

Physical Properties Dynamics of Oil Sands Products and their Influence on Spill Response

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Dedication

This thesis is dedicated to my granddaughter, Millie Grace Robertson, who was born with Hypoplastic Left Heart Syndrome. Although modern medicine prolonged her life, she passed away at age 16 months. Millie, you gave us joy; made us stronger and more compassionate souls.



*Millie Grace Robertson
December 23, 2016 to May 2, 2018*

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Abstract

If current trends continue, Alberta oil sands production could increase by a million barrels per day in the next decade. Demand would then overwhelm existing domestic transport routes, and one would predict pressure to mount for new pipelines and expansion of existing ones, and increased tanker traffic to provide access to new overseas markets. In Canada, mechanical recovery is the primary oil spill response option. It is effective, but only under relatively calm seas. Alternative oil spill countermeasures exist, such as chemical dispersant and *in situ* burning. The analysis here indicates that, if approved through legislation and applied in conditions to achieve best results, these alternatives could considerably reduce environmental and socio-economic impacts than mechanical recovery alone. Current Canadian contingency plans lack the decision-making tools to predict the effectiveness of oil spill countermeasures to treat and assess the risk from spills to protect sensitive aquatic areas.

Blended bitumen and conventional oils were selected and their physical properties and chemical compositions, relevant to ecological impacts and oil spill response, were characterized. Empirical models were developed to predict the rate and decay of water soluble chemicals released from spills of bitumen blends to provide implications for risk assessments. A decision matrix was created from newly developed models for the time evolution of the density and viscosity of oil to forecast windows of opportunity, where countermeasures are effective at treating spills and the conditions under which oil would sink in aquatic areas. Also, evaluation of seasonal climatic factors revealed that sunlight exposure, wind speed and temperature had a significant ($p < 0.05$) influence on weathering of oil. A new oil dispersion model was developed to estimate effectiveness values for dispersant to treat oil at points in time after its release. These new developments offer to strengthen critical elements that are often missing in contingency plans.

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Definition of Terms

Alternative Oil Spill Cleanup Options (Countermeasures) refer to chemical dispersant, in situ burning, and natural attenuation. These are alternatives to the containment and recovery, the primary oil spill response option to combat oil spills in Canada.

Biodegradation is a process where microorganisms, mainly bacteria and fungi, are responsible for the degradation of spills of petroleum hydrocarbon products in marine and coastal environments through a metabolic process called respiration that is required for cell maintenance and reproduction.

Bitumen Blends are new oil products produced by blending *crude bitumen* with a lighter hydrocarbon, often referred to as *diluent* (e.g. condensate, synthetic crude, combination of both, etc.) to reduce viscosity to a range where it can be transported by rail, pipelines and tankers. The diluent consists of a variety of water- and oil-soluble chemicals of varying composition depending on the type of hydrocarbon used in the blending process. The blending process produces a variety of new products with many common subtype names such as dilbit (*ca.* 30-50% condensate blended with crude bitumen); synbit (*ca.* 30-50% synthetic crude blended with crude bitumen); dilsynbit (*ca.* 30-50% condensate/synthetic crude blended with bitumen); and railbit (*ca.* 15 % diluent and typically shipped by rail) which was not used in this study.

Brackish water has more salinity (dissolved salt) than fresh water, but not as much as seawater in offshore areas. It is produced when fresh receiving water enters marine coastal areas.

BTEX is the collective name given to Benzene, Toluene, Ethylbenzene and the Xylene isomers (*p*-, *m*-, and *o*-xylenes).

Chemical Dispersant contains a surfactant or surface active agent, which partially mixes with both oil and water in the presence of mixing energy (e.g. waves, currents, or mechanical means). The process removes the oil from the surface of the water to the subsurface water column, where it is further mixed and rapidly diluted by waves and currents. In most cases, chemical dispersants are applied to treat surface spills of oil in offshore areas to prevent the oil from entering shoreline areas that are costly to clean. To remediate oil contaminated shorelines, dispersants formulations that differ from those

used in offshore areas are applied in combination with high pressure flushing to remove oil, and the oil and water mixture is subsequently recovered with vacuum pumps that divert it to holding tanks prior to disposal.

Containment and Recovery is a process that removes oil from the water surface by mechanical means and is achieved in combination with booming or containment of oil. The recovery process is restricted to calm sea conditions and having sufficient oil slick thickness and adequate storage and handling of the recovered oil-water layer. If conditions are favorable, booming and skimming technologies are typically only 10 to 15% effective at containing and removing oil from the surface of water, and preventing it from reaching sensitive habitats of coastal areas.

Crude bitumen is dense, viscous semi-liquid oil produced from the Athabasca oil sands in Alberta, Canada. It is a mixture of hydrocarbons indigenous to the fine-grained sands in which it is found.

Conventional oil is a type of oil produced using traditional extraction methods. It is liquid at standard temperature and pressure conditions, and thus flows without added stimulation.

COREXIT®EC9500A is the trade name for a chemical dispersant produced by Nalco Environmental Solutions, USA. New regulations have been passed to permit its usage to treat oil spills in offshore areas.

Density of a substance is its mass per unit volume. The density of oil relative to water, its specific gravity, governs whether particular oils will float on water. Most fresh crude oils will float on water. Bitumen and certain residual fuel oils, however, may have densities greater than water at some temperature ranges and may submerge in water. The density of spilled oil will increase with time due to weathering as lighter chemicals are degraded.

Diluent is light hydrocarbon fluid (e.g. condensate, synthetic crude, combination of both, etc.) consisting of water- and oil-soluble chemicals and have low density and viscosity values.

Dispersion is the entrainment (transport of fluid across an interface between two bodies of fluid by shear induced turbulence) of oil droplets in the water column and is driven by surface tension of the oil and water, viscosity of the oil, and mixing energy (e.g. waves, currents, and tides). Heavy crude oils such as bitumen blends are not expected to disperse

well naturally. This process can be enhanced in high energy waves by the application of a chemical dispersant (e.g. surface active agent), which lowers the interfacial tension by disrupting the intermolecular attractions (e.g. hydrogen bonds) between adjacent water molecules at the oil-water interface.

Dissolution is a process where the chemicals present in oil are water soluble depending on their chemical structure, where solubility decreases as carbon number (e.g. in molecular structure) increases. Dissolution can also be affected by hydrogen bonding intermolecular forces of attraction of water molecules with the π electron cloud of the benzene ring of monocyclic aromatics such as Benzene, Toluene, Ethyl Benzene, and Xylenes.

Empirical Expressions is another term used for models.

Emulsification involves the mixture of two or more liquids that are immiscible. This results when one liquid is dispersed as small droplets into another. With respect to oil and water, emulsions can be in two forms; one where oil is dispersed into water to generate oil-in-water emulsion and second when water is dispersed into oil to form water-in-oil emulsion. This process changes the physical properties of oil; increases the volume of the slick; slows the rate of degradation from other processes such as evaporation, dissolution, and biodegradation; and makes cleanup operations more challenging.

Evaporation is a process whereby a liquid is converted to a gas. The intermolecular forces (e.g. London dispersion, dipole-dipole, or hydrogen bonding) of attraction in liquids determine the rate of evaporation. As molecules increase in molecular weight with more electrons, van der Waals dispersion forces become greater; therefore, boiling point increases with molecular size. Dipole-dipole attraction exists when the positively charged region of one molecule is attracted to the negatively charged region of another molecule. Substances, whose molecules have dipole moment, generally have higher boiling points than those of similar molecular mass without a dipole moment. Hydrogen bonding is a term describing an attractive interaction between a hydrogen atom from a molecule or a molecular fragment, X-H in which X (e.g. F, O, N) is more electronegative than H, and an atom or a group of atoms in the same or a different molecule. The weaker the intermolecular forces in a liquid the more rapid the evaporation.

Herding Agent is a surfactant that is applied to the outer perimeter of an oil slick to herd

<p>the oil into a thickened state to allow containment for either <i>in situ</i> burning or recovery (skimming).</p>
<p><i>In Situ Burning</i> involves burning the oil where it is at sea. In some cases, an accelerant may be used to start the oil burn. Similar to mechanical recovery, <i>in situ</i> burning requires calm waters to be effective. Also, it should be conducted in daylight (for safety reasons), and because containment and herding of oil are limiting factors, and the burn must be a considerable distance from communities and wildlife that may come in contact with toxic smoke, <i>in situ</i> burning is typically about 95% effective, based on the volume of oil contained. Sometimes it may be deployed to remove oil from marshes.</p>
<p><i>Natural Attenuation</i> (no treatment) relies on nature's physical, chemical and biological processes to reduce or attenuate contaminant concentrations in the environment without any stimulation.</p>
<p><i>Non-conventional crude oil</i> is oil produced using non-conventional methods. For example steam assisted gravity drainage is an enhanced oil recovery technology for producing heavy oil and bitumen.</p>
<p><i>Photo oxidation</i> is a process where hydrocarbons, in particular aromatics, are readily oxidized in the presence of intense ultra-violet light from the sun. This photo chemical effect transforms water insoluble chemicals to alcohols, carboxylic acids, and ketones that are water soluble and more readily transferred and diluted in waterways.</p>
<p><i>Sedimentation</i> is the process where oil and suspended sediments or particulates in the water column interact to form oil-particle-aggregates that can become dense enough to sink to the bottom of an aquatic system.</p>
<p><i>Spill Treating Agent</i> (STA) is another term used for chemical dispersant. It also includes shoreline and herding agents. The active ingredient is a surfactant.</p>
<p><i>Spreading</i> of oil on water increases its footprint, but also encourages evaporation, dissolution, and exposure to photo oxidation. The distribution of oil spilled on the sea surface occurs under the influence of gravitational forces. In the early stages of an oil spill, gravitational forces and interfacial tension (e.g. dissolved hydrocarbons interfere with hydrogen bonding to reduce surface tension of water) cause increasing oil spreading, while inertia (e.g. resistance to change in speed or direction) and viscous forces (e.g. resistance to flow) retard it as the lighter chemicals evaporate or dissolve in the water</p>

column. Winds, water currents and tides are the three main factors that affect the transportation of oil released. Spreading can also be affected by temperature changes and the presence of ice regulated by seasonal effects.

Viscosity is a quantity that describes a fluid's resistance to flow. The viscosity of oil is a function of its chemical composition. As oil weathers, the evaporation of the lighter chemicals leads to increased viscosity. Viscosity also increases with decreased temperature, and decreases with increased temperature.

Weathering is the physical, chemical and biological processes acting on spilled oil. These processes include evaporation, dissolution, photo oxidation, dispersion, spreading, emulsification, sedimentation and biodegradation.

