduce. Major oil spills are rare and each of these rare events is unique - making generalizations from one case to another very difficult. Stochastic processes such as weather influence the fate and effects of oil spills in unpredictable ways.

The framework and tools for ERAs originally were developed for relatively small sites; their applicability to 1,000's of kilometres of pipeline crossing highly variable habitats with major physical and chemical gradients is questionable. Of necessity, risk assessors must select representative sites along these routes and the assessed risk is ultimately a comparison of modeled concentrations of hydrocarbons in water, sediment (or sometimes tissue) to a single benchmark of toxicity. Rarely, modeled concentrations are compared to a dose-response curve. Effects of exposure to several chemicals are usually assumed to be additive, although the validity of this assumption is highly questionable, particularly when chemicals with very different modes of action are combined. In particular, the interactive effects of oil and municipal and industrial effluents have not been considered for risk assessments in freshwater and coastal ecosystems. The existing condition of the receptor is almost never explicitly considered; e.g., if a fish population is already exhibiting poor condition due to the existence of other stressors in the receiving environment.

Given the limitations of the toxicological approach to risk assessment, there have been many calls for the incorporation of ecology into risk assessment. The use of spatially-explicit exposure modeling that incorporates seasonal habitat use by each receptor and superimposes contaminant gradients or patterns has been a significant advance; however, such modeling rarely appears within impact assessments. More commonly, a weight-of-evidence approach is used, which combines laboratory, field and modeling lines of evidence into an overall risk estimate. The evaluation of effects of exposure to multiple stressors is the subject of active research; however, the results of this research seldom are reflected in risk assessments.

In summary, although many improvements are needed in both exposure and effects evaluations within risk assessment, the most fundamental challenges centre on the framing of the risk assessment. Risk framing can be from the perspective of informing management, or it can be from the perspective of deciding whether the risk is acceptable to society (Hague et al. 2014). Public concerns about impacts may be very different from a petroleum company's concerns. Often, risk assessments are part of processes where questions can be asked of science and yet cannot be answered by science (Weinberg 1972 cited in Hague et al. 2014). Risk assessments cannot provide the level of confidence often demanded by the public and political decision-makers—to achieve the required confidence would take decades of research, and even then, we may not be able to adequately represent the complexity of ecosystems.

8.20 Assessment of Risks Associated with Transport of Crude by Rail

A major increase in crude-by-rail transport started around 2009. Since then, crude-by-rail transport in the US has increased by 40-fold or more (Etkin 2015). The bulk of the oil is crude oil from the North Dakota Bakken fields and the Alberta oil sands. A 42% increase has occurred in average annual spillage of oil by rail in the US but at a reduced rate per volume transported (Etkin 2015) (Table 1.4). However, accidents involving crude-by-rail are of particular concern because of the potential for fires and explosions and impacts on urban areas traversed by rail lines.

Etkin (2015) cited analyses showing a steep decline in the frequency of derailments per train mile, with about one mainline derailment for every 3.85 billion tons of freight (including but not limited to crude-by-rail). It has been estimated that about six crude-by-rail related derailments would occur annually. Consequences were determined by oil type, volume, location and timing.

For Bakken crude, the property of greatest concern is volatility leading to explosion and fire, e.g. the Lac Mégantic, QC, disaster. For diluted bitumen the greatest public concern is that oil will become submerged when it reaches a body of water. Bitumen blends vary considerably depending on the source, blending procedures and diluent used (Table 2.3); therefore, the potential for sinking will vary. However, the Kalamazoo spill and the results of modeling in support of risk assessments illustrate that sinking is a definite possibility when dilbit is spilled, depending upon weathering-related density changes, turbulence, salinity and the amount of sediment in the water.

Estimated spill volumes for crude-by-rail Unit Trains are presented below (from Etkin 2015). The ranges are based on a less conservative 9.2% release rate to a more conservative 16.7% release rate:

- 25^{th} percentile – 21 to 38 m^3 involving 2 cars
- 50^{th} percentile – 52 to 95 m^3 involving 5 cars
- 75^{th} percentile – 104 to 190 m^3 involving 10 cars
- 90^{th} percentile – 178 to 322 m^3 involving 17 cars
- 95^{th} percentile – 240 to 436 m^3 involving 23 cars
- Worst case – 1,274 to 2,313 m^3 involving 122 cars

In actual crude-by-rail spill cases in Canada and the US in 2013 and 2014, the lowest volume spilled was 17 m^3 and highest was 2,909 m^3, which was greater than the estimated worst case (Etkin 2015).

The higher percentile spill volumes (and the highest actual spill volume) are substantial spills, comparable to tanker spills and the larger pipeline spills. Therefore, preparedness and response plans should not discount the potential for higher-volume spills from crude-by-rail accidents. Challenges related to response to spills of Bakken crude transported within Canada include:

- Fires in populated areas or in locations where wildfires may be triggered; and
- The adequacy of first responder systems in locations that have seen a sudden increase in crude-by-rail (e.g., from the Estevan area of south-eastern Saskatchewan).

The Canadian Association of Fire Chiefs is reviewing the preparedness for crude-by-rail spills (Etkin 2015).

Responses to Bakken spills have included the use of sorbent and containment booms along with water spraying to corral oil for skimming and vacuum pumping. Sorbent pompoms and pads have been used in some areas (Etkin 2015).

Response to spills of dilbit would include the requirements for general preparedness for inland locations, consideration of the flammability of diluent, and development of capabilities for submerged oils.

Etkin (2015) noted that risk mitigation through prevention is key. Prevention measures would include training of railway personnel and first responders, positive train control, improvements in braking systems, and track inspections and maintenance. Newer tank car designs would reduce the potential for leakage or spillage. Reducing volatility of the oil (e.g., via conditioning of Bakken crude) would be another preventive measure. Canada and the US recently jointly announced forthcoming wide-ranging changes to rail safety regulations including braking systems, speed limits, improved tank car specifications, and rules regarding securing of unattended trains[8].

8.21 Overall Conclusions Regarding Assessment of Risks of Oil Spills

Assessments of the risks of hypothetical spills conducted in support of the environmental impact assessments of proposed pipeline projects in Canada have used unrealistic assumptions regarding spill response time, based upon experience to date. The more detailed and comprehensive risk assessments, such as those conducted for the proposed Northern Gateway Pipeline, were sufficient for risk-based prioritization of preparedness and response planning as well as mitigation via pipeline design. However, the consequences were likely underestimated given the assumption that it would take only a few minutes to recognize a pipeline breach and deploy shutoff valves.

The review of risk assessments also revealed a wide "range of practice" applied to assessments by different practitioners. The Panel was concerned about the breadth of this range, particularly since the range was demonstrated in submissions to the same regulator (the NEB). Therefore, in addition to research and monitoring to provide information needed to support risk assessments, there appears to be a need for an explicit 'standard of practice' regarding the assessment of risk of oil spills. This is particularly important given the high level of concern associated with the production and transport of oil.

There is an urgent need for investigations in Arctic Canada regarding the fate and behaviour of oil under Arctic conditions, the sensitivity (and resilience) of Arctic environments and the effectiveness of available spill response measures. Arctic marine systems include unique habitats, including the epontic habitat. Epontic communities are currently the subject of research; however, the potential effects of oil spills on these important communities should be investigated. The results of Arctic marine research should be consolidated periodically to serve as a baseline for monitoring activities (SL Ross 2014).

Investigations of oil spill effects must include collaboration with Indigenous peoples to ensure that traditional knowledge is incorporated into our overall understanding of the risks of oil spills.

There is a critical need for a coordinated and integrated database of information relevant to the assessment of risk of oil spills in Canada. The data needed for input to risk assessments in Canada are often either absent or widely scattered among government agency, industry, and academic sources. The highest priority should be accorded to assembling, and if necessary, sampling to build an understanding of pre-spill conditions at locations that are under the highest threat of contamination. The Panel suggests that efforts initially focus on geographical areas at risk that have received less attention with respect to oil spills (e.g. inland rivers, portions of the Great Lakes with the highest oil transport-related activities, and the Gulf of St. Lawrence).

There is a compelling need for coordinated environmental sensitivity assessment in Canada using standard tools and analytical approaches. This assessment must include integration of traditional knowledge and information about traditional uses of resources. The gap in sensitivity mapping is larger in inland Canada. Some industries are conducting their own sensitivity mapping; however, this information is generally proprietary. Sensitivity mapping efforts should be prioritized using screening tools that can identify the most likely sensitive watercourses subject to oil spills because of their location in proximity to production or transportation routes, characteristics that would affect fate and behaviour in such a way that risks are increased, and the presence of sensitive environmental components. Partnerships among industry, government and academia will be necessary if adequate coverage of receiving environments in Canada is to be achieved.

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[8] *e.g., http://www.cbc.ca/news/canada/montreal/lisa-raitt-u-s-counterpart-announce-broad-new-standards-for-rail-safety-1.3057150 (May 1, 2015).*

Regarding the potential for spills in the Canadian Arctic, SL Ross (2014) suggested:

- Consolidate the rapidly expanding knowledge about the aspects of the ecology of Arctic species relevant to monitoring (spatial distribution, populations, habitat use, seasonality);
- Prepare a review of research into effects of oil spills on Arctic marine and anadromous fish species (e.g., Arctic and polar cod, Arctic herring, Arctic char, Arctic cisco). *The Panel adds the need for consultation with Aboriginal peoples regarding their knowledge of fish species and the areas most sensitive to oil spills, e.g., char spawning areas;*
- Develop a decision tree to help decide whether a field monitoring program is required during a spill incident. *The Panel suggests that field monitoring would be required for all but small spills; therefore, the decision tree could be designed to assist in the determination of the scope of the monitoring program; and*
- Prepare a readily accessible up-to-date directory for all regional environmental emergency coordination centres in Canada, including the names and contact information for the senior personnel. *The Panel strongly endorses this recommendation.*

In addition to the above more general recommendations, SL Ross (2014) suggested that it would be useful to develop an understanding of the sensitivity of Canadian species to PAH-induced immunosuppression and the potential long-term consequences of it in Canadian fish populations during spills.

Focussing research and management on ecological resilience would be useful both in principle and for specific spill scenarios. As the NRC (2013) pointed out, resilience provides a valuable conceptual framework for managing complex systems because it focuses attention on how systems are affected by short-term disturbances and long-term stresses. Resilience can be either increased or decreased through management decisions. Analysis of the trade-offs inherent in management decisions would benefit from the use of a resilience framework.

Adopting resilience as a fundamental framework will require much more attention to the acquisition of baseline data, both for the natural environment and for the socioeconomic environment.

The Panel suggests that our focus should be on prevention of large spills and rapid and effective response to smaller ones because we will never be able to eliminate spills. Therefore, the Panel **recommends:**

- Identifying where most of the spills are occurring and why (e.g., pipeline spills into wetlands are more common than into rivers; truck spills are more likely to enter storm sewers and then rivers rather directly impact rivers; rail lines often run parallel to rivers and derailments may occur more frequently with certain load and geographical configurations, etc.);
- Examining past spill response records, plus the current risk management processes and regulations and their effectiveness and then honing in on the weak spots;
- Filling in critical data gaps regarding environmental sensitivity;
- Conducting relative risk assessments of the common spill location types overlain on the most sensitive receiving environments; and then
- Identifying the combination of spill source, receiving environment and level of preparedness that most urgently requires attention.

8.22 Research Needs and Recommendations

The following list presents knowledge gaps and corresponding recommendations, in order of priority.

8.22.1 *High priority research needs (short-, medium-, and long-term)*

8.22.1.1 Gap: Baseline information

Recommendation: Collect and Evaluate Baseline Information from High-Risk Areas (Short-term and Extending to Long-Term)

Research is needed regarding the current status of sensitive species and vulnerable habitats for specific, pre-defined locations in Canada representing a range of human disturbance, from relatively undisturbed to highly disturbed. This information can then be used as the base case for assessment of any future spill. The priority locations for collection of baseline information are those identified as high-risk in recent assessments conducted for Transport Canada (WSB and SL Ross 2014a,b), combined with information on areas with proposed new human activities that may increase the likelihood of spills and/or contribute to cumulative effects of spills (e.g., LNG terminals along the British Columbia coast). Input from Indigenous peoples and from key stakeholders should be part of the selection process for baseline collection areas.

8.22.1.2 Gap: National, accessible databases for use in assessment of oil spills

Recommendation: Establish a National Database of Information Relevant to Risk Assessment of Oil Spills, Preparedness and Response (Short-Term)

Baseline Data: There is a critical need for a coordinated and integrated database of information relevant to the assessment of risk of oil spills in Canada. (e.g., data collected for EIAs, EEM programs, compliance monitoring (e.g., for municipal or industrial discharges), research programs, etc.). The Panel is aware that some databases are already established (e.g., for EEM data); however, there is no readily accessible, national portal to metadata on freshwater systems. Since the assembly of such a database would be a huge undertaking, the Panel suggests that efforts initially focus on geographical areas at risk that have received less attention with respect to oil spills (e.g., inland rivers, the Great Lakes).

The Panel strongly recommends that the national database include data for the Arctic.

Experimental and Monitoring Data: To support predictive numerical models and operational guidelines for spill response, there is a need for a rigorous database on the fate, behaviour and effects of various types of oil spilled and the efficacy of current and emerging oil spill countermeasures over a range of environmental conditions.

8.22.1.3 Gap: Shoreline sensitivity in the Arctic

Recommendation: Extend Shoreline Sensitivity Mapping to Selected Arctic Locations (Short-term to Medium-Term)

The Panel strongly supports the continued mapping of shoreline sensitivity and calls for this mapping to be extended into Arctic areas.

Shoreline mapping should be conducted in areas where oil and gas exploration and development is already occurring or is expected, e.g., Beaufort Sea and the Mackenzie Delta. The mapping should also consider other human activities that would affect relative risk, such as mining, where large port facilities have been proposed involving not only transport of the minerals out but fuel in, and increased commercial shipping traffic through the Northwest Passage, which brings greater risk of fuel oil spills.

8.22.1.4 Gap: Shoreline sensitivity in inland Canada

<u>Recommendation:</u> Extend Sensitivity Mapping to Inland Freshwater Habitats (Short-Term to Medium-Term)

The current lack of inland shoreline sensitivity information in the open literature is a serious gap affecting the ability to apply risk-based preparedness and response planning. Prioritization of areas requiring mapping could be based upon evaluation of the intensity of human use, the current knowledge of the relative sensitivity of ecosystems and the availability of information from various sources. For example, high-priority areas for mapping might include areas upstream and downstream of hydroelectric dams.

Sensitivity mapping should be coordinated and should use standard tools and analytical approaches. This assessment must include integration of traditional knowledge and information about traditional uses of resources.

8.22.1.5 Gap: Efficacy of oil spill responses for various types of oil

<u>Recommendation:</u> Conduct Experiments on Efficacy of Current and Emerging Oil Spill Countermeasures (Short-Term to Medium-Term)

More data are required regarding the efficacy of current and emerging oil spill countermeasures for various types of oil spilled over a range of environmental conditions. This will require support for the conduct of field trials that incorporate controlled releases of oil. The consensus of scientists in oil spill countermeasure research is that major advances in the development and validation of spill response technologies are being hampered by our inability to conduct controlled field experiments with oil. Such field experiments involving intentional releases of oil must use scientifically valid and statistically sound experimental designs that use multiple replicate control and treated plots to enable calculation of experimental error.

8.22.1.6 Gap: Sufficient information to conduct NEBA for Arctic spills

<u>Recommendation:</u> Compare the Risks of Various Methods and Intensities of Cleanup under Arctic Conditions (Short-term to Medium-term)

Research comparing sites that have been subjected to various methods and intensities of cleanup to sites with minimal or no cleanup should be conducted under conditions relevant to the Canadian Arctic, building upon the experience in Prince William Sound. Experimental designs should include the range of crude oils that may be produced and transported in the Arctic, as well as the specific fuel oils already transported to Canadian Arctic communities. Well-controlled field experiments would be of great benefit; therefore, the current prohibition of experimental oil spills in the field should be re-examined.

8.22.1.7 Gap: Finer-scale relative risk analysis that allows focused preparedness and response planning

<u>Recommendation:</u> Conduct a Series of Focused Risk Assessments as a Follow-up to Recent Assessments (Short-Term)

The Panel recommends that a set of focused relative risk assessments be conducted building upon the Transport Canada marine spill results by focussing on high-sensitivity areas within each of the assessment zones in order that preparedness and response plans can include explicit plans for the areas with the highest potential consequences.

Follow-up risk assessments should be focused on specific areas at a finer scale than recent relative risk assessment. In addition, areas can be selected based on environments with multiple anthropogenic and natural stressors and measureable levels of impact and/or potential for future human disturbance. For example, these areas might include portions of the Bay of Fundy, the Gulf of St. Lawrence and the Strait of Georgia. Areas with high natural stressors, or which are sensitive to global factors that, at present, do not have high levels of anthropogenic stressors might include the Labrador Sea, the MacKenzie River delta and Hudson Strait. Once the priority areas for follow-up risk assessments have been identified, methodology refinements should be applied. Recommended refinements are presented in **bold** in Sections 8.11, 8.12 and 8.13.

8.22.1.8 Gap: Limited data from past spills in Canada

Recommendation: **Take Advantage of 'Spills of Opportunity' (Short-term and Extending to Long-term)**

If spills do occur, maximum advantage should be derived from the opportunity to study the fate, behaviour, and effects of the spill in the short, medium, and long-term. Studies of the relative effectiveness of response measures should also be part of a suite of investigations associated with all significant oil spills in Canada. Pre-approved funding should be put aside for spills of opportunity that would incorporate a combination of research and monitoring. Responsibility for each component of spill studies must be clear and research and monitoring efforts must be well coordinated to eliminate redundancy and to ensure that all required study components are implemented. It may be appropriate to select areas that would not receive treatment; these 'set aside' areas would then serve as a medium and long-term source of data for comparison of treated versus untreated sites.

8.22.2 Medium-priority research needs (medium-term and long-term)

8.22.2.1 Gap: Risks of residual oil in Arctic ecosystems

Recommendation: **Evaluate the Consequences of Long-Term Residual Oil in High-Risk Marine Habitats (Medium-term)**

The consequences of long-term residual oil in high-risk marine shoreline, estuary, marsh and lagoon areas both north and south of the 60^{th} parallel require further research. Chedabucto Bay is a good candidate for part of this evaluation. Other study areas should be selected on the basis of where consequences might be highest. The results of the research would provide much-needed input to NEBA regarding the most appropriate level of cleanup.

8.22.2.2 Gap: Risks of deposition to deep sea sediments

Recommendation: **Evaluate the Consequences of Deposition of Oil to Deep Sea Sediments (Medium-term)**

Research into the consequences of deposition of oil to deep sea sediments in the Arctic, as well as deep sea sediments south of the 60^{th} parallel in Canada, would provide part of the required knowledge base for support of decisions regarding offshore oil and gas exploration and oil transport. The current state of knowledge is totally inadequate with respect to supporting confident assessment of risk to deep sea systems.

8.22.2.3 Gap: The potential contribution of hyporheic flow to oil spill risk in rivers

<u>Recommendation:</u> Investigate the Role of Hyporheic Flows in Contributing to Exposure to Oil (Medium-term)

Research is needed on the relative role of hyporheic flows in contributing to exposure of fish to hydrocarbons after a spill. A range of experimental conditions using relevant concentrations and both weathered and unweathered oil should be tested on salmonid species under conditions that represent actual field conditions in terms of variables such as flow, temperature, substrate and dissolved oxygen. Experimental results can be used to evaluate whether monitoring of hyporheic flows after spill events would be feasible and justifiable.

8.22.2.4 Gap: Data supporting assessment of effects on ecosystem services

<u>Recommendation:</u> Investigate the Socioeconomic Impacts of Oil Spills in Support of Assessment of Effects on Ecosystem Services (Medium-term to Long-term)

Measurement of socioeconomic impacts of oil spills as a first step in implementing an ecosystem services approach to oil spill impact assessments. A standard set of indicators of socioeconomic effects should be developed for marine and freshwater systems in Canada, in consultation with First Nations, industry, academics and government agencies. These indicators should have explicit links to ecosystem services. If possible, measurement of effects on culturally important ecological services should be included.

8.22.3 Long-term research needs

8.22.3.1 Gap: Effects of oil spills on trophic dynamics

<u>Recommendation:</u> Conduct Research on the Effects of Oil Spills on Trophic Dynamics of Aquatic Ecosystems

In the Canadian context, the current level of understanding of trophic dynamics in identified high-risk offshore and inshore marine habitats requires evaluation in order that critical gaps in understanding are identified. For example, there may be specific critical features of Bay of Fundy trophic dynamics at specific locations (e.g., estuaries) that, if affected by oil spills, would have much greater consequences than spills in other areas of the Bay. Alternatively, the pelagic trophic dynamics of the Bay of Fundy are fundamental to maintenance of many highly-valued ecosystem services. Currently, it would be extremely difficult to differentiate risks among inshore and offshore areas (and thus to guide cleanup and follow-up monitoring programs).

8.22.3.2 Gap: Potential for population-level effects

<u>Recommendation:</u> Conduct Long-term Research on Effects of Different Oils on Populations of Aquatic Biota

The Panel recommends that there be support for long-term research into effects of different oil types on populations of aquatic biota, especially fish, marine mammals, and waterfowl. Such long-term research requires stable funding and effective collaboration among disciplines such as environmental chemistry, toxicology and ecology. Spills of Opportunity could provide the impetus for the initiation of long-term research.

8.22.4 Operational preparedness needs

Standardized Sensitivity Mapping

National-scale relative risk assessments used for preparedness and response planning must be based upon reliable and consistent data and analysis; therefore, standardized methodology for environmental sensitivity mapping is an *urgent requirement*.

Post-Spill Monitoring Program Development and National Guidance

The Panel strongly recommends that national guidance regarding monitoring after oil spill events be developed, involving consultations among industry, government, Indigenous communities and community stakeholders. The guidance would be designed to produce information that is reliable, adequate, credible and consistent. The guidance should include provisions for adjustment in response to specific characteristics of the receiving environment. The guidance should also include requirements for standard baseline datasets (tailored to specific receiving environments). The guidance could be divided into two parts: 1) which information to collect without exception; and 2) which information gathering can be deferred until the full scope of the spill and its potential effects are better understood. The guidance should include information on data quality requirements, including determination of minimum sample sizes, standard sampling protocols and laboratory quality assurance/quality control.

The Panel recommends the development of a national, consensus-based set of indicator species for each of Canada's major marine offshore and inshore zones (perhaps using the zones developed by WSP and SL Ross (2014). Once these indicator species have been selected, coordinated research programs among academia, industry and government should be developed which: a) compile existing information; b) identify and prioritize critical data gaps; and c) conduct research to fill the priority data gaps.

Standard guidance for monitoring the fate of spilled oil in all major environmental compartments of lotic systems is required. This guidance would include measurement of oil in sediments, as noted above, but would extend to measurement in water, pore water and biota.

Standard guidance is required for measurement of oil contamination of sediments in flowing waters in Canada. This guidance should consider the range of lotic receiving environments and logistic constraints common to remote locations. The guidance should include the de minimis level of investigation required for decision-making regarding cleanup requirements and techniques, as well as for determination of acceptable residual levels of oil.

The Panel supports the recommendations of SL Ross (2014) regarding monitoring programs in Canadian aquatic systems. These recommendations are listed in Section 8.14.

Update and Refine Risk Assessment Methods for Use in Support of Project Applications or Preparedness Planning

The Panel's review of risk assessments performed as part of pipeline applications revealed opportunities for improvement.