List of Common Abbreviations

Dilbit-crude bitumen diluted with condensate.
Dilsynbit-crude bitumen diluted with a mixture of condensate and synthetic crude oil.
Synbit-crude bitumen diluted with synthetic oil
Blended Bitumen-includes all oil sands products (dilbit, dilsynbit and synbit)
IFO 180-Intermediate Fuel Oil 180 (has a viscosity of 180 cSt at 50 °C)
AWB-Access Western Blend (dilbit)
CLB-Cold Lake Blend (dilbit)
ρ -density
v-viscosity
WCS-Western Canadian Select (dilsynbit)
GC-gas chromatography
MS-Mass Spectrometry
SARAs-saturates, aromatics, resins, and asphaltenes
BTEX- Benzene, Toluene, Ethyl Benzene, and Xylenes.
DE-dispersion effectiveness
STA-spill treating agent
ASTM-American Standard Test Method

Chapter 1: This Study

1. Research Statement

Canadian contingency plans are inadequate for protecting vulnerable, sensitive aquatic areas from potential heavy oil spills that are forecasted to occur as a result of an increased production of over one million barrels per day of oil sands products. Oil spill response capabilities are limited to mechanical recovery, and while other alternative options exist, responders currently do not have the authority to use them and the modelling tools needed to more effectively and promptly aid in making decisions on the selection and limitations of alternative response options to treat and assess the environmental impacts of spills of oil sands products in diverse aquatic ecosystems.

1.1 Research Objectives

To address the gaps in scientific knowledge, an ecological simulator (circular flume tank) was designed and fabricated to simulate a water current pathway to transport oil and the natural processes that weather it on the surface of water. A multi-ring, floating oil containment barrier controls oil slick thickness and permits time-series sampling of oil as it weathers in the simulator. During the course of the research, the project advances from conducting flume tank experiments to developing models to show changes in the physical properties that are relevant to responding to spills of oil sands products that have weathered on water over time. The project advances further to create a decision matrix from the simulation outcomes to forecast windows of opportunity where alternative oil spill countermeasures are effective and timely at treating oil after its initial release, and when the oil becomes dense enough to sink in aquatic systems.

More specifically, the research addresses the following objectives:

- *To characterize various bitumen blends and comparative conventional oils to provide information pertinent to spill response and ecological impacts;*
- *To develop an empirical model to show dissolution of monocyclic aromatic in water released from the diluent of surface spills of bitumen blends and evaluate the effect of season (spring and summer) and the associated climatic factors on the dissolution of monocyclics in water, so that the information can be used in the preparation of environmental risk assessments;*
- *To advance empirical models for the time evolution of oil physical properties and integrate it with information on the effectiveness of various oil spill response options to produce a decision-making matrix to aid spill response;*
- *To evaluate seasonal climatic effects on the changes in density and viscosity of oils weathered on water; and*
- *To develop empirical models to estimate the ‘window of opportunity’ and limitations of COREXIT®EC9500A to treat spills of weathered oil at sea.*

The outcomes of the study provide new aids to strengthen contingency plans and effective response to spills of oil sands (blended bitumen) products.

1.2 Summary of Research Findings

The dissertation contains eight chapters including ‘this study’ (Chapter 1), ‘introduction’ (Chapter 2) and ‘conclusions and contributions’ (Chapter 8). Chapters 3 to 7 are summarized below.

Chapter 3: *Composition of Bitumen Blends Relevant to Ecological Impacts and Spill Response* outlines the characterization of a number of blended bitumen products and comparative conventional oils (Heidrun and IFO 180) to provide information pertinent to

spill response and ecological impacts. Bitumen blends contain monocyclic aromatics (e.g. benzene, toluene, ethylbenzene and xylenes) and straight-chain saturates, but in different proportions compared to IFO 180 and Heidrun crude. The fraction of these chemicals that are present depends on the diluent used to produce the products, and they are readily degraded after the initial release. Bitumen blends were also found to contain polycyclic and heterocyclic aromatics and their alkylated homologues in different proportions compared to the conventional oils. The presence of these chemicals is most likely derived from the crude bitumen and is of environmental importance, since they are more toxic and carcinogenic than saturates. Bitumen blends were richer than conventional oils in the high molecular weight resins and asphaltenes. These recalcitrant chemicals greatly affect the physical properties (e.g. density and viscosity) that are relevant to oil spill response, especially long after the initial spill. Non-weathered bitumen blends have similar physical properties, since they are engineered to meet pipeline specifications. In contrast, IFO 180 was more dense and viscous than the bitumen blends, but Heidrun was less so.

Chapter 4: *Seasonal Effect Data on Monocyclic Aromatics Dissolution from Surface Spills of Bitumen Blends: Implications for Environmental Risk Assessments* outlines the development of a dissolution model to show the release rate and decay of monocyclic aromatics from the diluent (thinning agent) as bitumen blends weather on brackish water over time to strengthen environmental risk assessments. Of the climatic factors assessed, air and water temperatures and sunlight had a significant ($p < 0.05$) effect on all oils. This would suggest that both evaporation and photo-chemical weathering of these chemicals was occurring when they dissolved in water, but mostly in summer-time. Season (Spring and Summer) had a significant ($p < 0.05$) effect on the release rate and decay of

monocyclics in water from surface spills of bitumen products containing condensate, as the diluent. The study also demonstrated that a significant portion (~96%) of the monocyclics, released from surface spills of blended bitumen, was lost by evaporation. The data was coupled with species sensitivity data from the literature and the findings suggest that marine mammals and birds are at high risk due to inhalation and ingestion of monocyclic aromatics through feeding and oiling of body surfaces in the vicinity of a spill in coastal areas. Also, studies on oil acute toxicity to fish should reflect photochemical weathering of monocyclics in water released from the diluent during surface spills of bitumen blends.

Chapter 5: *An Oil Spill Decision Matrix in Response to Surface Spills of Various Bitumen Blends* details the creation of an oil spill decision-matrix in response to surface spills of various bitumen blends. Weathering studies were conducted on five oil products (two conventional oils and three bitumen blends) in the Department of Fisheries and Oceans' flume tank with two oil slick thicknesses, 4.0 and 7.0 mm. It was found that there was a significant difference in the time evolution of oil properties (density and viscosity), raising doubt on the validity of weathering models that do not consider the thickness of oil slicks. Also, the empirical data were fitted to new expressions for the time evolution of the densities and viscosities of these oil products. The findings from the 4.0 mm results were incorporated with data from the literature to create a decision-matrix on the factors to consider during response to spills of blended bitumen products. The matrix indicated that most response options, including chemical dispersants, work much more effectively within 48 hours of the initiation of weathering. After that window of opportunity closes, natural attenuation or *in situ* burning is the only options remaining.

Chapter 6: *Seasonal Climatic Factors that Affect Changes in the Density and Viscosity of Bitumen Blends Naturally Weathered on Water* shows when an oil spill happens, the seasonal climatic conditions under which it occurs will influence natural weathering processes acting on the spill. In these experiments, dilbit, dilsynbit, synbit and conventional crude were naturally weathered on seawater under the north-temperate spring and summer conditions of Atlantic Canada, to examine changes in their density and viscosity to enhance our understanding of the natural attenuation of bitumen blends to aid spill response planning. The empirical data from each experiment was fitted to a previously developed hyperbolic function, with their coefficients of determination, R^2 , ranging from 0.86 to 0.99. Regression analysis suggested that various climatic factors (temperature, wind speed and sunlight exposure) had a significant ($p < 0.05$) influence on the changes in the density and viscosity of bitumen blends weathered in spring and summer conditions. Sunlight had a significant ($p < 0.05$) influence on the weathering of the conventional crude, Heidrun. Season had a significant ($p < 0.01$) effect on changes in the density and viscosity of the oils weathered on water. Therefore, the climatic factors influence on the weathering of oil is possibly driven by oil type and the season in which a spill occurs. The results indicate that evaporation and photo-chemical weathering had a major influence on the natural attenuation of the tested bitumen blends.

Chapter 7: *Estimating the Usefulness of Chemical Dispersant to Treat Surface Spills of Oil sands Products* depicts that natural and chemically enhanced dispersion rates were determined for four oil products (dilbit, dilsynbit, synbit and conventional crude) under breaking wave conditions (0.4m) in an outdoor wave tank facility to determine the influence of spring and summer temperature conditions. The results showed that the

dispersion effectiveness (DE) ranged from 0 to 7%. The application of dispersant significantly ($p < 0.05$) increased the DE by an order of magnitude. Except for the conventional oil, seasonal temperature changes (4 to 20 °C) had a significant ($p < 0.05$) effect on the DE of the test oils. With differences in the type of oil, weathering state, and seasonal conditions this study provided a data set of DE values covering a broad range of oil viscosities that were fitted to a linear regression model. The model was then combined with a previous model compiled from Chapters 4 and 5 predicting oil viscosities as a function of time, to produce a model that predicts the DE as function of time. Such a relation could be used by responders tackling oil spills.

Articles Published from this Research and Cited in This Thesis:

- King, T.; Mason, J.; Thamer, P.; Wohlgeschaffen, G.; Lee, K.; and Clyburne, J. (2017a). Composition of bitumen blends relevant to ecological impacts and spill response. *Proceedings of the 40th AMOP Technical Seminar* (pp. 463-475). Alberta, Canada: Environment and Climate Change Canada. (Chapter 3)
- King, T.; Robinson, B.; Cui, F.; Boufadel, M.; Lee, K.; and Clyburne, J. (2017b). An oil spill decision matrix in response to surface spills of various bitumen blends. *Environmental Science: Processes & Impacts*, 19(1), 929-939. (Part of Chapter 4 [tank design] and all of Chapter 5)
- King, T.; Robinson, B.; Ryan, S.; Lee, K.; Boufadel, M.; and Clyburne, J. (2018). Estimating the usefulness of chemical dispersant to treat surface spills of oil sands products. *Journal of Marine Science and Engineering*, 6(4), 128; <https://doi.org/10.3390/jmse6040128>. (Part of Chapter 6 and all of Chapter 7)

Chapter 2: Introduction

2. Canadian Oil Production

Global demands for oil products are on the rise, which increases the risk of an oil spill through production and transport of oil products. Canada's Alberta oil sands contain vast deposits of extra heavy crude oil (also called bitumen) in three main geological areas: Athabasca, Peace River and Cold Lake/Lloydminster. Together, these three production fields contribute significantly to the nation's 171 billion barrels of oil which ranks Canada third in the world for oil reserves (National Resources Canada, 2017). Oil sands heavy crude oil represents two million barrels per day (b/d) of the four million b/d of crude oil produced within Canada (Canadian Association for Petroleum Producer [CAPP], 2017). With improved extraction procedures to remove crude bitumen and a variety of lighter hydrocarbons fluids to dilute it, production of Canadian oil sands products is forecasted to increase by greater than a million b/d during the next decade (National Academies of Science [NAS], 2016; CAPP, 2017).