- Risk assessment scenarios should assume a more likely combination of factors (less than full-bore rupture with a longer elapsed time to response) that are more relevant and comparable to actual spill incidents. These scenarios would also be viewed as more credible by stakeholders sensitized by recent spills that experienced long delays before shutdown.
- Detailed risk assessments conducted in support of applications for new projects such as pipelines and production facilities should include winter conditions.
- Stochastic fate modeling for complex, sensitive receiving environments is recommended.

- The sites of interest used in the EEPP assessment merit being re-analysed using more sophisticated analytical tools and approaches—particularly with respect to fate and transport and the level of sophistication with respect to acute and chronic toxicity, shoreline effects and overland flow effects with season.

Apply Research Results, Engagement with Indigenous peoples and Stakeholders and Economic Analyses to Address the Longstanding Remediation Question "How Clean is Clean Enough?"

Effects on ecosystem services can be evaluated using data obtained from laboratory studies, large-scale open-air experiments, long-term field research and baseline data surveys. These data should be compiled and interpreted with the intention of determining acceptable, science-based chemical and biological endpoints of spill remediation. Long-term monitoring of follow-on effects after experimental spills and spills of opportunity would inform regulatory guidelines for cleanup endpoints.

The benchmarks for an acceptable level of residual oil should always include social and economic factors. Social factors must include input from Indigenous peoples. Social and economic factors could include residual effects on ecosystem services such as recreational or commercial fishing, drinking water sources and parks or other protected areas.

Inclusive Preparedness Planning

Preparedness planning should consider information from Indigenous, provincial, territorial and municipal sources in order that smaller-scale, higher-risk locations can be identified. Many of these areas have already been mapped at a finer scale than presented in the Transport Canada relative risk assessment. Provincial laws and regulations must be considered in preparedness to ensure harmonization and avoidance of redundancy.

Develop a Spill Risk Calculator Tool

The Panel suggests that a Spill Risk Calculator tool for Canada would be beneficial to preparedness planners and responders. This tool can be based upon methods used for the assessment of oil spill risks in Alaska (Reich et al. 2014).

CHAPTER 9: SUMMARY CONCLUSIONS AND RECOMMENDATIONS

The Royal Society of Canada (RSC) Expert Panel on The Behaviour and Environmental Impacts of Crude Oil Released into Aqueous Environments was asked to address the following questions:

1. How do the various types of crude oils, including diluted bitumens, compare in the way they behave when mixed with fresh, brackish or salt waters under a range of environmental conditions?
2. How do the various crude oils compare in their chemical composition and toxicity to organisms in aquatic ecosystems?
3. How do microbial processes affect crude oils in aquatic ecosystems, thereby modifying their physical and chemical properties, persistence and toxicity?
4. Are the research and oil spill response communities able to relate, with reliable predictions, the chemical, physical and biological properties of crudes to their behaviour, persistence, toxicity and ability to be remediated in water and sediments?
5. How should these scientific insights be used to inform optimal strategies for spill preparedness, spill response and environmental remediation?
6. Given the current state of the science, what are the priorities for research investments?

During its deliberations the Panel considered accidental releases of conventional (light, medium and heavy) crude oils and unconventional crude oils (including diluted bitumen), at exploration and production sources or as they are transported between ports and storage sites, to refineries or to users.

Following a review of available information, the Panel concluded that large spills of crude oil into marine or freshwater systems in Canada from oil production facilities, tankers, pipelines, rail and truck transport that cause significant ecological damage are infrequent, and the probability of spills decreases with increasing spill size (Chapter 1). The Panel noted that comprehensive statistical records for spills into the marine environment of Canada were much more readily available than for inland spills into fresh water. Thus, in the case of freshwater spills, the Panel had to search through individual investigative reports from the Transportation Safety Board (TSB), Alberta Energy Regulator (AER) and the media. Furthermore, as illustrated by the AER (2013) report on pipeline performance that provided data on spill incidence and volume, spills of crude oil were not always distinguished from refined product spills. Instead, statistics were presented as ‘hydrocarbon liquids’. This disparity in spill record keeping for the freshwater environment of Canada should be resolved.

Despite the relative infrequency of crude oil spills into aqueous environments in Canada, the consequences of spills into sensitive waterbodies can be substantial, not only economically but also impacting human health, safety and the environment. This concern is commensurate with the key questions posed by the sponsors and stakeholders.

With the anticipated growth of Canada’s offshore oil and gas industry and the production and transport of unconventional oils, such as diluted bitumen, accidental releases of oil from offshore platforms, pipelines and other sources were considered to be within the scope of this report. The Panel focused on the Canadian environment. However, it reviewed and considered the applicability of case studies from the United States and other countries to ensure full coverage of pertinent information. For example, current knowledge on the effects of and response to subsurface blowouts was provided by the Gulf of Mexico Deepwater Horizon (DWH) oil spill, and the consequences of and response to a release of dilbit spilled into a freshwater environment was represented by the Kalamazoo River, MI, oil spill. The Panel has made an effort to acknowledge the large number of research papers and environmental impact statements recently published on oil spills, as well as major ongoing research initiatives. The conclusions and recommendations made by the RSC Expert Panel in this report, under its remit to address the questions of its Terms of Reference, are subject to revision as new findings from environmental impact assessments and oil spill response technologies emerge.

Question 1: How do the various types of crude oils, including diluted bitumens, compare in the way they behave when mixed with fresh, brackish, or salt waters under a range of environmental conditions?

The Panel provided an overview on the chemical composition of petroleum hydrocarbons, the types of conventional and unconventional oil (including dilbit) transported in Canada, their bulk properties, and information on the processes that influence their weathering in the environment (Chapter 2). The Panel concluded that the behaviour of these oils when mixed with fresh, brackish or salt waters is dependent on their inherent physical and chemical properties, which are influenced by the environmental conditions at the specific areas of concern. Our understanding and ability to accurately predict the behaviour of some oils in the environment following accidental spills are still limited. This is due to analytical challenges, incomplete experimentation and complex interactions among oil weathering processes, remediation strategies and environmental conditions.

Each oil spill will be a unique combination of oil and receiving environment characteristics. However, the review of oil spill cases revealed that some generalizations can be made (some having more uncertainty associated with them than others).

Season and weather are dominant factors determining both the initial and ultimate fate and effect of all oil types. The lighter the oil, the more it is affected by spreading and evaporation and the easier it is to treat effectively, regardless of the environment in which it is spilled. The higher the ambient temperature, the faster is the evaporation and dissolution and the more extensive is the spreading. Medium oils (e.g., most conventional crude oils) are generally less volatile than lighter oils, which increases the potential for impacts on waterfowl and wildlife. However, medium and light oils are amenable to relatively rapid biodegradation. Heavy oils and diluted bitumens (e.g., Bunker C, dilbit, synbit and railbit), which have fewer components that dissolve in water or evaporate to the atmosphere are more resistant to evaporation and biodegradation and thus their potential long-term damage to the environment, waterfowl and fur-bearing animals is greater. Cleanup of heavy oils and bitumens is extremely difficult for both marine and inland spills because of their specific gravity, viscosity, flash point properties and high asphaltene content.

In addition, the direct effect of weather conditions on turbulence influences the physical dispersion of oil and the likelihood of successful dispersant use, especially for light and medium oils where some degree of mixing-energy is required for breakup of oil into small droplets. However, turbulence can also increase emulsification of oils, especially heavier oils, causing moussification or the production of water-in-oil emulsions, which resist evaporation, spreading and biodegradation. Dilbit is an exception because it resists the formation of water-in-oil emulsions. Turbulence is also an important factor in the formation of oil-particle aggregates (OPAs; significant with respect to some diluted bitumens and their potential for sinking).

High winds with associated wave action and currents can deposit oil onto windward shorelines and into more protected areas such as lagoons. High waves, tides and seiches can result in oil burial along sandy shorelines followed by re-exposure. Wind-driven surges can drive oil into the high intertidal zone or, in freshwater systems, deep into marginal wetlands or riparian habitats. Spills occurring immediately after high rainfall events can transport and subsequently deposit oil over wide areas of the floodplain of rivers, resulting in significant stranding when flows subside. These effects are applicable to all oil types, regardless of their properties.

The persistence of residual oil along shorelines correlates with shoreline energy level (e.g., waves, tides and ice), with oil persisting longer in low-energy and low-temperature environments. Cobble/boulder beaches with fine-grained interstitial materials, lagoons with fine sediments, backwater channels and shoreline marshes have been linked to the sequestration of conventional crude oil in a relatively un-weathered state for long periods of time due to protection from physical weathering and/or biodegradation in hypoxic conditions. Heavier oils are less amenable to this sequestration action as they tend to remain on the surface and resist seeping into the interstitial area of the shoreline.

The fate of oil spilled into rivers is affected by river flow, river channel characteristics and sediment characteristics and processes. High-flow conditions at the time of the spill will increase turbulence and the presence of suspended particulate matter that, in turn, contribute to the formation of OPAs that will sink and accumulate in deposition zones where they may be re-suspended by subsequent high-flow events. Biological processes within sediments can also elicit the re-suspension of oil and associated sheen production on the water surface. River channels that have been subject to bank hardening (e.g., by placement of riprap or rubble) have higher velocity flow, leading to the potential for transport of spilled oil farther downstream and/or stranding of oil among the bank materials. There is also a potential for entrainment of oil into porous bed sediments of shallow, high gradient rivers by surface-ground water interactions (hyporheic flows), although this possibility has not yet been evaluated in detail.

The fate of oil spilled into lakes is affected by lake morphology and mixing characteristics. Conventional crude oils spilled into shallow, wind-swept, well-mixed lakes will be subject to rapid dispersion if the spill occurs during open-water seasons. Oil, especially the heavier types, spilled into deeper lakes with thermal stratification may, in part, be sequestered in cold, low-oxygen, deepwater sediments with subsequent low biodegradation rates if OPAs are formed and subsequently sink.

Brackish and saline waters have greater density than fresh water, which affects the sinking of oil. In theory, as a dilbit loses its light components to evaporation, it may reach sufficient density to sink even in seawater, especially if it forms OPAs. The longer-term fate and effects of oil deposits within marine sediments is the subject of current research.

Question 2: How do the various crude oils compare in their chemical composition and toxicity to organisms in aquatic ecosystems?

The Panel provided an overview of what is known about oil toxicity and ecological impacts of oil spills to aquatic environments based on previous review articles and current literature (Chapter 4). Numerous case studies (e.g., *Exxon Valdez*) have documented various levels of habitat destruction that have resulted from oil spills. Although an overview is provided on the toxic effects of oil spills on various biota (i.e., plants, invertebrates, fish, reptiles/amphibians, birds and mammals) within the Panel's report, a major focus was given to fish, which were the subject of the greatest number of research papers. This is not surprising as the concern over oil spills is largely focused on impacts to fisheries due to their socioeconomic importance. Furthermore, many of the interactions between oil chemistry and its toxicity to fish may also apply to other species.

Studies with fish have shown that acute lethality is associated primarily with low molecular weight (LMW) components of oil, such as monoaromatics (e.g., BTEX), diaromatics (naphthalene and alkyl naphthalenes) and short-chain alkanes ($< C_{12}$). LMW petroleum hydrocarbons are sufficiently hydrophobic to partition rapidly into lipid membranes and to cause mortality by narcosis. Typically, as oil weathers following a spill, most narcotics hydrocarbons are lost within two days by volatilization, biodegradation and dilution. As a consequence, lethal concentrations in water are not maintained for prolonged periods unless the discharge of oil is continuous. Thus, observed fish kills are typically brief and localized because of the rapid loss of the acutely lethal LMW oil components through dilution and weathering. However, extensive fish mortalities have been observed in rivers where a point source of oil was rapidly transported downstream before significant weathering occurred (e.g., pipeline break, Pine River, BC).

The acute toxicity of hydrocarbons to aquatic biota can be estimated from octanol-water partition coefficients (K_{ow}), the ratio at equilibrium of the concentrations of a compound in n-octanol (a water-insoluble phase that mimics tissue lipids and floats on water) to the concentrations in the underlying water. Mortality typically occurs when tissue concentrations reach a 'critical body residue' or median lethal dose (CBR or LD50) of approximately 5 mmoles/L of tissue lipid. These predictable relationships have been used as the basis for mathematical models for assessing the risk of acute lethality following potential oil spills from proposed developments, such as pipelines, and for assessing the potential lethality of hydrocarbon mixtures measured during actual oil spills.

Chronic and sublethal effects of oil on fish are associated with either chronic exposures (e.g., oil stranded in sediments) or with delayed or lingering effects of acute exposures. Over the lifetime of a species, exposures to oil may occur via respiratory uptake of hydrocarbons from water (most common), direct contact with oil droplets (an emerging area of research) or the diet and maternal transfer to eggs (not well studied). Effects range from initial cellular genetic and molecular responses to long-term organismal impacts on rates of reproduction, growth, disease, mutations/cancer and survival.

In contrast to acute toxicity, 3-5 ring medium and high molecular weight (MMW and HMW, respectively) polycyclic aromatic hydrocarbons (PAHs), including aromatic heterocycles, such as alkyl dibenzothiophenes, are thought to be primary causes of chronic toxicity to fish. Embryos appear to be the fish life stage most sensitive to oil exposure, presumably due to interference with the large number of genes that must be up-regulated or activated at precise stages during embryonic development for normal development to occur. Most studies report the effects of waterborne oil, usually by reference to the concentrations of TPAHs and total petroleum hydrocarbons (TPHs) in test solutions that affect 50% of test organisms. The EC50 and LC50 values for chronic exposures have been reported to range from 0.3–60 µg/L TPAH and 0.03 – 11 mg/L TPH. Because of their lower volatility, alkyl PAHs persist in water longer than monoaromatics continuing to partition from oil into water over weeks to months if residual oil persists.

It might be expected that the relative risks of acute and chronic toxicity of different oils could be predicted by simply ranking them in order of the concentrations of their different constituents. Unfortunately, the expected correlations were not observed in studies with marine fish and invertebrates. Toxicity may be confounded by the relative proportions of different alkyl PAHs, the presence of unidentified compounds (including additives) or by generation of polar hydrocarbon derivatives during weathering of the oil.

Differences in the relative proportions of different PAHs in oil may influence the toxicity of diluted bitumens, such as the product dilbit. Dilbits are prepared from bitumen, a highly-weathered oil depleted in alkylnaphthalenes, which are the alkyl PAH of lowest chronic toxicity. Thus, dilbit contains a higher proportion of the more toxic 3- to -5-ring alkyl PAH mixture than do conventional crude oils, so that chronic toxicity at a given concentration of TPAH may be greater than expected. Only one report has been published on the chronic embryo toxicity of dilbit. In this study with Japanese medaka, chronic toxicity across an array of crude and refined oils suggested that dilbit may be slightly more embryo-toxic than average. Until equivalent data for other species have been reported, any conclusions about the perceived toxicity of dilbit may be confounded by species differences in sensitivity to oil. There is some evidence dilbit elicits acute toxicity in benthic invertebrates and that its toxicity varies with sediment characteristics.

It is often difficult to express quantitative relationships between PAH concentrations in oil and toxicity because the physical characteristics of oil modify toxicity by controlling droplet formation and the rate of partitioning of hydrocarbons from oil to water. The proportion of waxes, resins and asphaltenes will control the physical characteristics of oil, which in turn affect the dispersability and biodegradability of oil in water. Thus, relative to light oils, heavy oils including dilbit are more difficult to disperse mechanically in water, are less likely to form fine droplets, biodegrade more slowly, and may appear less toxic than light oils because their toxic constituents are less bioavailable.

The Panel's report includes tables and references that contain compositional and physical data for crude oils that represent petroleum types transported in Canada and globally. Based on current analytical capabilities, the petroleum hydrocarbons produced and/or transported within Canada appear to fall along a chemical continuum spanning condensates to bitumen. Condensates are considered acutely toxic due in part to elevated BTEX concentrations. Conventional oils with lower proportions of BTEX can exhibit chronic toxicity associated with alkyl PAHs and resins.

The results of studies to date suggest that the direct toxic effects of dilbit in both freshwater and marine ecosystems do not seem to differ dramatically from other oils. However, the binary nature of dilbit currently confounds extrapolation of toxicity from its individual components: diluent and bitumen. The acute toxicity associated with the diluent may be dispelled by evaporation, and the heaviest residues (the asphaltenes) in the bitumen are likely biologically inert. However, the likely extent of diluent evaporation (conversely, the biological availability of diluent in weathered dilbit) is currently unknown. Furthermore, the toxicity of resins and/or products of photooxidation is poorly understood.

The impacts of spilled oil on aquatic species depend as much on the extent of their exposure to oil as on the inherent toxicity of oil. Exposure to oil will vary with the interactions among the fate and behaviour of spilled oil and the habitat characteristics, behaviour and physiology of different species. Research is needed to identify those species that will be most exposed to oil with extreme properties, including very light (e.g., Bakken crude) and very heavy oils (e.g., HFO), and the ecological factors that will enhance exposure (e.g., turbulent mixing of rivers or weathering). Research is also needed to better understand the differences between dilbit and Bakken light crude versus conventional crude oils in terms of their acute and chronic toxicity. The hydrocarbon composition of various oils can play a major role in explaining these differences. Although acute lethality can be attributed to LMW components of oil and chronic toxicity to the alkyl-substituted 3- to 5-ring PAHs, research is needed to identify the most toxic constituents of oil, particularly polar hydrocarbons generated by weathering, biodegradation or photooxidation that are not often analyzed in oil or water.

It is important to note that most vertebrate species (e.g., fish, birds, mammals) can metabolize and excrete hydrocarbons. In contrast, invertebrate filter feeders do not metabolize or excrete petroleum hydrocarbons quickly; thus, contaminated zooplankton can accumulate significant quantities of droplet oil. Although contaminated invertebrates can contribute to the dietary exposure of predators, it appears that petroleum hydrocarbons do not typically biomagnify to high concentrations in food webs.

Question 3: How do microbial processes affect crude oils in aquatic ecosystems, thereby modifying their physical and chemical properties, persistence and toxicity?

The Report outlines in Chapters 2, 3 and 6 how microbial communities in aquatic environments interact with spilled oil to change its properties, behaviour and effects on other biota. Interactions that affect physical properties include stabilizing emulsions via cell attachment to oil:water interfaces, enhancing oil dispersion in water through secretion of biosurfactants and biodegradation.

The chemical composition of oil dictates its susceptibility to biodegradation (i.e., the proportions of biodegradable alkanes and aromatics versus recalcitrant steroids, resins and asphaltenes). In competition with abiotic evaporation and dissolution processes, biodegradation selectively converts certain lighter alkanes and aromatics to gases (CO_2 and/or methane), water and biomass while leaving the heavier, complex oil components as residues. This altered chemical composition changes the physical properties of the residual oil, making it more dense and viscous than the original. In turn, this physical change progressively reduces further biodegradation of the residual oil since biodegradation is also influenced by the physical state of the oil (e.g., viscosity that affects the oil:water interfacial surface area available for microbial attachment and attack). Biodegradation, being an enzymatic process, is directly affected by temperature, and because microbial cell growth is the ultimate outcome of biodegradation, its rate is affected by availability of growth-promoting nutrients such as soluble nitrogen and phosphorus sources. Even under ideal environmental conditions, biodegradation of the multitude of components within a crude oil is a relatively slow process that may take weeks, months or even years to remove a significant mass of spilled oil, and oil that is buried in anaerobic sediments may persist for decades or longer. A residue of original petroleum components, including asphaltenes and resins, will always remain, in addition to partially degraded hydrocarbons and metabolic end products (e.g., CO_2, CH_4, H_2S), the mass of which will depend on the interplay between environmental conditions, petroleum chemistry and microbial community composition.

The predominance of aerobic versus anaerobic conditions dictates which enzymatic pathways are effective, the rate of microbial attack and the end products. Oil biodegradation is faster and more efficient under aerobic conditions, such as in a well-aerated water column or in the uppermost layer of sediment, but it is slower in environments dominated by anaerobic conditions, such as buried sediments. The range of susceptible hydrocarbons under anaerobic conditions appears to be more limited than with aerobic degradation, and the end products and residual oil composition therefore differ from aerobic processes. For this reason, wetlands, salt marshes and mud flats that have significant anaerobic strata are among the most sensitive and difficult ecosystems to clean after an oil spill. Bioremediation may be the best approach for wetland cleanup because it is among the least intrusive strategies for these sensitive environments. However, even bioremediation requires some human intervention that may cause additional harm to the contaminated site by trampling of oil into the anaerobic sediment, which may diminish bioremediation of the site and promote oil persistence *in situ*. Natural attenuation may be the cleanup method of choice if trampling cannot be avoided. The beneficial interaction of hydrocarbon-degrading microbes and plant roots in soils and wetlands (phytoremediation) may enhance biodegradation and decrease persistence of buried oil.

The types of microbes present at a spill site dictate the lag time before biodegradation begins, the subsequent rate and extent of biodegradation and hence the behaviour and persistence of the residual oil. Hydrocarbon-degrading bacteria are ubiquitous, but they tend to be present in higher proportions in chronically oil-impacted sites because they have an advantage over microbes that cannot utilize hydrocarbons. For the same reason hydrocarbon-degraders may flourish after an oil spill even in a pristine site, given favorable conditions. Thus, the history of a spill site may indirectly influence progression of bioremediation or, conversely, oil persistence. Extensive and rapid rate of biodegradation requires the metabolism of a consortium of hydrocarbon degraders working in conjunction with non-hydrocarbon degrading microbes.

Given these general factors, it is evident that light oils are inherently more biodegradable than heavier oils and leave lighter residues. In contrast, only small proportions of heavy crudes are readily biodegradable, and the residues will persist even with active intervention. In the case of dilbit,it is not yet clear whether all of the diluent is actually available for biodegradation, is protected by virtue of molecular association with the bitumen or is simply unavailable to microbes because of the limited surface area of viscous weathered dilbit. Considerable research is required to address this knowledge gap under different environmental conditions.

In the process of selectively biodegrading petroleum components, microbes can reduce or increase the toxicity of an oil spill. For example, very light oils (e.g., jet fuels and gasolines) contain high concentrations of acutely toxic compounds that are susceptible to biodegradation. Although such light compounds may be quickly lost by abiotic processes (particularly evaporation and dissolution), biodegradation may reduce acute toxicity if they are retained in an environment (e.g., in deep water or buried in sediment or trapped under ice). In some conventional oil spill scenarios natural attenuation can effectively lower the risks to aquatic life and human consumers of fish and shellfish, despite persistent residues, because: a) biodegradation may produce primarily non-toxic residues; b) the residual oil is not being released back into the water in amounts sufficient to significantly affect aquatic life; or c) residual oil compounds (e.g. asphaltenes) are not bioavailable. This was well illustrated by the *Arrow* tanker oil spill case study. Microbial degradation by indigenous bacteria (i.e., natural attenuation) contributed to the reduction of toxic fractions within the heavy Bunker C fuel oil stranded within the beach sediments at some sites. At present, information is insufficient regarding the effectiveness of monitored natural attenuation as an oil spill countermeasure for a dilbit spill in the aquatic environment.

Conversely, in unfavorable conditions microbes may be unable to completely convert hydrocarbons to gases, water and biomass. Instead, partially oxidized metabolites that are more polar (more water-soluble) and more mobile in an aqueous system may accumulate. Because of the diverse hydrocarbon isomers present in petroleum, an enormous number of possible metabolites could be produced. The toxicity of most is untested either as pure compounds or, more realistically, as mixtures of polar metabolites. In some cases the metabolites generated by microbial attack are known to have carcinogenic potential. By analogy to the resins fraction, many are likely to have chronic toxic effects. Additional research is needed to address this question of chronic toxicity due to incomplete microbial metabolism of crude oil components.