Crude bitumen is too viscous to transport, so it is diluted to a viscosity range required for transport by rail, pipelines and tankers. As products like this become more common, new oil spill cleaning options are needed to counter their harmful effects. Application of spill treating agents during a spill ultimately changes the fate of the oil, but the aquatic conditions under which they are applied must also be considered when evaluating their efficacy. Oils behave in a variety of ways depending on their composition, the environment into which they are introduced, and their fate changes over time. The physical and chemical properties of various oil sands products must therefore be characterized to understand their interaction with and effects on the environment. Oil

spilled in aquatic settings is exposed to natural weathering including evaporation, dissolution, dispersion, sedimentation, emulsification and biodegradation. The weathering processes determine the ultimate fate of the oil and influence decisions on the best approach to remediate a spill. Lack of information on the fate of oil products spilled under various aquatic conditions impedes remedial choices and applications, increases response times and the likelihood of oil persistence in the environment, thus increasing clean-up costs and potential longer-term environmental impacts associated with a spill.

2.1 The Destructive Impacts from Oil Spills

According to an Angus Reid Institute Poll (2016), the majority (67%) of Canadians are concerned about the potential for oil spills in aquatic systems. This is fueled by the devastating environmental, economic, and health impacts that can occur during a spill. In addition to water, air and sediment contamination; environmental impacts to aquatic species can be extensive. Oil can affect small species of fish or invertebrates and coat feathers of birds and fur of mammals, reducing their ability to maintain body temperatures. Oil can kill plants along shorelines and marsh areas. Subsurface species will have reduced exposure to oil (assuming that the majority of the oil does not sink), while species near the surface and in intertidal zones will have the highest exposure. Highly mobile species may be able to migrate away from contaminated areas, reducing their exposure and impact, while sedentary species might not. Filter-feeding species tend to accumulate oil while feeding and are particularly susceptible (Law and Hellou, 1999). Larvae and early developmental stages of species are more vulnerable to oil toxicity (Rice et al., 2001). Sensitive species with slower reproduction rates take longer to recover from a spill incident (Conan et al., 2001).

Oil spills can cause economic impacts to fisheries that suffer direct losses from product decline, fishery closures, loss of market value, demand and brand damage (Negro et al., 2009). Direct losses to businesses that depend on commercial fisheries such as docks, processors, distributors, and supply companies lose product inputs and markets (Negro et al., 2009). In addition, brand damage from an oil spill can impact businesses providing accommodations, transportation, guides, recreational fishing, and tourism-related retail. These market impacts can spread beyond the direct oil spill zone. For example, waterways may be closed and the greater their use the larger the effect due to closure.

There can be health impacts to humans from eating contaminated seafood. Exposure to oil vapors in vicinity of the spill could lead to chronic effects in humans and aquatic species (Law and Hellou, 1999). Contaminated water can affect those that ingest it or use it in food processing systems for human and/or animal consumption. Oil can adhere to sediment and gravel/sand beaches; thus affecting the quality of life of those that use these areas for recreational and other purposes. Social impacts from job loss, shorter life expectancy, increased stress, suicides, substance abuse and crime can create further social costs (Rodin et al., 1992). The damage to wildlife and pristine coastlines can be devastating to local residents. The corresponding surge of cash, the emotional impact of the spill, and the disruption of the local economy can result in severe social stresses such as alcoholism and drug abuse, family violence, marital breakups, psychological disorders, and arrests (Rodin et al., 1992).

2.2 History of Blended Bitumen Spills in Canada and the US

2.2.1 Pipeline Spills

Over the past decade, three noteworthy blended bitumen (see definition of terms) spills have been reported in North America. The first was a bitumen blend spill (~63,000 gallons Albian Heavy, a blend of synthetic crude and heavier oil) that occurred in 2007 from a pipeline operated by Kinder Morgan. Oil from the ruptured pipeline entered a storm sewer system and eventually entered the Burnaby Inlet (BC, Canada) resulting in damages to the marine environment and affecting 1200 m of shoreline (TSB, 2008). There was no report to confirm that any of the spilled oil submerged in the adjacent waterways. In this case, 95% of the product was recovered with a cleanup cost of \$15 million.

A second spill occurred in July 2010, when the Enbridge Line 6B pipeline ruptured releasing 843,000 gallons of Alberta's blended bitumen into Talmadge Creek which flows into the Kalamazoo River near Marshall, Michigan (US Environmental Protection Agency, 2017). The Enbridge Line 6B spill contained two bitumen blends, namely 77% Cold Lake Blend (30% condensate blended with 70% crude bitumen or dilbit; see definition of terms) and 23% Western Canadian Select (50% blend of synthetic crude/condensate blended with 50% crude bitumen or dilsynbit; see definition of terms) (Lee et al., 2015). The lighter hydrocarbon blended with crude bitumen was expected to evaporate quickly or be released as water soluble chemicals into the water column. Natural evaporation and periods of heavy rainfall and increased suspended river sediments interacted with the weathered heavy oil causing it to become dense enough to sink a few days post-spill. Spill responders were challenged in their effort to clean up the

spill using conventional technologies and developed new cleanup methods on site to recover sunken oil. The spill was recognized as one of the largest inland spills in US history with a hefty cleanup cost of over a billion US dollars (Enbridge Energy Partners, 2014).

Another spill from Exxon's Pegasus pipeline, in 2013, released between 130,000 to 400,000 gallons of oil sands product that impacted the community of a suburb in Mayflower, Arkansas US. Again, cleanup proved to be extremely challenging for responders, since land-based oil spills can seep into groundwater, contaminating aquifers and flowing into streams, rivers and lakes. In this case it was reported that the spilled product entered a drainage ditch and eventually entered Lake Conway, a popular destination for fishing and recreation (Government of Canada, 2013). Residents of Mayflower were showing symptoms of exposure to harmful volatile chemicals (e.g. monocyclic aromatics) more than four weeks after the spill (Conservation Council of New Brunswick, 2015). The spill cleanup cost was estimated to be \$75 million (Greenfield Advisors, 2017).

In all three cases, the variance in the fate and behaviour of the blended bitumen products demonstrated how the product type, site location and environmental factors can result in different response challenges. These examples also highlight the fact that there is a significant lack of independent scientific data on the consequences of oil sands product spills in diverse aquatic settings. Much of the limited information on how these products weather (degrade) in aquatic systems and the challenges in recovering and remediating them comes from the experiences of the Kalamazoo and Mayflower spills. Numerous other spills have been reported over the last few decades in Canada (Global News, 2013)

and with oil production and transportation expected to increase in the next several years, improved spill modeling capabilities are required to advance response efforts, and use of alternative spill cleanup options to mitigate oil spills.

2.2.2 Oil Tanker Spills

There have been numerous oil tanker spills reported throughout the literature, including the Exxon Valdez in Alaska, US in 1989, the Odyssey spill offshore Nova Scotia, Canada in 1988 (International Tanker Owner Pollution Federation [ITOPF], 2017), and the Arrow (Lee et al., 1999) and Kurdistan (Vandermeulen and Buckley, 1985) spills also offshore Nova Scotia in 1970 and 1979 respectively, to name a few. Case studies have shown that each spill incident is a unique blend of many factors including the type of oil, the mechanism of release, the volume of the spill, 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 (Lee et al., 2015).

According to a report by SL Ross (1999) it is estimated based on model predictions that the Maritimes region (Atlantic coastal provinces) of Canada by far is at the greatest risk for a tanker spill. It is estimated that half of expected spills in the country will be in this region, because of the approximately 20,000 tankers that move through Canadian waters each year, the majority (85%) are on the Atlantic coast (Anderson and Spears, 2012). Future proposed/expanded pipelines (Energy East and Kinder Morgan Trans Mountain expansion from Alberta to Burnby, British Columbia) in Canada would introduce 281 new tankers carrying an estimated 1.1 million barrels per day of Alberta heavy oil products off the Atlantic coast (National Resource Defence Council, 2016;

Axelrod et al., 2016) and a 300% increase in container ship and oil tanker traffic transporting an estimated 600,000 barrels per day of oil sands products off the Pacific coast (Living Oceans Society, 2011; Burnaby Public Library, 2017). Given these predictions of increased transport of heavy oil products, the Atlantic and Pacific coasts are at a greater risk of spills of oil due to potential accidents.

2.3 Spill Response and Science Challenges

In Canada, the only methods currently available to recover oil in the event of a spill are booming and skimming (see definition of terms). The effectiveness of these techniques is limited by sea states (calm only) and climatic conditions, and at best typically account for only 10 to 15% of the total oil that can be recovered (ITOPF, 2012) leaving the rest to natural attenuation where heavy oil contamination can exist for decades as was the case with the Arrow oil tanker spill that occurred in 1970 off the coast of Nova Scotia (Lee et al., 1999 and 2003).

Alternative response options exist, such as chemical dispersant and *in situ* burning, which, if approved and applied under the right conditions, can prove to be more useful at reducing the kind of environmental and socio-economic impacts (Tanker Safety Expert Panel, 2013) that were identified in section 1.2.

2.3.1 Changes to Legislation to Strengthen Environmental Protection

The Government of Canada has introduced new legislation documenting that “Canada is committed to modernizing its offshore oil and gas regime by implementing a world class regulatory system and strengthening environmental protection” (Canada Gazette, 2015, Part I: <http://gazette.gc.ca/rp-pr/p1/2015/2015-07-04/pdf/g1-14927.pdf>). Part II of the legislation records a list of spill treating agents (STA) acceptable for use in

the event of a spill in offshore areas (Canada Gazette, 2016 <http://www.gazette.gc.ca/rp-pr/p2/2016/2016-06-15/html/sor-dors108-eng.html>). To date, the chemical dispersant COREXIT®EC9500A is the only STA that has been identified as being acceptable for use in marine waters, and the Canada-Nova Scotia and Canada-Newfoundland and Labrador Offshore Petroleum Boards (C-NSOPB and C-NLOPB), and National Energy Board [NEB] which was replaced with the new Canadian Energy Regulator in February 2018) can authorize its use in consultation with the Federal Minister of Environment and the Department of Environment and Climate Change Canada. In order to receive approval to use an STA, the responsible party (entity that is liable for the spill) must demonstrate that it will result in a net environmental gain in comparison to natural attenuation and/or other recovery and remedial options. Further amendments to Canadian regulations to include alternative response options (i.e. *in situ* burning) could occur over the next few years and science is required to provide advice on their effectiveness when applied under different environmental conditions and to assess whether there is a net environmental benefit from their use.

2.3.2 Gaps in Science on the Use of Dispersant to Treat Surface Spills of Bitumen

Blends

A limited number of studies have been conducted on the use of chemical dispersants to treat spills of blended bitumen products in aquatic systems. The efficacy of chemical dispersants, used to treat surface slicks of bitumen blends, is largely unknown. In addition, the chemical composition of blended bitumen products can differ depending on the type of crude bitumen and the lighter fluid that is used to dilute it (Mech, 2011; King et al., 2014), and therefore selection of an ideal dispersant to treat different types of

spills may prove challenging. In the absence of data specific to blended bitumen products, the application of dispersant to spills of some conventional hydrocarbon products such as heavy fuel oils (e.g. a high proportion of relatively heavy asphaltenes) might in part be comparable. However, testing is required in order to confirm this hypothesis. Recent studies by the Government of Canada (2013) and King et al., (2015a&b) have shown that chemical dispersant may provide some effectiveness to treat a relatively fresh spill of Cold Lake Blend, if conditions are ideal to do so. The Royal Society of Canada's expert panel report on "*The Behaviour and Environmental Impacts of Crude Oil Releases in Aquatic Environments*" (Lee et al., 2015) identified the need to address the application of chemical dispersant to treat blended bitumen spills in aquatic systems. However, more importantly raised by response organizations and the Canadian Coast Guard (personal-communications) is that there is a need to develop models that include factors (e.g. oil type, seasonal effects, and natural weathering) that limit and establish a 'time window of opportunity' for dispersants to be effective in treating a variety of blended bitumen spills after the initial release. Before amendments may be considered to Canadian legislation to include alternative response options, science is needed to predict the effectiveness of alternative response options to treat spills of oil sands products weathered under various environmental conditions to more efficiently and promptly aid decision-making on the choice and limitations of such options.

2.3.3 Gaps in Modelling the Weathering of Oil to Advise Spill Response

Heavy or residual oils are expected to lose about 5% of their volume in the first few days following a spill (Fingas, 1999). The natural weathering processes transform the oil into substances with physical and chemical characteristics that vary from the original

source material. Therefore, the degree of oil weathering can greatly affect spill response and efforts to determine the risks of a spill.

Oil weathering encourages dissolution, which is a very important process from a toxicity point of view. Less than 1% of oil dissolves in water, but it is this fraction that impacts aquatic life (Saeed and Al-Mutairi, 1999). Oil contains water soluble monocyclic aromatics (Benzene, Toluene, Ethylbenzene, and Xylenes collectively known as BTEX) that are acutely toxic to marine organisms, because they are more bioavailable to aquatic life than the oil (Lee et al., 2015). A recent study revealed that BTEX associated with spills of condensate bitumen blends (dilbit) is a better predictor of lethality and pericardial edema in the early life stages of Zebra fish than polycyclic aromatic hydrocarbons (PAHs) or the water insoluble fraction (Philibert et al., 2016). However, the water soluble portion of the diluent (condensate in this case) is only expected to cause fish toxicity in confined coastal waters (Fingas, 2015), in areas where there is a slow rate of evaporation and dilution of spilled oil. For the assessment of environmental impacts in coastal waters, there is a need for information on the influence of seasonal changes on the weathering of bitumen blends including modelling its rate of water solubles from the diluent released during a spill.

In their crude form, bitumens from Athabasca and Peace River have a density of >1.0 g/mL and a viscosity of about 500,000 cSt, and Cold Lake and Lloydminster bitumens are typically less dense (range from 0.9700 to 1.016 g/mL) and viscous (averaging 275,000 cSt) (Fingas, 2015). When crude bitumen is blended with a diluent (lighter hydrocarbon fluid) the new products have an average density of 0.927 g/mL and viscosity <300 cSt (Fingas, 2015) (water has a viscosity of 1.0 cSt). At a temperature of

15 °C, fresh water has a density of 1.000 g/mL, seawater density ranges from 1.025 g/mL to 1.033 g/mL and brackish water is between the two; meaning that when spilled, any blended bitumen product will initially float in fresh, brackish and marine waters. If upon natural weathering all the diluent is lost and the crude bitumen approaches its original density, it could potentially sink in fresh water or brackish water of lower density, but remain floating in marine areas. Much of the concern over the density of weathered bitumen blends arose as a result of the sinking of some product after a spill in Lake Michigan (US Environmental Protection Agency, 2017). However, there is debate whether all of the diluent fraction of bitumen blends can be lost by natural weathering (Fingas 2015) or whether the residual bitumen will retain some of the diluent as a partially blended product, presenting unique properties (Winter and Haddad 2014). This is particularly important for predicting if weathered dilbit (condensate blended with crude bitumen), dilsynbit (condensate/synthetic crude blended with crude bitumen), and synbit (synthetic crude blended with crude bitumen) will float or sink in water. When oil sinks, response options to treat surface slicks are no longer applicable, and it is more challenging to track and monitor submerged oil. There is a requirement to predict under what specific environmental conditions oil sands products could potentially sink, to assess the risk and advise spill response operations.

Viscous oils spread slowly and affect the ability of pumps and skimmers to recover oil during a cleanup (ITOPF, 2012). Viscosity can reduce the effectiveness of chemical dispersants to remediate oil spills (National Research Council [NRC], 1989), and *in situ* burning efficiency declines with weathered heavy oils (Fingas, 2015). Spill behaviour models specific to blended bitumen do not exist and existing commercial

models for conventional oil do not allow parameter-specific modifications. A response to an oil spill event can be seriously hampered due to a limited database of chemical and physical properties of non-conventional oil (i.e. blended bitumen) products that can be coupled with high resolution data for ocean circulation models. Scientific expertise, information and tools to generate the foundational knowledge and prediction required for determining the fate, transport and effects of substances in the coastal and near-shore ocean environments is needed to reduce the risk of heavy oil spills, since their impacts on wildlife; ecosystems, coastal and Indigenous communities and local economies can be substantial.

Chapter 3: Composition of Bitumen Blends Relevant to Ecological Impacts and Spill Response

A version of this chapter was originally published in 2017 in the proceedings of the Arctic and Marine Oil Spill Technical Seminar, Environment and Climate Change Canada (ECCC), ON, pp. 463-475. All papers are peer-reviewed and are obtained from the author(s), by written request to Emergencies Science and Technology Section (ESTS) or by contacting ECCC Library Services.

3. Introduction

Alberta, Canada contains large deposits of extremely heavy crude oil or bitumen. The crude product is rock-like at room temperature and too viscous to transport to refineries or markets. In order to meet conventional oil pipeline specifications, the crude bitumen is diluted with a lighter hydrocarbon fluid to reduce its viscosity and improve flow. The most common specification for pipeline inputs is a maximum density of 0.940 g/cm³ and viscosity of 350 cSt at 15°C (Fingas, 2015). The maximum density specification equates to an American Petroleum Institute (API) gravity value of 18.9°. Based on API classifications, bitumen blends fall into the heavy oil category, since their API value is <22.3° (Speight, 2014).

Oil sands heavy crude oil, which is upgraded bitumen, blended with diluent or upgraded crude oil, represents approximately two million barrels per day (b/d) of the four million b/d of crude oil produced and transported in Canada (CAPP, 2017). In many of the new national pipeline projects being contemplated (e.g. Northern Gateway, Energy East and expansion of the Kinder Morgan Trans Mountain Pipelines), bitumen blends

would be transported by pipeline to coastal ports, where they would be transferred to tankers destined for international markets.

Five types of bitumen blends shipped throughout Canada were selected for this study. The possible fate and behaviour of surface spills of bitumen blends on water have been compared to those of lighter oils (e.g. light or medium crudes) in the early part of a spill, but changing to the behaviour of heavier fuel oil as weathering occurs (Enbridge Northern Gateway, 2011). For this reason, Heidrun (medium crude oil, lighter than bitumen blends) and Intermediate Fuel Oil 180 (IFO 180, a fuel oil heavier than bitumen blends that is diluted with a diesel distillate) were selected as comparative oil products. Unlike crude bitumen blended with condensate, the physical properties of IFO 180 are not expected to rapidly change in the early stages of a spill at sea (Colcumb et al., 2005). An assumption could be made that these bitumen blends have similar physical properties, so they behave similar to each other or to conventional oils in the same class when spilled in aquatic environments. However, the chemical composition of these blended bitumen products varies more widely than conventional crudes, because the characteristics of each blend depend on the source of bitumen, extraction method, type of diluent, and ratio of diluent to crude bitumen, which varies with seasonal temperature during shipment (Adams et al., 2013). The amount of diluent mixed with crude bitumen can vary from 30 to 50% depending on where it is produced and the time of year it is transported by pipeline (Lee et al., 2015). Here we provide a means to understand and compare the difference in chemical composition and physical properties among the various bitumen blends and some conventional oils, as they relate to environmental impacts and oil spill response.

3.1 Materials and Methods

3.1.1 Oil Products

The following oil products were tested:

- Access Western Blend-Winter (AWB-W, also dilbit), a crude bitumen blended with 30% condensate
- Cold Lake Blend-Summer (CLB-S, also dilbit), a crude bitumen blended with 20% condensate
- Cold Lake Blend-Winter (CLB-W, also dilbit) is crude bitumen blended with 30% condensate,
- Synthetic bitumen (Synbit), a bitumen diluted with 50% synthetic crude oil
- Western Canadian Select (WCS), a bitumen blended with a 50% mixture of condensate and synthetic oil and in some cases, referred to as a dilsynbit
- IFO 180, a residual fuel blended with about 6 to 7% heavy diesel petroleum distillate (Uhler et al., 2007)
- Heidrun, a conventional crude oil

3.1.2 Physical and Chemical Measurements of the Oil Products

All oil samples were analysed using an Anton Paar SVM 3000 Viscometer/Densimeter to obtain viscosity (ASTM D7042, 2014) and density (ASTM D5002, 2010) in triplicate measurements at 15, 25, 40 and 50 °C all at a precision of ± 2 C. SARAs (saturates, aromatics, resins and asphaltenes) were measured using Iatroscan thin layer chromatography/FID (Maki and Saski, 1997). All seven oils were prepared in dichloromethane at a concentration of $5.0 \text{ mg}\cdot\text{L}^{-1}$ to allow direct comparison. Detailed chemical composition was obtained by gas chromatography (GC, Agilent 7890B) coupled to a mass spectrometer (MS, Agilent 5977A) in selected ion monitoring (SIM) mode using electron ionization based on similar parameters outlined in method 8270D (Environmental Protection Agency, 2007). The MS mass transfer line was held at 280°C.