Another factor affecting chronic toxicity of the oil itself (versus its metabolic products) is that as lighter components of the oil are biodegraded, the proportion of alkyl PAHs and resins in the residual oil increases, thus increasing the chronic toxicity associated with these components. In addition to these chemical effects, the increase in oil density and viscosity due to biodegradation of light fractions can increase the likelihood of detrimental physical impacts on higher organisms including plants.

The mechanism by which microbial processes affect dilbit toxicity has yet to be fully resolved because the binary nature of dilbit confounds simple extrapolation of toxicity from the individual components.

Question 4: Is the research and oil spill response community able to relate, with reliable predictions, the chemical, physical and biological properties of crudes to their behaviour, persistence, toxicity and ability to be remediated in water and sediments?

The environmental behaviour of unconventional oils and blended oils currently cannot be predicted with confidence, which affects spill response planning and decisions. Each oil spill is unique, due to the specific chemical nature of the oil and the complex interaction with different environmental and climate factors. Thus, to account for the environmental variables that might be experienced in a dilbit spill, a multitude of combinatorial trials would be required before empirical rules of its behaviour can be developed.

The toxic effects of oil are well described for a limited array of aquatic organisms, most notably acute toxicity in fish embryos due to their high sensitivity, inability to avoid exposure and the obvious concerns over the impacts of oil spills on the fisheries. Much less is known about the effects of oil on other responses of fish (e.g., sexual maturation, reproduction, behaviour) or on other species, in part because research has not been focused and systematic (e.g., see review of toxicity to algae, Chapter 4) or it is simply lacking. In addition, the interactions of oil exposure and toxicity with environmental stressors, including temperature, salinity, oxygen concentrations, pH, spawning migrations and other anthropogenic contaminants, would be important variables in this research. It is critically important to determine if acute sublethal exposure of aquatic organisms (e.g., fish embryos) to oil causes delayed or lingering toxicity evidenced as a reduced abundance in the years following an oil spill.

A major impediment to quantitative predictions of oil toxicity is the quality of toxicity data for risk and impact assessments. Problems include a lack of methods to distinguish dissolved from droplet oil, the high cost of analytical methods to adequately characterize exposures, and time-varying concentrations in toxicity tests. The application of toxicity data in ecological risk assessments is also limited by the availability of models capable of linking acute and chronic toxicity to the chemical characteristics of hydrocarbons. The current models that predict acute lethality reasonably well do not apply to situations where concentrations of oil in water vary over time, as would be the case during an oil spill. The routine applications of these models also do not generate estimates of the error of calculated toxicities, despite considerable variations between observed and predicted toxicities for individual compounds. Models to predict chronic toxicity have not been developed from data on chronic toxicity, but rely on the incorrect assumption of a constant ratio between acute and chronic toxicity.

Ecological impact assessments of spilled oil, especially dilbit, are also limited by a lack of ecological research in oil-contaminated ecosystems. Long-term time-series research ranging from days to years on 'spills of opportunity' or experimental oil spills is needed to establish mechanistic and statistical links among hydrocarbon exposure of aquatic species, biomarker responses, the prevalence of signs of toxicity and pathology, the distribution, abundance and production of individual species, and ecosystem structure and function. In particular, research is needed on the fate, behaviour and effects of oil in freshwater ecosystems using designs and methods that reflect differences in spatial scales, processes, water movements and biological communities relative to marine ecosystems.

A knowledge gap remains in understanding the potential impacts of oil, or chemically-dispersed oil, in deepwater and Arctic ecosystems where dispersant use is contemplated. The complex interactions among extreme low temperatures, the unique physiologies of coldwater species, the solubility kinetics of hydrocarbons in water, exposure times, pharmacokinetics of hydrocarbon uptake and toxicokinetics for different mechanisms of acute and chronic toxicity of oil must be investigated. With respect to freshwater and terrestrial ecosystems, our understanding of the impacts of spilled oil on permafrost ecosystems and northern wetlands, which are characterized by complex water flows and plant and animal species highly adapted to harsh conditions, is severely lacking.

Chronic impacts may also result from a cascade of effects originating with acute exposure to the spill and/or to lingering effects of residual oil. For example, mortality induced damage to the structure of a population or community (e.g., a killer whale pod) will alter food web dynamics (e.g., elimination of a predator leading to increased abundance of the prey species and increased feeding pressure on primary producers). Toxicity can also cause indirect effects, such as energetic costs associated with the metabolism of PAHs and other hydrocarbon compounds, that result in lower body weight and increased mortality or higher susceptibility to predation. Such effects and their ecological significance are not fully understood and hence not properly considered in risk assessment models.

In terms of modeling, the oil spills of interest for the community are those that cover large areas because the smaller ones can be more or less contained and treated. Therefore, the thrust of modeling oil transport from a response point of view has been on parametrizing small-scale processes while attempting to capture the bulk of the large-scale transport. In other words, the small-scale information has been sacrificed in favour of the large-scale. Unfortunately, this means that most oil spill models designed for response, such as NOAA's GNOME, are not designed to provide concentrations that could be readily used for predicting toxicity effects. For example, a model that conserves mass and uses a computational block of 1 km x 1 km would not distinguish whether the mass of oil is spread within that block or whether it is localized within a 10 m x 10 m sector of that block. While the mass is the same in both cases, the latter provides a concentration that is 100 times greater. Also, oil spill models developed for response cannot be used to design the optimal parameters for applying dispersants. In contrast, models designed for research are sufficiently sophisticated to allow their use in toxicity studies and for evaluating remediation scenarios. Nevertheless, as modeling is becoming more acceptable as a predictive tool, sophisticated models are becoming more common. The goal is to achieve effective communication between the response community and the academic community that can lead to collaboration, such as occurred with the droplet model from jets VDROP-J developed in academia and currently being adopted by NOAA in their model ADIOS2.

To support the application and accuracy of predictive models following spill events, research and implementation of autonomous, remotely operated detection devices (e.g., AUVs and ROVs) and other remote sensing technologies should be encouraged, as well as the development of new or refined biomarkers and fingerprinting methods for conventional and unconventional oils (including dilbit) and oil spill treatment agents such as dispersants, in water, sediment and biological materials recovered from freshwater and maritime systems. Uncertainty, in the form of incomplete information, errors in sampling, subjective judgement, random variations of and dynamic interactions among operating factors, approximations and assumptions in measurement, and changes of environmental conditions, will always be a challenge in oil spill response operations. Reduction in the level of uncertainty is needed in the measurement of environmental factors, spill modeling and response decision-making and implementation.

The Panel recommends the conduct of biodegradability studies on conventional and unconventional oils commonly transported in Canada, especially dilbit, to delineate the maximum biodegradation rates expected under actual environmental conditions. Comparison to multiple control conditions will be essential for rigorous interpretation of the results. A controversy still remains over the use of oil dispersants for spill response. Consideration should be given to the use of mathematical decision-making tools to optimize the dose, logistical and operational processes for their application, as well as the development of more effective and eco-friendly dispersant formulations.

The existing models for simulating response processes (e.g., booming, *in situ* burning, skimming, dispersion and bioremediation) and predicting their effectiveness (individually and collectively) are limited in terms of accuracy and adaptability to different environmental conditions. This is especially true for cold waters and Arctic environments. Furthermore, once the response has ended, it becomes a matter of evaluating the effectiveness of natural attenuation (i.e., a reduction in contaminant levels and habitat recovery) and risk from residual oil. The development of standardized methodologies and targeted post-spill monitoring programs are needed to accurately determine the levels of response efficacy and the risks of residual oil.

The challenge exists on how to determine what level of preparedness is appropriate for each area of response and of concerns across Canada. Despite the importance of oil type, the Panel concluded that the overall impact of an oil spill, including the effectiveness of an oil spill response, depends mainly on the environment and conditions (weather, waves, etc.) where the spill takes place and the time lost before remedial operations.

In terms of prevention, there is a need to assess the current level of preparedness in light of relative risks in order to identify major geographic areas of concern and those with deficiencies in response capability. The risk assessment commissioned by Transport Canada should be expanded from marine spills to freshwater environments. In addition to cumulative impacts of response actions, socioeconomic factors should be more effectively reflected in the net environmental benefit analysis (NEBA) process to minimize impacts on a region's environment and economy and the wellbeing of its people. In terms of risk assessments, it is important to stress that our ability to distinguish the effects of oil spills (even on the scale of the DWH) depends upon the availability of pre-spill baseline information, an understanding of natural variability and an understanding of the effects of multiple anthropogenic stressors. The risks of oil spills must also be evaluated in the context of large-scale oceanic and climatic phenomena and changes that are occurring at unprecedented rates.

In the marine environment, preliminary data suggest that the early post-spill behaviour of dilbit would not differ substantially from the behaviour of conventional crude oil. However, dilbit fate and behaviour depends on various and sometimes unpredictable environmental factors, such as the level of mixing energy and level of contact with suspended particles. Thus, questions remain about our level of confidence in selecting and developing suitable response strategies and cleanup equipment for both contingency planning and response management. To reduce the level of uncertainty, rapid and effective response operations are paramount. Regardless of oil type, rapid response will limit the spatial extent of floating oil, prevent extensive contact with soils, sediments and organic materials along the spill flow path, and minimize shoreline stranding. The nature of the crude oil is less important than the rapidity and efficacy of the response. For example, rapid on-water response by an oil recovery unit to the spill of diluted bitumen from the punctured Kinder Morgan pipeline in Burnaby, BC, minimized subsequent environmental damage. However, if such a spill had occurred in a more remote area, the consequences might have been more substantial.

Cold and harsh environments in northern Canada and the Arctic are usually characterized by a wide range of wind speed and direction, limited visibility, low temperature, rough water surface, ice coverage, etc., posing substantial challenges for oil spill prevention, preparedness and response. To protect the habitat and its resources within the Arctic and sub-Arctic regions, vulnerability and risk analyses are needed to support contingency planning and response operations. Currently, there is a drive within Canada and internationally (e.g., Northern Region Persistent Organic Pollution Control Laboratory – Memorial University; Churchill Marine Observatory – University of Manitoba; Arctic Joint Industry Partnership – International Association of Petroleum Producers) to increase understanding of the fate and behaviour of oil in water and ice conditions (solid, slush and frazil ice) and during active periods of formation and breakup of annual and multi-year ice, as well as the impacts on ecosystems. This experimental information on the effect and efficiency of different response methods under Arctic conditions is urgently needed to improve the ability to forecast and manage oil spill response operations in a more timely, eco-friendly and cost-effective manner.

Most of the knowledge of oil spill response technologies has been developed through results from studies in the laboratory, mesocosm test systems and actual case studies (with limited controls and treatment replication). It is the consensus of the Panel and general scientific community that controlled field trials are needed to advance the development, validation and acceptance of operational spill response strategies, especially for subsurface blowouts, Arctic oil spills and freshwater shorelines.

Question 5. How should these scientific insights be used to inform optimal strategies for spill preparedness, spill response and environmental remediation?

Baseline data are needed to distinguish oil impacts from natural environmental variability and for the selection of spill response options to be taken (e.g., dispersant use). The identification of operational endpoints for oil spill response operations raises the difficulty of addressing the question "how clean is clean?" Usually this is a site-specific question because habitat recovery depends largely on a variety of species at risk identified through baseline surveys.

Anticipating the challenges of oil spill response in remote, northern areas and cold waters and planning for each contingency would help decrease the likelihood of undue delays and inappropriate response techniques. Recovery of oil spilled in the Arctic can be expected to be relatively ineffective; therefore, prevention must remain a major focus.

Delays in response typify oil spill case studies. Common causes of delays include lack of preparedness and response capabilities, deficiencies in regulatory oversight and lack of communication and coordination among government agencies, Indigenous communities and industry. Involvement of Indigenous communities in decision-making regarding cleanup and monitoring is occurring and will continue to contribute to the baseline knowledge required to support focused preparedness planning.