The extracts of oil were chromatographically separated on a Supelco column (SLB™-5ms, 30 m × 0.25 mm × 0.25 µm film thickness) using the following GC conditions: cool on-column injection with oven track mode (track 3°C higher than the oven temperature program) 85°C hold 2 min, ramp at 4°C/min to 280°C, hold 10 min. In addition, BTEX (benzene, toluene, ethylbenzene, and xylenes) were determined by an accredited lab, AGAT Laboratories (N.S., Canada) using a purge and trap coupled to GC-MS.

3.2 Results and Discussion

3.2.1 Chemical Composition of Oils

3.2.1.1 BTEX

The monocyclic aromatics, BTEX, make up *ca.* 1% (w/w) of the total crude oil (Njobuenwu et al., 2008). They are neutral chemicals and are non-polar; however, they are soluble in water due to hydrogen bonding interactions and have low K_{ow} values (<4). They are considered to be potentially more acutely toxic than the water insoluble aromatics (e.g. PAHs), because they are more bioavailable to aquatic life (Lee et al., 2015). For the tested oils, BTEX ranged from as low as 0.11% (w/w) for IFO 180 to as high as 1.96% (w/w) for AWB-W. BTEX values for the other test oils fell within this range (Table 3.1). In Table 3.1, significant figures applied to BTEX values are based on the method measurement and not to be confused with SARAs values, which are based on a different method. Since many bitumen blends contain BTEX, it could be used as a potential surrogate to predict the rate of diluent release from surface spills of the oils on water. It could also be used to assess the risk associated with a spill in the first few days following release. However, research is required to determine the rate of diluent released from bitumen blends in water.

Table 3.1: BTEX and SARAs in Crude Oils.

Crude Oil	BTEX	Saturates (S)	Aromatics (A)	Resins (R)	Asphaltenes (A)
	%w/w				
AWB-W	1.96	14	23	46	17
CLB-W	0.89	13	35	38	14
CLB-S	0.59	12	14	60	14
Synbit	0.56	20	10	57	13
WCS	0.87	20	10	52	18
IFO 180	0.11	27	42	27	4
Heidrun	1.21	38	40	20	2

3.2.1.2 SARAs

BTEX is not included as the part of the SARAs percentage by weight values, since these chemicals would be lost to evaporation during the application and drying procedure of the method. Two conventional oils, IFO 180 and Heidrun crude, were characterized and compared to the selected bitumen blends (Table 3.1). Crude oil is comprised of four main classes: saturates, aromatics, resins and asphaltenes (SARAs). The distribution of these classes will vary depending on oil type. Light and medium crude oils (API gravity 23.3 to >31°) contain a greater percentage of the less viscous and dense saturates and aromatics (Paliukaitė et al., 2014). Heidrun and IFO 180 have higher amounts of saturates and aromatics compared to the bitumen blends. The synbits (synbit and WCS) have almost twice as much saturates as the condensate bitumen blends (AWB-W, CLB-W and CLB-S), but fewer aromatics.

The remaining fractions are resins and asphaltenes and have polar substitutes. The distinction between the two is that asphaltenes are soluble in aromatics, whereas the resins are more so in pentanes. Asphaltenes exhibit complex chemistry (e.g. combining

cooperative binding by Brønsted acid-base interactions, hydrogen bonding, metal coordination complexes, and interactions between cycloalkyl and alkyl groups to form hydrophobic pockets, in addition to aromatic π - π stacking) that strongly affects the physical properties (e.g. density and viscosity) of crude oils (Gary et al., 2014; Badre et al., 2006). Resins are small compounds compared to asphaltenes and are largely responsible for the adhesion properties of the oil (Fingas 2011). Heavy crudes (API gravity value $<23.3^\circ$) contain a greater percentage of the more dense and viscous resins and asphaltenes (Paliukaitė et al., 2014). In this comparative study, the bitumen blends contain a greater percentage of resins and asphaltenes compared to Heidrun and IFO 180. These recalcitrant chemicals have large, tightly packed, molecular structures >500 amu (Groenzin and Mullins, 2000) that are not expected to cross tissue membranes of aquatic organisms to induce toxicity (Khan, 2007). They are more likely to become dense enough through weathering to sink in aquatic environments, or adhere to suspended sediments and sink.

3.2.2 GC-MS Characterization of Saturates and Aromatics

The low molecular weight classes of saturates and aromatics are of environmental concern, since they may contribute to toxicity in fish exposed to crude oil spilled in the marine environment (Lee et al., 2015). Saturates are the non-polar, low molecular weight fraction of crude oils comprised of cyclic (e.g. C_nH_{2n}), straight-chain and branched (e.g. C_nH_{2n+2}) hydrocarbons. Aromatics (e.g. C_nH_{2n-6}) are made up of one or more benzene rings, including their alkylated homologues, and are more polarized.

The GC-MS data (Tables 3.2 and 3.3) represents aromatics with 2 to 6 ring structures, their alkylated homologues, and straight chain saturates (C_{10} to C_{35}). The

AWB-W, CLB-W, and WCS have similar levels of saturates; however, CLB-S has less due to the fact that it contains 10% less diluent compared to the others. IFO 180 contains the greater amount of saturates (based on C₁₀ to C₃₅) per gram of oil compared to dilbit and dilsynbit. Although individual concentrations of saturates vary, Heidrun and synbit have comparable total amounts. For blended bitumen products, a greater percentage of the total saturate concentrations fall between C₁₀ (*n*-Decane) and C₂₀ (*n*-Icosane) even though different diluents are used to blend crude bitumen. These constituents are considered readily biodegradable when spilled in aquatic areas (Lee et al., 2015). Crude bitumen is a highly degraded, extra heavy, oil product made up mostly of branched and cyclic hydrocarbons that are resistant to biodegradation (National Academies, 2016). Therefore, the dominant presence of straight-chain hydrocarbons found in bitumen blends is derived from the diluent, and this is the portion of the product that is readily biodegradable during a spill.

For all oil types, alkylated PAHs are dominant compared to the parental ones. AWB-W has less alkylated PAHs compared to the other blends. The difference most likely derives from the origin of the crude bitumen. Many of the parental PAHs detected in the oils are on the United States Environmental Protection Agency (US EPA) priority pollutant list and these are considered to be more toxic and carcinogenic than saturates (Lee et al., 2015). The biodegradation rates decrease as the number of fused aromatic rings increase, so 4 to 6 ring PAHs and their alkylated homologues are more environmentally persistent than 2 to 3 ring PAHs. The chronic toxicity of oil is largely attributed to the 3 to 5 ring alkylated PAHs (Adams et al., 2014). Heterocyclic aromatics (i.e. Sulfur in the ring structure) and their alkyl homologues were detected in the oils and

are thought to be more toxic (Madison et al., 2015) and have slower biodegradation rates compared to other hydrocarbons (Oberoi and Philip, 2016). These chemicals require more attention in toxicity and biodegradation studies to best assess the risks associated with surface spills of blended bitumen products in aquatic areas.

Table 3.2: Saturates in Bitumen Blends, IFO 180 and Heidrun Crude. C-Carbon.

Compound	C#	CLB-W	AWB-W	IFO 180	WCS	CLB-S	Synbit	Heidrun
$\mu\text{g}\cdot\text{g}^{-1}$								
n-decane	C ₁₀	1,225	1,068	90	1,145	577	1,684	1,013
undecane	C ₁₁	1,003	897	120	968	416	1,559	1,154
dodecane	C ₁₂	664	643	160	768	371	1,340	1,200
tridecane	C ₁₃	594	573	220	616	295	1,133	1,083
tetradecane	C ₁₄	551	540	340	560	268	1,033	970
pentadecane	C ₁₅	468	496	440	453	217	855	903
hexadecane	C ₁₆	337	341	440	304	119	500	641
heptadecane	C ₁₇	374	323	490	320	124	485	673
pristane	pris	225	203	270	337	132	77	424
octadecane	C ₁₈	305	303	460	264	98	392	546
phytane	phy	274	183	180	344	146	141	412
nonadecane	C ₁₉	276	274	470	229	82	336	458
eicosane	C ₂₀	206	205	440	180	67	245	364
heneicosane	C ₂₁	195	196	530	179	67	218	335
docosane	C ₂₂	181	177	610	166	66	195	323
tricosane	C ₂₃	161	165	720	143	53	151	278
tetracosane	C ₂₄	151	148	710	119	50	127	252
pentacosane	C ₂₅	142	123	680	122	43	118	230
hexacosane	C ₂₆	129	114	560	111	52	103	221
heptacosane	C ₂₇	112	111	480	115	71	109	217
octacosane	C ₂₈	77	86	390	92	58	96	183
n-nonacosane	C ₂₉	56	76	270	71	35	59	154
tricontane	C ₃₀	50	53	120	60	56	66	122
n-heneicontane	C ₃₁	43	44	110	38	23	33	96
dotriacontane	C ₃₂	31	33	110	31	22	31	68
tritriacontane	C ₃₃	25	28	70	27	19	21	61
tetratriacontane	C ₃₄	13	20	60	20	11	14	41
n-pentatriacontane	C ₃₅	21	24	50	11	19	12	26
Σ Alkanes		7,889	7,447	9,580	7,793	3,557	11,133	12,448

Table 3.3: Parent and Alkylated PAHs in Bitumen Blends, IFO 180 and Heidrun Crude; C1-C4 are the Alkyl PAHs (Methyl, Dimethyl, Trimethyl and Tetra).

Compound	CLB-W	AWB-W	IFO 180	WCS	CLB-S	Synbit	Heidrun
	$\mu\text{g}\cdot\text{g}^{-1}$						
Naphthalene	44	33	90	60	28	73	746
C1-C4 Naphthalene	1,595	413	2290	1,584	1,291	561	7,517
Acenaphthene	11	10	30	18	18	12	28
Acenaphthylene	8	8	80	8	9	9	11
Fluorene	19	19	30	29	21	7	140
C1-C4 Fluorene	495	176	480	511	470	421	866
Dibenzothiophene	37	34	10	35	36	31	65
C1-C4 dibenzothiophene	1,104	396	220	898	1,102	630	751
Phenanthrene	73	15	120	65	66	35	222
Anthracene	7	7	20	7	7	7	21
C1-C4 Phenanthrene	880	485	1750	898	933	704	1,605
Fluoranthene	9	9	10	10	10	7	20
Pyrene	7	7	60	14	11	38	28
C1-C4 Pyrene	330	306	1400	346	339	386	424
Naphthobenzothiophene	21	8	20	18	22	14	19
C1-C4 Naphthobenzothiophene	612	619	490	404	412	340	265
Benzo[a]Anthracene	6	6	60	9	10	9	12
Chrysene	16	12	90	18	17	15	30
C1-C4 Chrysene	212	216	1540	263	244	307	289
Benzo[b]Fluoranthene	7	7	10	9	8	9	13
Benzo[k]Fluoranthene	3	2	10	5	5	5	6
Benzo[e]Pyrene	7	7	30	8	7	9	14
Benzo[a]Pyrene	7	7	20	9	7	8	8
Perylene	7	11	20	14	13	16	6
Indeno[1,2,3-cd]Pyrene	4	5	10	6	6	6	6
Dibenz[a,h]Anthracene	4	4	10	5	5	5	5
Benzo[ghi]Perylene	6	6	10	6	6	10	6
Σ PAH	302	217	710	352	312	326	1,405
Σ AlkylPAH	5,228	2,611	8,170	4,904	4,791	3,349	11,717

3.2.3 Physical Properties of Oils

API gravity is calculated as

$$API\ gravity = \frac{141.5}{SG_{oil}} - 131.5$$

where specific gravity of the oil, $SG_{oil} = \rho_{oil}/\rho_{water}$, and ρ is density. API <10° is extra heavy, 10-22° is heavy, 22-31° is medium, and >31° is light. Based on calculated API gravity values, the blended bitumens and IFO 180 are classed as heavy oils and Heidrun is a medium crude oil (Table 3.4). The blended bitumen products have densities and viscosities that have been engineered to meet pipeline specifications, so are all quite similar except CLB-S, which contains 10% less diluent to compensate for temperate conditions during summer. IFO 180 is more dense and viscous (hence the lower API gravity) than the blended bitumen products, whereas Heidrun is less so.

Table 3.4: Physical Properties of the Oil Products.

Oil	Diluent	Density g/cm ³	Viscosity cSt	API°	Class
AWB-W	Condensate	0.9189	244	22.3	Heavy
CLB-W	Condensate	0.9240	237	21.5	Heavy
CLB-S	Condensate	0.9375	575	19.3	Heavy
Synbit	Synthetic crude	0.9304	205	20.4	Heavy
WCS	Condensate/Synthetic crude	0.9214	211	21.9	Heavy
IFO-180	7% Distillate	0.9685	2340	14.5	Heavy
Heidrun	none	0.9132	68.9	23.3	Medium

The kinematic viscosities of the tested oils decreased exponentially as a function of temperature increase (Figure 3.1). All the blended bitumen products produced similar curves, except CLB-S, likely because it contains 10% less diluent than CLB-W. Heidrun

crude and IFO 180 are respectively the least and most viscous. Oil density declined linearly as temperature increased (Figure 3.2). At 15°C, all oil types had a measured density less than that of fresh water (e.g. 1.000 g/cm³), so would initially float after a spill at sea. IFO 180 and Heidrun displayed the highest and lowest densities respectively. Although not considered here, it is known that temperature also affects the pour point (temperature below which oil will not pour and begins to solidify or gel) and flash point (temperature at which the oil produces vapors sufficient to ignite into flames) of crude oils (Lee et al., 2015; National Academy of Sciences, 2016). However, these physical properties, in addition to seasonal temperatures, would be affected by the natural weathering of oil in aquatic environments.

How blended bitumen products behave when spilled is largely dependent on the rate of diluent separation from the blend. If the rate is high, the asphaltenes and resins have a greater effect on the physical properties (e.g. density and viscosity) of the oil in the early stages (hours to days) of a spill. Through natural weathering of the oil, a density exceeding 1.000 g/cm³ can result in sinking of the oil in fresh water, making spill response more challenging. In addition, if the oil viscosity exceeds 10,000 cSt, it limits the effectiveness of chemical dispersants applied to the slick (National Research Council, 1989; Genivar, 2013). Oils with a viscosity >100,000 cSt, which is significantly lower than crude bitumen, can impede oil recovery operations when booms and skimmers are deployed (ITOPF, 2012). *In situ* burning is another response option that has been successful for removing oil, depending on oil type, from the water surface, and can be quite effective (e.g. 90 to 99%) in the first 96 hours following an oil spill (National Academies, 2016). The oil slick must have a thickness > 2 mm in order for it to ignite,

and efficiency of burning decreases for heavy oils and weathered products (Fingas, 2015). A high asphaltene content (> 6 %) can cause ignition delay and poor combustion, which would limit *in situ* burning as a spill response option for some heavy oils (Speight, 2004), including bitumen blends. Controlled burning could result in 50 to 75% removal of heavy oil, such as diluted bitumen, provided the weathering of the oil is limited to within a day (National Academies, 2016).

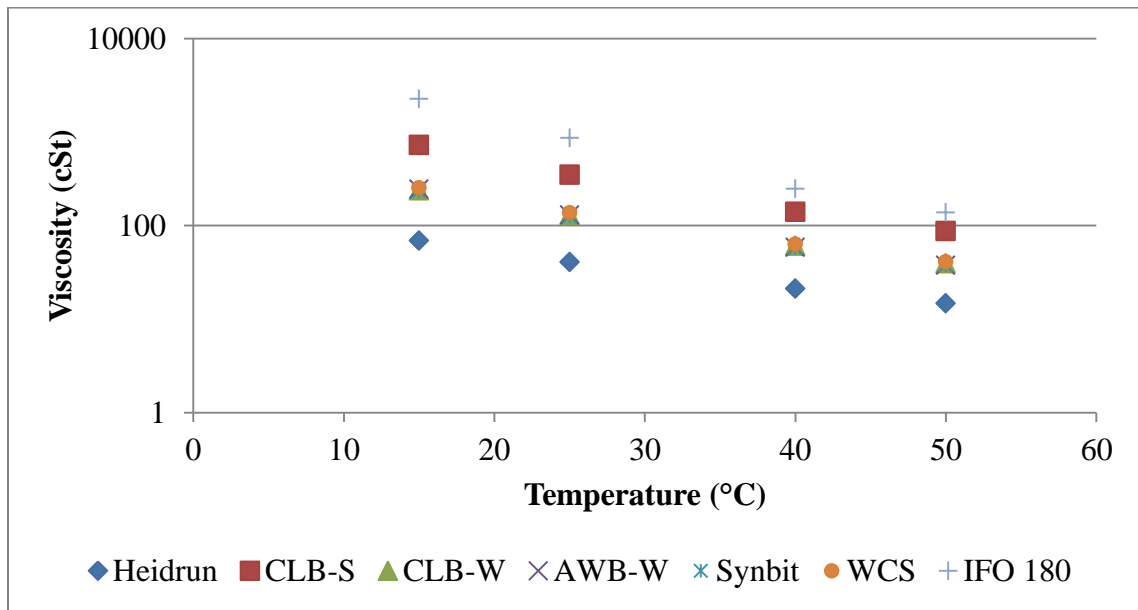


Figure 3.1: Kinematic Viscosities of Seven Oil Types as a Function of Temperature.

Previous studies by King et al. (2014) demonstrated that condensate-bitumen blends (e.g. AWB-W and CLB-W) can reach a density greater than or very close to that of fresh water when naturally weathered on brackish water (directly from the Bedford Basin, Halifax Nova Scotia) for two weeks. Even though the products initially had similar physical properties, their chemical composition appeared to affect how they weathered on the surface of water. This was a strong indication that no two blended bitumen products behave the same when spilled on water, which makes assessing the risk and response efforts more challenging. Spill responders face challenges when making

decisions and predicting time windows for which response technologies will be effective at recovering or remediating surface spills of bitumen blends (Lee et al., 2015). Since blended bitumen products can vary in chemical composition, which can influence the oils' physical properties post spill, empirical evaporation models are required to predict changes in the physical properties of products that are relevant to oil spill response. In addition, there is a requirement for sound science to support regulations on the use of oil spill countermeasures (e.g. dispersants) and to strengthen the connection that science plays in spill response decision-making.

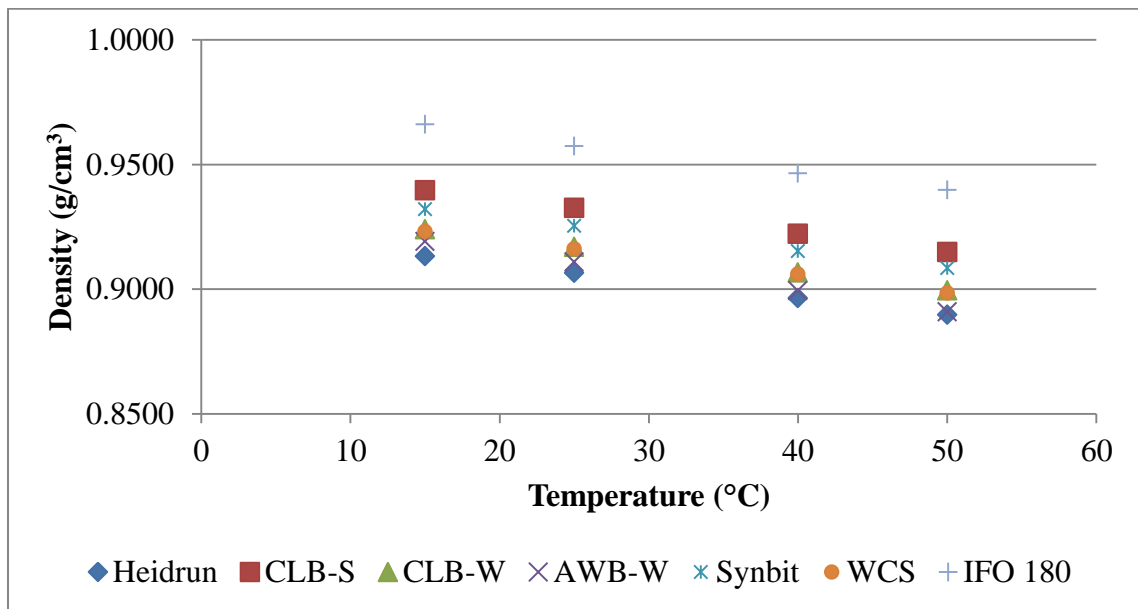


Figure 3.2: Densities of Seven Oil Types as a Function of Temperature (±2 °C).