Human intervention often can cause more harm than the spill itself. Aggressive shoreline cleanup methods, such as high-pressure washing and physical removal of oiled vegetation and debris along the shore of lakes and rivers, can impart substantial negative effects on biological communities, including indirect and cascade effects that can delay recovery. Thus, responders should be sure to consider the impacts of their response actions will have on the ecosystem even from the contingency planning stage. In some cases, monitored natural attenuation (natural recovery) may be the best response option for stranded or submerged oil since the negative effects of cleanup may be significant. Consultation not only with Aboriginal communities but also with ecologists knowledgeable in the contaminated environment is essential for protecting these important habitats. Furthermore, NEBA should also consider sociological factors because of public concerns over matters such as the return of a high amenity sites (e.g. highly-valued beaches and watercourses) to their pre-spill state.

Research is needed to further understanding of the effects of spilled oil in Arctic and permafrost ecosystems and how best to develop appropriate response strategies that mitigate the damage without further harm. Little has been done to advance knowledge of how to deal with a subsurface blowout in ice-covered marine environments. While the National Energy Board has identified the need for additional precautionary measures (e.g., same season relief well capacity), further research is needed to aid in development of oil detection and response decision support. With the advent of Arctic drilling for oil and hydrocarbons, improved methods are needed to detect and monitor the behaviour and transport of spills on, in and under ice and within the water column in the event of a subsurface deep sea blowout. In addition, oil interactions with permafrost and spring melt are associated with a number of challenges and unknowns that include site access for spill response, rapid spreading of oil during freshet, slow rates of weathering and how hydrocarbons interact with ice and suspended particulate matter.

Current technologies, equipment and response personnel are needed to be fully capable of effectively responding to major inland or offshore spills in northern Canada and Arctic regions. To advance operational spill response guidelines in these extreme environments, improvements in the understanding of the ecological effects of various oil spill cleanup measures need to be developed.

More research is needed to rapidly determine the highest-risk combination of environmental characteristics when dealing with dilbit. For example, further studies are needed to understand under what circumstances a dilbit product is most likely to sink and its weathering would be slowest. In addition, more research is needed to understand the behaviour of dilbit and other heavy fuel oils in a range of environments, including near-shore and offshore marine, estuarine, and freshwater lakes, rivers and wetlands, under various combinations of climate, water chemistry and biological community conditions. This new information will help to optimize the selection of current spill response strategies and to support the development and validation of emerging technologies, including biodegradation of mousse (water-in-oil emulsions). Details on the factors that influence mousses and tar balls are needed to better understand their formation, properties and treatment.

Based on the Panel's review of the physical and chemical properties of petroleum hydrocarbons, the overall behaviour of both conventional and unconventional oils currently transported within Canada fall along a continuum for which existing oil spill technologies have been used. Unfortunately, a full understanding of the fate and transport of conventional and unconventional oil, such as dilbit, and associated impacts under different environmental conditions is insufficient. This compromises our ability of select and develop suitable response strategies and cleanup equipment.

In terms of priorities, just as conventional oils have been studied for years, greater focus should be given to dilbit, heavy fuel oils, emulsified oils and possibly tar balls in a range of environments, with special emphasis on identified high-risk coastal areas and cold northern parts of Canada. The results of these studies will help to identify and predict the level of impact following a spill, aid in the selection of the optimal spill response strategies, support the development and validation of emerging technologies and provide needed assistance in the assessment and understanding of the risks following a high impact spill.

Most literature on oil persistence is from marine environments. More information on oil persistence in riverine, lacustrine and mud flat environments would be beneficial for risk assessments and response operations. Also, more information is needed on high gradient, high energy rivers and hyporheic zones connected to groundwater resources where there is a potential for mixing of oil into water by physical dispersion and widespread distribution.

Emphasis has recently been given to *in situ* 'green' technologies for the remediation of oil-contaminated sites that have higher public acceptance. Although much progress has been made over the last decade, green spill response technologies, such as phytoremediation (a technique based on enhanced oil biodegradation rates by plants and their associated rhizosphere microorganisms) and biodispersion (by potentially eco-friendly dispersants based on biosurfactants which are surface-active chemicals produced by microorganisms) should be tested and validated as cost-effective cleanup options. Although anaerobic biodegradation of hydrocarbons is still poorly understood, methods to accelerate the process are being considered for the treatment of oil sequestered within riverine, lacustrine, estuarine or marine sediments where it could persist for decades. Innovative methods (such as introduction of bioventing, air sparging or dissolved air flotation as response options) to stimulate anaerobic processes in the environment are needed to accelerate the rate of oil-impacted sediment remediation and habitat recovery.

Responses to oil spills usually consist of a series of dynamic, time-sensitive and complex processes subject to time and resource limitations, as well as environmental and technical constraints. The effectiveness of the response relies on the efficient use of available information (oil, weather, wave, etc.) and resources (devices, manpower, money, etc.) in response decision-making and implementation. Inadequate response decision support is one of the major challenges that limit the efficiency of current response practices. Due to limited attention and investment, existing response decision support systems are rare and lack dynamic and interactive support from other assessment tools (e.g. risk analysis, impact assessment, spill modeling, process simulation, etc.) and field validation. These are especially true for the Arctic regions and waters where harsh environmental conditions limit the time period available for response.

Question 6. Given the current state of the science, what are the priorities for research investments?

The behaviour, fate and effects of spilled oil are highly site-specific and decisions on oil spill cleanup and on assessing environmental and socioeconomic impacts are highly dependent on science. As illustrated in this RSC Panel report, the science is often lacking or highly uncertain due to the large number of variables that affect oil behaviour, fate and effects. There is an urgent need in Canada to develop science-based guidance and protocols for oil spill impact, risk assessments and cleanup. Guidance documents should provide scientific information and technical data on the various types of hydrocarbons transported, their potential effects and baseline information on potential sites exposed to high-risk -- material essential for the application of science-based decisions in oil spill response operations. This initiative requires a national level of coordinated scientific research in both the laboratory and the field (including experimental field trials with controlled releases of oil) that involves both support and funding from Indigenous communities, federal and provincial government agencies, private sector industries, academia and the public. The core needs of this proposed program are listed within seven high-priority research themes identified by the RSC Panel to improve spill prevention and the capability and effectiveness of oil spill response operations in Canada:

1. *Research to better understand the environmental impact of spilled crude oil in high-risk and poorly understood areas, such as Arctic waters, the deep ocean and shores or inland rivers and wetlands.*

2. *Research to increase the understanding of effects of oil spills on aquatic organisms at the population, community and ecosystem levels.*

3. *A national, priority-directed program of baseline research and monitoring to develop an understanding of the environmental and ecological characteristics of areas that may be affected by oil spills in the future and to identify any unique sensitivity to oil effects.*

4. *A program of controlled field research to better understand spill behaviour and effects across a spectrum of crude oil types in different ecosystems and conditions.*

5. *Research to investigate the efficacy of spill responses and to take full advantage of 'spills of opportunity'.*

6. *Research to improve spill prevention and develop/apply response decision support systems to ensure sound response decisions and effectiveness.*

7. *Research to update and refine risk assessment protocols for oil spills in Canada.*

Appendix A. Routine laboratory analytical methods for chemical characterization of crude oil contamination in the environment

Crude oils are complex mixtures of thousands of chemicals; various combinations and proportions of these chemicals impart different properties on the oils (Chapter 2). Analysis of such mixtures, particularly complex high molecular weight (HMW) components, including resins and asphaltenes, remains technically challenging. No single method is sufficient to reveal and identify all components simultaneously and for some purposes it is unnecessary. Therefore, methods including those described below can be used singly or in combination to provide a range of information from bulk composition to detailed chemical 'fingerprints' of a crude oil spilled in the environment. A summary of analytical methods used in spill response (a subset of all available methods) is presented below and in **Table A1**. A recent review of additional methods used for analysis of crude oils ('petroleomics') is available (Rogers and McKenna 2011).

The concept of Total Petroleum Hydrocarbons (TPH) is important in oil analysis. TPH is a single value for each distinct crude oil, and represents the total mass of all hydrocarbons in that oil, including the volatile and extractable (non-volatile) hydrocarbons that are recovered and detected using a specific method. When used in the context of an environmental sample, TPH often refers to the total hydrocarbons that can be extracted from the sample (EPH or extractable petroleum hydrocarbons). Many methods are available, and each will yield a different TPH value for a sample depending on the properties that the method analyzes, as described below. Therefore, the TPH value must be accompanied by a definition of the method used to obtain the value, and only recognized, standard methods, such as those vetted and archived by ASTM International (www.astm.org; formerly the American Society for Testing and Materials), the US-EPA, and ISO standards, should be used.

A potential complication relevant to spilled oils recovered from the environment for analysis is that non-petroleum hydrocarbons, such as plant oils and waxes, may be co-extracted from soils rich in vegetation or plant debris, and subsequently be detected by methods outlined below, thus contributing to TPH values without accurately reflecting the oil itself.

Infrared (IR) spectroscopy is a simple, non-destructive, rapid and inexpensive analytical technique developed for analysis of oils and greases that provides bulk composition data and allows estimation of physical properties of oils (Khanmohammadi et al. 2012). Typically, petroleum is extracted from an environmental sample (usually water or soil) using a solvent (historically Freon 113, now replaced with a non-fluorocarbon solvent like cyclohexane; ASTM [2011]), and a beam of infrared light is passed through the extract. Absorption of particular IR wavelengths yields a spectrum based on the type and abundance of chemical bonds in the extract and provides a measure of TPH. In theory, most hydrocarbons will be detected quantitatively using this analysis, except for the very light and very heavy compounds because the former may evaporate and the latter may not be soluble in cyclohexane. A drawback is that the standard method as applied to crude oils does not identify specific chemicals in a mixture and the presence of water (e.g., in oil samples recovered from the environment) interferes with accurate measurements.

Fluorescence spectroscopy (FS) is simple, non-destructive and non-specific, like IR, but employs ultraviolet (UV) wavelengths (Steffens et al. 2011). When some aromatic hydrocarbons are irradiated with UV they re-emit that light at a different wavelength. This light can be captured and analyzed as a proxy for TPH concentration. The simplicity of the measurement lends itself to remote sensing of crude oil in aquatic systems. Several instruments in different configurations have been developed to detect and estimate petroleum concentrations in real time. For heavy oils the fluorescence signal is broad and short-lived, although it is more robust for lighter oils (Steffens et al. 2011). FS only gives an estimate of the aromatics present in a sample and thus is inaccurate for estimating total hydrocarbons.

Gravimetric analysis is a rapid, inexpensive laboratory technique for determining TPH, typically after solvent extraction of the oil from an environmental sample. The mass of material that dissolves in the solvent and then remains after the solvent is evaporated is weighed. Unless combined with another analytical method, gravimetry cannot determine which specific chemicals within a class are present (or have been lost to the environment), but it can determine bulk changes in the oil and therefore indicate changes in gross properties. This method is unsuitable for light oils or dilbits that suffer large evaporative losses, but is more appropriate for heavier crudes and may be particularly useful for analyzing oil samples that present difficulties for other techniques, such as heavy oils and bitumens that have high resin and asphaltene contents and resist detailed chemical characterization. However, the measurement will include any non-petroleum materials in the sample that are extracted by the solvent used.

Liquid-Solid Column Chromatography and Fractionation. Oil that is recovered from the environment using extraction solvents subsequently may be subjected to chromatographic fractionation. Typically, the light fractions in the oil are depleted by artificial weathering in a laboratory fume hood (‘topping’ the oil) to make subsequent steps easier and because these light molecules would be lost during the fractionation procedure anyway. After determining the mass of oil that has been lost during topping (by mass difference), the asphaltene fraction is removed by precipitation using either n-pentane or n-hexanes, dried and weighed. The de-asphalted oil (also called the ‘maltenes’) is then passed through a glass column containing adsorbent(s) like silica. Discrete fractions (e.g., SARA; Chapter 2) comprising chemicals in different solubility classes are then eluted using solvents of different polarity (**Figure A1**). The masses of the fractions are determined after evaporating the solvents so that gravimetric changes, such as those caused by weathering (Chapter 2), can be discerned. Additionally, the saturate and aromatic fractions can be subjected to detailed chemical analysis using, for example, GC-FID or GC-MS, described below, to yield additional insight into the oil’s composition. Thus, chromatography and fractionation can provide quantitative information, as well as composition, within technical limitations of detection.

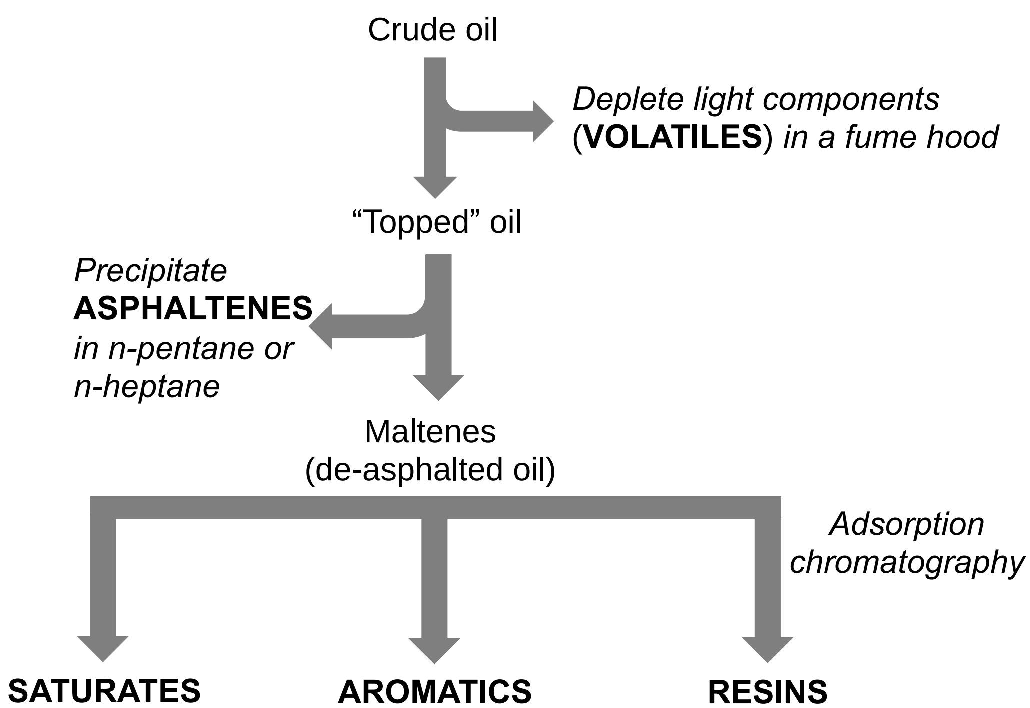

Figure A1 Liquid-solid chromatography and fractionation yielding SARA (saturates, aromatics, resins and asphaltenes) fractions of crude oil (Chapter 2), plus volatile hydrocarbons determined from mass of initial oil minus mass of topped oil.

Gas Chromatography (GC) uses principles similar to those of the adsorption chromatography fractionation method described above, but uses elevated temperature and gas flow across the adsorbent phase rather than liquid solvents at ambient temperature to separate individual chemicals in the oil. Long, small-bore capillary columns (e.g., fused silica columns of 30 m length, 0.25 mm diameter with an ultra-thin adsorbent film of 0.25 µm) enable separation of complex chemical mixtures. Different adsorbents are available to separate specific chemical classes, providing a characteristic 'fingerprint' (chromatogram) of the oil where, ideally, each peak represents a single chemical (**Figure A2**). In practice, a finite range of molecular sizes and composition having boiling points below 524 °C can be detected using GC, routinely from C_6 to C_{30}. Only materials having no or low polarity are resolved, i.e., many saturates and aromatics, but few resins (asphaltenes are removed before GC analysis to prevent fouling of the column and instrument). Therefore, TPH values obtained by this method are limited to only GC-detectable and -resolvable compounds. This is important when analyzing weathering losses from heavy oils in which the large majority of material is not GC-detectable, because any changes observed by GC represent only minor mass changes in the total oil composition.

GC methods are in common use because of the broad range of hydrocarbons that are detected selectively and sensitively, and because identification of individual compounds can be achieved by coupling various detectors to GC analysis, including flame ionization detectors (GC-FID) and mass spectrometers (GC-MS), among others.

GC-FID uses a non-selective hydrogen flame to ionize and detect a broad range of compounds that are separated by and elute from the GC column. It is a sensitive and reproducible method commonly used for detecting ~C_6 to C_{30} hydrocarbons and some resins, but is not suitable for large, polar molecules such as asphaltenes. It is commonly applied to analysis of the most readily biodegradable fractions, the saturates and aromatics. However, even within these fractions, the presence of myriad isomers can render resolution of individual compounds difficult; in that case, the chromatogram is characterized by a 'hump' comprising unresolved peaks called the Unresolved Complex Mixture (UCM). The UCM is the dominant feature in chromatograms of heavy oils. Examples of GC-FID chromatograms are shown in **Figure A2**.

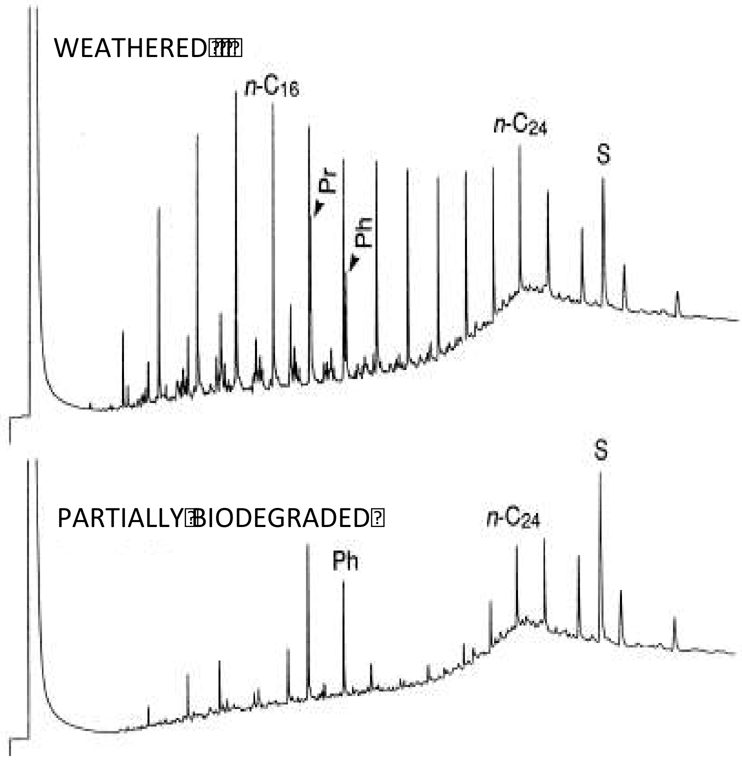

Figure A2. Examples of GC-FID chromatograms showing the GC-detectable saturate fraction of an Alaska North Slope crude oil. *Top: weathered oil, showing evaporative loss of 'light ends' below C_{12}; Bottom: weathered and partially biodegraded oil, showing selective removal of n-alkanes below C_{24}. Numbered peaks: n-C_{16} and n-C_{24}= n-hexadecane and n-tetracosane, respectively; Pr and Ph= pristane and phytane, respectively (biomarkers that are slow to degrade); S= squalane, a reference hydrocarbon added to the oil as an internal standard. The remaining taller peaks represent the n-alkane series, differing by a single –CH_2 group, and the shorter peaks represent multiple different isomers of iso- and cyclo-alkanes. The 'hump' toward the right-hand side represents the unresolved complex mixture (UCM), comprising isomers that are not resolved by the GC conditions used.*

GC-MS: The mass-selective detector yields highly detailed information about individual chemicals as they elute from the GC column, including inferred compound identity. However, although it is very sensitive, it may not be able to discern differences between multiple isomers that are common in crude oils. GC-MS is not used to measure bulk properties, such as TPH, but is more of a 'fine tool' to discern specific GC-detectable changes in oil composition.

A major disadvantage of all GC-based methods is that only certain classes of chemicals are resolved on a given adsorbent column and the detectors are only suitable for certain classes of petroleum components. For example, whereas saturated and aromatic hydrocarbons within a molecular weight range (e.g., ~C_6–C_{30}) are routinely detected using GC-FID and GC-MS, larger saturated and aromatic compounds and the resins and asphaltene fractions are particularly difficult to resolve and/or are undetectable by either method. GC-MS is particularly useful for routine analysis of changes in the specific chemical composition of an oil as it weathers or biodegrades, but usually does not provide comprehensive information, as it does not detect or identify large compounds.

An important consideration of GC analysis is that 'disappearance' of a peak from the oil chromatogram ('oil fingerprint') does not necessarily mean that the corresponding chemical has been completely removed from the environment. It is possible that the compound has been only slightly altered, e.g., by photooxidation (see Chapter 2) or by partial biodegradation by microbes, with the majority of the hydrocarbon skeleton remaining intact but being too polar to be detected or resolved by GC. Thus, GC chromatograms must be analyzed carefully so as not to over-interpret the fingerprint and thereby overestimate degradation.

High Temperature Simulated Distillation by Gas Chromatography (GC-HT SimDis or HTSD) separates the components of petroleum in the order of their boiling points (Roussis and Fitzgerald 2000), generating bulk compositional information about the oil. It is particularly useful for analysis of oils with high contents of waxes, resins and asphaltenes that cannot be measured using conventional GC methods. The curve generated by detecting boiling ranges as the analytical temperature increases to >700 °C can be used to compare different oils or to refer to calibration curves to estimate the oil's composition. The shape of the boiling point distribution curve (i.e., cumulative % mass loss with increasing temperature) reflects the proportions of low- and high-boiling point components in the oil.

An example is shown in **Figure A3**, comparing HTSD for a conventional oil (ASMB), an intermediate fuel oil (IFO-180) and two dilbit samples (Cold Lake and AWB**; Table 2.2**). A simplistic interpretation of the distillation curves is that a greater proportion of ASMB components have lower boiling points (are lower molecular weight) than those of IFO-180; Cold Lake and AWB have similar compositions and include light ends present in much lower proportions than the bulk of the oil and are similar in content to those in ASMB.