3.3 Conclusions

Crude oils and bitumen blends contain mixtures of low molecular weight, water soluble, to very large, insoluble chemicals. They are comprised of four major chemical classes that include saturates, aromatics, resins and asphaltenes, and the percentage by weight of these can vary depending on oil type. The bitumen blends contain a greater percentage of resins and asphaltenes compared to Heidrun and IFO 180. These

recalcitrant chemicals have large, tightly packed molecular structures >500 atomic mass units that are not expected to induce toxicity, because they are unlikely to cross tissue membranes of aquatic organisms. As the bitumen blends weather at sea, the presence of these persistent chemicals could greatly affect the physical properties that are relevant to spill response and increase the propensity of the products to sink in aquatic environments.

BTEX was present in all oil types, ranging from 0.11 to 1.96 % (w/w). These compounds can induce acute toxicity in marine organisms, and can be easily measured in environmental samples. Their presence in bitumen blends is derived from the diluent added to the crude bitumen. BTEX detected in water could be used to assess the risks and predict the rate of water solubles chemicals released from the diluent during surface spills of bitumen blends. However, simulations to evaluate BTEX release to the water column post spill are required.

The saturate profiles detected in bitumen blends differed from the conventional oils. The straight-chain hydrocarbons in the range of C₁₀ to C₂₀ were dominant in bitumen blends, but were likely derived from the diluent and not the crude bitumen. Synbit contained total saturate amounts similar to Heidrun crude oil. CLB-S contains less diluent compared to CLB-W; thus, it contained the least total saturates (C₁₀ to C₃₅ straight-chain) of all test oils. SARAs results showed a high saturate percentage for IFO 180, but this method of measurement does not distinguish straight-chain from cyclic and branched saturates. The straight-chain saturates detected in oil products would be readily susceptible to microbial degradation when spilled at sea.

US EPA priority parental PAHs were detected in all test oils. Their alkylated homologues were the most prevalent chemicals associated with the products. These were

lower in AWB-W compared to the other bitumen blends, which is most likely due to the bitumen's origin. Also, they were lower compared to the conventional oil products. These chemicals are of environmental importance, since they are more toxic and carcinogenic than saturates. In addition, heterocyclic aromatics and their alkylated homologues were detected and are thought to have lower biodegradation rates and greater toxicity compared to PAHs.

The physical properties (density and viscosity) of bitumen blends were similar, which is understandable, since they are engineered to meet pipeline specifications. The exception was CLB-S, which contains less diluent than the other bitumen blends. During an oil spill, evaporative loss removes the lighter components of the diluent, and consequently increases the density and viscosity of the residual oil. Models are required to predict changes in these physical properties to determine when bitumen blends might sink, to aid decision-making in the selection of the most appropriate oil spill countermeasures and to support regulations on their use in aquatic environments.

Chapter 4: Seasonal Effect Data on Monocyclic Aromatics Dissolution from Surface Spills of Bitumen Blends: Implications for Environmental Risk Assessments

The details of the flume tank designed for this thesis and introduced in this chapter were published in 2017 in the Royal Society of Chemistry (RSC) Journal of Environmental Science: Processes and Impacts, 19(1): 928-938. The RSC grants permission to use the whole article in a thesis (<http://www.rsc.org/journals-books-databases/journal-authors-reviewers/licences-copyright-permissions/#deposition-sharing>).

4. Introduction

Heavy bitumen products from the Canadian oil sands in Alberta represent approximately two million barrels per day (b/d) of the 4 million b/d of crude oil produced and transported in Canada (CAPP, 2017). Within Canada, there is a plan to transport crude bitumen to coastal areas, where it would be eventually shipped by tankers to global markets. Crude bitumen is a semi-liquid product that is too viscous for transport via pipeline. A number of methods can be used to resolve this problem. One is a chemical treatment process where large molecules that can't be distilled are "cracked" into lighter molecules. The process involves a hydrocracker (e.g. fluid coker) at 400 °C (NRC, 2015) that breaks up long chain bitumen molecules into short chain ones through a thermal conversion process known as 'coking'. These short chain molecules can include heavy gas oil, light gas oil, and naphtha (a flammable liquid hydrocarbon mixture of straight chain saturates and cyclic hydrocarbons molecules of 5 to 6 carbons atoms). The mixture is then processed through a hydro-treater operated at high temperature that uses a catalytic reactor to remove impurities (e.g. nitrogen and sulfur), replacing them with

hydrogen. The final product consists of naphtha mixed with light and heavy gas oils in a single blend known as synthetic crude oil (NRC, 2015), which can then be readily shipped to oil refineries to be further upgraded. An alternative and less expensive method is to dilute or blend the crude bitumen with a lighter fluid (e.g. condensate, synthetic crude, combination of both, etc.) to the viscosity range required for transport by rail, pipelines and tankers. With global demands for oil increasing, bitumen production and transport is likely to increase over the next decade; thus, increasing the potential risk for accidental spills. Within Canada, the proposed Kinder Morgan Trans Mountain Pipeline (TMPL) expansion from Alberta to Burnaby, BC, if approved, would create a twinned pipeline that would approximately triple the nominal capacity of the system from 300,000 barrels per day, to 890,000 barrels per day (Burnaby Public Library, 2017; Natural Resources Canada, 2017). It has been estimated that 20,000 tankers move crude oil and refined products through Canadian waters each year, with the majority (85%) on the Atlantic coast (Anderson and Spears, 2013). The proposed Energy East Pipeline would involve 281 new tankers carrying an estimated 1.1 million barrels per day of heavy oil products off the Atlantic coast (National Resource Defence Council, 2016; Axelrod et al., 2016; CAPP, 2017). Currently, this project is on hold, but may be revisited as oil prices rise. While the transport of various bitumen blend products through Canadian coastal areas is below previous anticipated levels due to the regulatory/environmental issues and the current economic value of bitumen products abroad; the rates of activity are nevertheless expected to increase with future changes in global market demand.

Lee et al., (2015) identified knowledge gaps related to the potential toxicity of the water soluble fraction released from diluent during spills of bitumen blends to aquatic

species. The monocyclic aromatics (BTEX - Benzene, Toluene, Ethyl Benzene and Xylenes) make up ~1% (w/w) of conventional crude oils (Njobuenwu et al., 2008). Like conventional crude oil, nonconventional crudes such as bitumen blends contain 0.6 to 2 % w/w BTEX, which is in the diluent blended with bitumen (King et al., 2017a). Once released into the environment, BTEX is volatile and evaporates quickly into the atmosphere. These chemicals are nonpolar, but polarizable and partially soluble (e.g. low K_{ow} values <4) in water due to hydrogen bonding with the π -electron cloud of the benzene ring and the hydrogen atoms of water (Feng et al., 2016). They are potentially considered to be more acutely toxic than the water insoluble polycyclic aromatic hydrocarbons (PAHs) because they are more bioavailable to aquatic life (Lee et al., 2015). Negri et al. (2016) identified BTEX or the monocyclic aromatics as the major chemicals released from condensate to the water column when exposing Coral Reef larva to the water accommodated fractions. A recent study revealed that BTEX, associated with spills of condensate bitumen blends, is a better predictor of lethality and pericardial edema in the early life stages of Zebra fish, a model species, than PAHs (Philibert et al., 2016).

In an open ocean environment, exposure to the BTEX released from an oil spill would be minimal; lasting only 24 to 48 hours as evaporation and dilution over a large area is expected to be rapid. However, acute toxicity can be widespread when there is a continuous source of oil released rapidly (i.e. subsurface blowout) and where conditions are unfavorable for rapid dilution, evaporation and biodegradation (Hodson et al., 2011), where the water soluble fraction could last longer than 48 hours. These conditions are most likely to occur when oil is spilled near coastal areas.

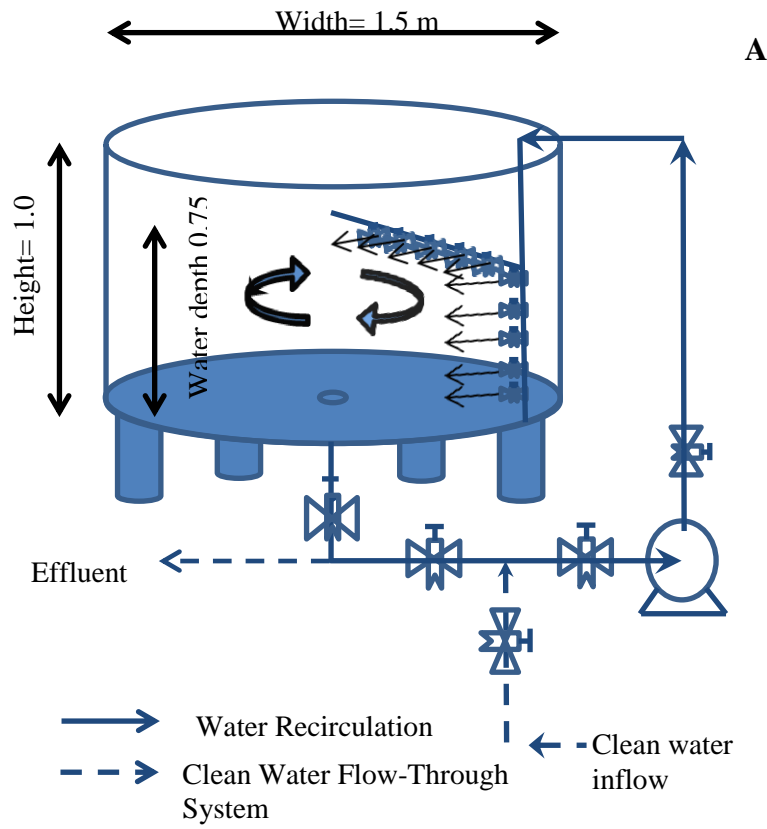
When oil is spilled in the aquatic environment, petroleum hydrocarbons undergo many diverse processes (e.g. evaporation, dissolution, photo oxidation, sedimentation, biodegradation, and uptake by biota) which collectively determine its fate and impacts on the aquatic environment. Of these, dissolution is a very important process, from an ecological impact point of view, where the water soluble components (monocyclics or BTEX) released from an oil slick is available to aquatic species and dissolution also plays a major role in dilution of those same chemicals. Variation in environmental conditions (such as wind speeds, air and water temperature, rainfall amounts, and sun light) with season and how they affect the monocyclic aromatics dissolution process; especially for diluted bitumens, where the fate of such hydrocarbons is not yet understood (Lee et al., 2015). Since BTEX is of ecological significance and present in the diluent (e.g. condensate and synthetic crude) used to blend bitumen, it was selected for this study. For comparison, a conventional oil (e.g. Heidrun) was weathered under similar test conditions. The oil was selected, since its BTEX composition (1.2 % w/w) was within the range of what was detected in the bitumen blends (Chapter 3 or King et al., 2017a). In this study, the aim is to address the identified gaps in scientific knowledge by: 1) conducting research to determine the extent and kinetics of the dissolution of monocyclics in water from simulated spills of oil; 2) the effect of season (spring and summer) and the associated climatic factors (such as wind speed, air and water temperature, rainfall amounts, and light intensity) that could influence the dissolution of monocyclics released from the diluent of three diluted bitumen based unconventional (which cannot be produced using conventional methods) crude oil products; Access Western Blend, Synthetic Bitumen, Western Canadian Select, and a comparative

conventional crude, Heidrun; and 3) using the information generated from the research coupled with literature findings on species sensitivity data derived from toxicity studies with dissolved components of oil to provide implications for risk assessments.