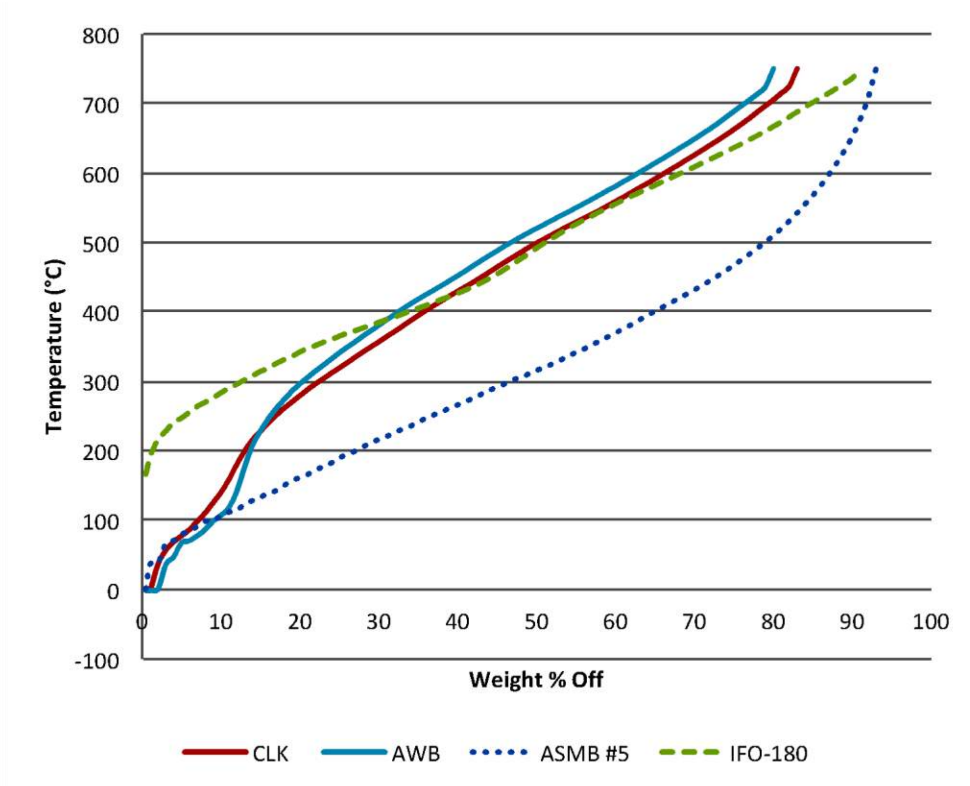

Figure A3. High Temperature Simulated Distillation *(HTSD) plot showing the simulated boiling point distributions for Cold Lake (CLK) and Access Western Blend (AWB) dilbits, Alberta Sweet Mixed Blend (ASMB) conventional crude and Intermediate Fuel Oil 180; see Table 2.2 for oil descriptions. Figure courtesy of Dr. H. Dettman, National Resources Canada – CanmetENERGY, Devon, Alberta.*

Non-routine analytical techniques

Two other techniques used for petroleum analysis are ElectroSpray Ionization Fourier transform ion cyclotron resonance mass spectrometry (ESI FT-ICR-MS) and Nuclear Magnetic Resonance (NMR) (Rogers and McKenna 2011). Both are highly sophisticated and require extremely expensive instruments, as well as skilled operators, but they provide fundamental insights into petroleum composition that is not afforded by more routine analytical techniques.

Other methods are available (e.g., high performance liquid chromatography [HPLC]; Table A2) but they are typically used for more specialized analysis.

Table A1. Summary of chemical analysis methods commonly used in oil spills

Name of method	Description of method	Advantage of the method	Disadvantage of the method	Reference
Infrared spectroscopy (IR)	• Provides miscellaneous information about complex mixtures (e.g., hydroxyl and carbonyl groups)	• Can analyze the hydrogen bonding in the crude oil mixture • Measurement of a great number of structural parameters • Helps determine oil age	• Gives more qualitative than quantitative information • Cannot detect some compounds • In some cases should be combined with other spectroscopic techniques, such as NMR spectroscopy • Includes standards only for 'oils and greases', not specifically for petroleum	Brown et al. 1975; Butt et al. 1986; Fernández-Varela et al. 2006; Gautam et al. 1998; Lynch and Brown 1973
Gas Chromatography (GC)	• Separates and analyzes complex oil components that can be vaporized without decomposition • Sample is carried through a column by the gas phase; chemical and physical properties of components differentiate their rate passing through the column, resulting in different retention times • Separated substances leaving the column are quantitatively detected by an electronic signal, which can be later detected by using detectors with different sensitivity and selectivity, such as flame photometric detector (FPD), flame ionization detector (FID), and the thermal conductivity detector (TCD).	• Quick analysis; small sampling amount • Well analyze light oil • FID: very sensitive and selective • TCD: universal detector; low selectivity, low sensitivity • FPD: identify heavily biodegraded oils, sulphur heterocycles and others	• Limited use in heavy crude oil analysis • FID: ideal for limited compounds; compounds are destroyed • TCD: not very sensitive; compounds are destroyed	Butt et al. 1986; de Andrade et al. 2010; Gaines et al. 1999; Kenkel 2002; Kim et al. 2013; Payne et al. 2008; Simanzhenkov and Idem 2003; Yim et al. 2011
Mass spectrometry (MS)	• Gives information on compound structures, such as molecular weight and formula • Used for compound identification and new compound detection • MS techniques include electron impact (EI), chemical ionization (CI), field ionization (FI), and fast atom bombardment (FAB) • Combine with chromatographic methods: GC-MS, HPLC-MS	• Identify compound structure	• Instrument can be expensive • Results may require technically sophisticated interpretation	Eide and Zahlsen 2005; Li et al. 1997; Rostad 2006; Sun et al. 2009; Tzing et al. 2003; Wang et al. 2002
High performance liquid chromatography (HPLC)	• Use high pressure to force chemical compounds to pass through a metal column • Detector used: UV absorption (UV), refractive index (RI) or fluorescence (F)	• Can analyze compounds with low volatility that are inappropriate for GC analysis • Can analyze some compounds that GC is unable to analyze (e.g., heavy crude oil) with precision in a short time	• Limited use in crude oil analysis due to the limited compound species determined • Unable to detect some compounds, depending on the detector used • UV and F only detect some species; F lacks sensitivity and is influenced by temperature	Fish et al. 1984; Kenkel 2002; Pasadakis et al. 2001; Speight and Speight 2002

APPENDIX B

Table B1 Major properties of oil, analytical methods and relevance to oil behaviour

Parameter	Description of parameter	Analysis method	Relevance with application and cleanup measurements	References
Viscosity	• Measure of flow resistance • Liquids with lower viscosity flow faster • Dependent on oil composition; hence, the viscosities of crude oils vary. • Oils with greater saturates and aromatics fractions and lower asphaltenes and resins content have lower viscosity • Weathering of oil increases its viscosity • Generally exponentially dependent on temperature	• Viscometer: determines the flow rate of the oil under standard conditions; higher flow rate indicates lower viscosity • Rheometer: measures liquid flow in response to applied force • ASTM method D445	• Viscous oil spreads on water surface slowly and penetrates soils/sediments slowly • Oils with high viscosity affect the efficacy of pumps and skimmers	Aske et al. 2002; Beal 1946; Beggs and Robinson 1975; Lambert 2003; Morrison and Murphy 2006; ASTM 2015
Density	• Mass of a unit volume of oil, expressed as g/mL or kg/m^3 • Density of oil typically 0.7-0.99 g/mL, (versus seawater density; 1.03 g/mL) • Most oils float on seawater, except for a few bitumens • Heavily weathered oils tend to have greater density • Oil density is more temperature-dependent than is water	• Density meter (densitometer) • ASTM method D 5002	• Light grade and heavy oils • Submerged oil detection (e.g., acoustic remote sensing); surface oil detection (e.g., optical remote sensing) • Heavier oils are more persistent and may pose greater challenge for remediation	Aske et al. 2002; ASTM 2005; Fingas et al. 2006;
Specific gravity (relative density)	• Ratio of oil density to receiving water density • Varies with temperature • Quality indicator of oil by American Petroleum Institute (API), or API gravity	• ASTM method D287 -12b: Standard test method for API gravity of crude petroleum and petroleum products (hydrometer method)	• Gives approximate hydrocarbon composition and heat of combustion • Affects oil storage, handing and combustion	ASTM 2012a; Fingas 2010
Surface tension	• Net stresses at the boundaries between different substances • Expressed as the increased energy per unit area, or as force per unit length (mN/m)	• Tensiometer • du Noüy ring method • ASTM method D971	• Affects oil spreading • Relates to the final size of the oil slick • Lower surface tension leads to thinner and larger extent of slick	Aske et al. 2002; ASTM 2012b; du Noüy 1925;
Flash point	• The temperature at which the vapor over the liquid can be ignited • Flammable liquid	• Flash point analyzer • ASTM method D1310 (for low viscosity oil), and ASTM method D93 (for heavier oil)	• Safety indicator for spill cleanup process (light fuels such as gasoline can ignite under most ambient conditions)	ASTM 2007; ASTM 2013
Pour point	• The temperature at which oil ceases to flow in a five second-period • Ranges from -60 °C to 30 °C for crude oils • Lighter, less viscous oils have lower pour points	• ASTM method D97	• Limited use as an indicator of oil status • Important for oil recovery and transport	ASTM 2012b

APPENDIX C

Table C1: Additional details of composition and properties of relevant crude oils and refined products. *Data excerpted from various sources**

Oil type (source province or country)	API gravity (°)	specific gravity at 15°C	% sulphur	% saturates	% resins	% asphalt-enes	% waxes	adhesion (g/m^2)*	% dispersion (agent)
Condensates and refined products used as diluents									
Sable Island condensate (NS)	40	0.82	0.03	88	0	1			
Fort Saskatchewan condensate blend (AB)	68	0.67	0.14	73					
Cold Lake Diluent (AB)	69	0.70	0.25						
Naphtha (AB)	57	0.75	0.07	85					
Southern Lights Condensate Diluent (US)	80	0.68	0.03						
Suncor Synthetic Crude Crude Oil/ SCO (AB)	33	0.86	0.2	82	1	0			40 (Corexit 9500)
Light crude oils									
Alberta Sweet Mixed Blend (ASMB) Reference oil #4 (AB)	36	0.84	0.6	65	5	33	4	13-61	40 (Corexit 9500)
Macondo (MC252) (USA)	35	0.84	0.3				0		
Norman Wells (NWT)	38	0.83	0.4	86	2	1	2		35 (Corexit 9500)
Transmountain Blend (BC)	34	0.86	0.8	81	2	4	7		
Statfjord (Norway)	38	0.84	0.3	68	6	2	8	14-62	40 (Corexit 9500)
Arabian Light (Saudi Arabia)	32	0.86	1.9	76	6	4	3	17-35	19 (Corexit 9500)
West Texas Intermediate (USA)	36-41	0.85	0..9	79	6	1	3	12-32	28 (Corexit 9500)

Medium crude oils									
Alaska North Slope (ANS) middle pipeline (USA)	30	0.89	1.1	52	9	5		28-33	46% (Corexit 9500)
Atkinson Point (NWT)	24	0.91	0.9	48	14	3	1		
Prudhoe Bay-A (USA)	29	0.88	1	53	10	4	4	24-29	10 (Corexit 9500)
Gullfaks, Troll (Norway)	29	0.88	0.3	60	5	1	4	23-35	25 (Corexit 9500)
Shale oils									
Bakken (USA)	42		variable; usually <0.3						
Waxy crude oils									
Hibernia (NL)	35	0.85		73	7	2	5	12-160	11-21 (Corexit 9500)
Terra Nova (NL)	36	0.85	0.4	62	6	2	9	10-80	14
Sour crude oils									
Midale (SK)	31		1.5	51	9	5	5		25 (Corexit 9500)
BC Light (BC)	41	0.82	0.6						
Western Canadian Blend (WCB) (AB)	22	0.92	3						
West Texas Sour (USA)	30	0.78	1.5	51	9	5	5	21-25	25 (Corexit 9500)
Heavy oils and diluted bitumen									
Bunker C fuel oil (Fuel Oil No. 6) (international)	11	0.99	0.5	25	17	11	2	85-421	6-14 (Corexit 9500)
Cold Lake blend (dilbit) (AB)	23	0.92	4.7					13-977	
Albian Heavy Synthetic (AB)	20	0.94	2.3	42	26	6			15 (Corexit 9527)
Access Western Blend (AWB) (AB)	23	0.92	4						

Wabasca Heavy (AB)	16	0.96	5	41	28	9			<10 (Corexit 9527)
Western Canadian Select (WCS) (AB)	19-22	0.93	3						
Synbit Blend (AB)	21	0.93	2.9						
Athabasca bitumen (undiluted) (AB)	8	1.01	5			5			
Cold Lake bitumen (undiluted) (AB)	9.8	1.0002	6.9			13	2		0 (Corexit 9527)
Orimulsion-100 ultraheavy oil and water (Venezuela)	8	1.01	2.3	17	16	20			

***** range of adhesion values represents different weathered states***

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Chapter 4

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Chapter 8

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