4.1 Materials and Methods

4.1.1 Circular Flume Tank

The circular flume tank is located outdoors at the Bedford Institute of Oceanography, Dartmouth, Nova Scotia, Canada. Fabricated from fiberglass; the tank measures 1.0 meter (m) in height x 1.5 m in diameter and 4.7 m in circumference (Figure 4.1, see King et al., 2017b for further details). The design of the flume system allows oils to weather under exposure to mild sea-like conditions including current flow, rain, air and water temperature variations, wind speeds, and sun light. The tank was filled with water (from the Bedford Basin was filtered sock filters (25 μm inside two 5 μm filters [Atlantic Purification Ltd., NS, Canada] to remove suspended particles) to a depth of 0.76 m (~30 inches) which equates to a water volume of 1.31 m^3 (1310 litres). The inlet of the circulating pump ($\frac{3}{4}$ HP ReeFlo1 phase, 1725 RPM, 115 VAC) was connected to a manifold (a vertical and horizontal injection system constructed of 0.038 m (1½ inch) polyvinylchloride (PVC) pipe with evenly spaced 0.013 m (½ inch) spigots (with ball valves to control water flow) submerged below the water surface. Water was removed by the $\frac{3}{4}$ HP pump through an outlet (2 inch or 0.051 m PVC pipe), located at the bottom center of the tank. The test stream was set up to recirculate water, producing uniform rotational water current velocities radially in a clock-wise direction, and reducing flow short-circuiting along the tank bottom. Water currents on the surface averaged 20.7 ± 0.4 cm/s (0.4 knots).



A



B

Figure 3.1: A) Schematic of the Circular Flume Tank (not to scale) B) Photo of tank.

4.1.2 Oil Products

The following oil products were tested: Access Western Blend (AWB, dilbit) stock, which is bitumen blended with 30 % condensate; Western Canadian Select (WCS, dilsynbit) which is bitumen blended with 50% mixture of condensate and synthetic crude oil blended with crude bitumen; Synthetic bitumen (synbit) which is 50% synthetic crude mixed with crude bitumen; and Heidrun is a conventional crude oil for comparative purposes. The physical properties and BTEX composition of the oils are found in Table 34.1 (Supporting Materials) and King et al. (2017a). As expected, the bitumen blends have similar physical properties (Table 3.4) since they are engineered to meet pipeline specifications and are classed as heavy oils based on American Petroleum Institute (API) gravity values. A representative for conventional crudes, Heidrun (medium crude oil) is lighter and less viscous than the bitumen blends.

Table 4S.2 (Supporting Materials) shows the concentration of the BTEX compounds in various oils along with the %w/w of saturates, aromatics, resins, and asphaltenes. The amount of BTEX in Heidrun (conventional crude) falls within the range of amounts in the various bitumen blends. In summary, AWB and Heidrun crude oils showed the highest concentration of BTEX, and in all oils toluene followed by xylene made up the major proportion of the \sum BTEX concentration.

4.1.3 Floating Microcosm

A 0.019 m ($\frac{3}{4}$ inch) thick sheet of Polyoxymethylene (chemical resistant) was cut into a circular disk with a diameter of 0.51 m (20 inches) to serve as a floating microcosm (Figure 4.2). The majority of the oil slick is in the center of the individual disks and oil doesn't stick to them. The polyoxymethylene disk and inserts are white in color. They do

not absorb sunlight and thus their temperature does not increase noticeably relative to that of the water it floats in. A total of 21 holes (of which 20 are used) with a diameter of 0.062 m (2 ½ inches) were cut into the sheet, and each hole served as a containment ring for oil. A piece of StyrofoamTM cut with similar dimensions, including the holes for oil containment, was fixed to the bottom of the floating microcosm to enable floatation and direct contact with the water surface. In addition, cylindrical inserts (0.062 m i.d. and 0.064 m length) were placed into each hole to allow easy application and retrieval of oil during the experiments.

The floating microcosm was placed into the circular flume tank under static (e.g. no flow) conditions. Then, sufficient amount (260 mL) oil was placed into numbered rings to achieve the desired measurable concentration of the water solubles (e.g., BTEX and diluents) to be released in the water column as the oil weathered over time. Once the oils were added to the rings the circulating pump was turned on, which generated the planned water current (20.7 ± 0.4 cm/s). When an oil spill occurs it can take up to 48 hours, depending on environmental conditions, to respond to it. A time window of 192 hours (8 days) was selected for this study to provide enough information on the changes in the BTEX concentrations released to the water column as the oils weather to assess the risk to aquatic life.

4.1.4 Flume Tank Studies: Sample Collection

Samples were collected at the following time points (hours): 0, 3, 8, 24, 48, 72, 96, 120, 144, 168, and 192. Time zero represents a sample of the unweathered oil. Water salinity and temperature were measured prior to each sampling event. Triplicate water samples, for BTEX analysis, were collected at a depth of 0.65 m from a sampling tube

placed in the water column that siphoned water to the surface and directly into a purge and trap vial.

4.1.5 Analyses of Oil and Water Samples Procured During Flume Tank Studies

The triplicate water samples were analysed by purge ant trap coupled to a gas chromatograph with mass spectrometry detection (EPA method 8260C) to measure BTEX concentrations. The BTEX analyses of the oils were completed by an accredited laboratory (AGAT Laboratories, Dartmouth NS, Canada).

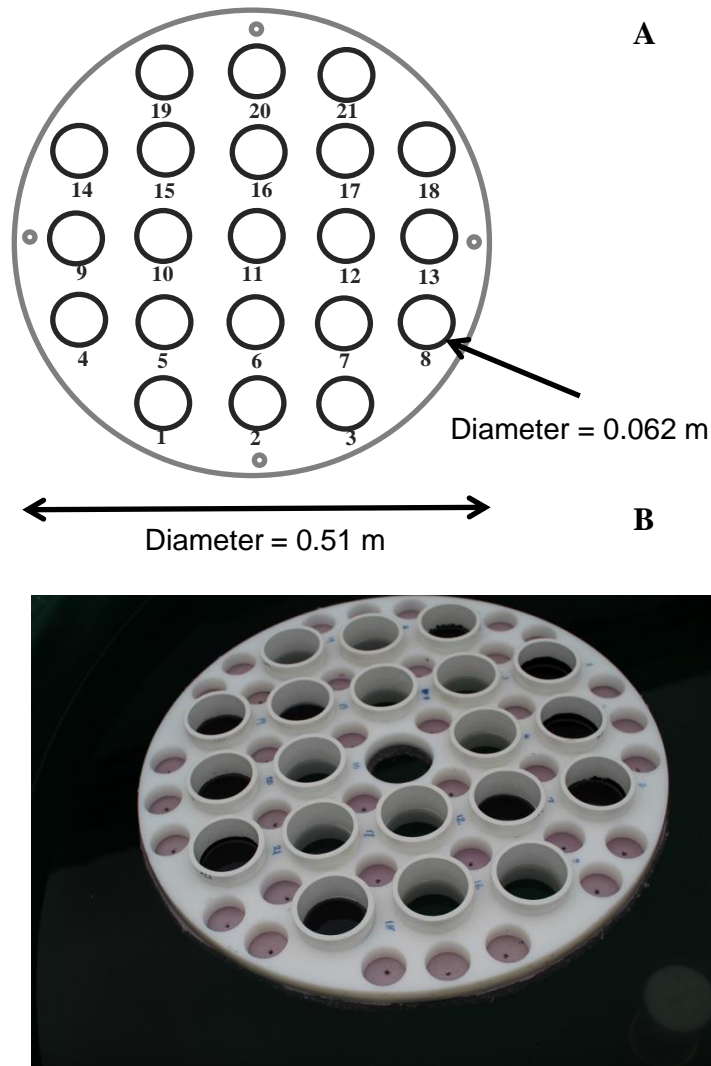


Figure 4.2: Floating Microcosm: A) schematic (not to scale) and B) photo.

4.1.6 Measurements Taken During Natural Weathering of Oils in a Flume Tank

The air temperature, rainfall amounts and wind speeds were recorded by a weather station located near the tank. The salinity and water temperature measurements were monitored using a hand held meter (YSI model #30-1-FT; Yellow Springs, USA) at each time point. Light intensity (sun light, night time and cloud cover) and water temperature was measured hourly for the length of the experiments using a HOBO Pendant Data Logger made by ITM Instruments Inc.

4.2 Results and Discussion

4.2.1 Time-Series Averaged BTEX Concentrations in the Water Column and Seasonal Climatic Factors Influence on the Weathering of Oil

Time-series averaged individual chemical amounts that make up the averaged Σ BTEX concentrations detected in the water column, at a depth of 0.65 m, for the oils are shown in Supporting Materials (Tables 4S.7 to 4S.10 and Figure 4S.1). Benzene and toluene made up a major portion of the BTEX detected in the water column. The lowest BTEX concentrations in water were detected for synbit and Heidrun crude oil. Natural weathering of AWB (dilbit) and WCS (dilsynbit) showed the highest concentrations of BTEX released in water. BTEX concentrations in water released from all oils were persistent for a longer period in spring than summer.

Figures 4.3 and 4.4 illustrate that the averaged Σ BTEX concentration in the water column increased rapidly to a maximum value, and then decreased at approximately 1/10 of the rise rate, indicating an exponential decline. The dissolution of diluent in water from oil differs from that of a pure compound due to the competition of other chemicals present in the oil reaching the oil-water interface and subsequently the water column (Lee

et al., 2015). The more polar compounds in the bitumen blends, such as the resins and asphaltenes, tend to migrate to the oil-water interface. However, they also tend to remain at the interface due to their low solubility in water. Therefore, these compounds are likely to hinder the dissolution of the remaining oil components in the water (Lee et al., 2015). Gary et al. (2014) reported that there are many complex intermolecular forces of attraction in the structure of asphaltenes, including where toluene is physically trapped in the structure of these complex chemicals and this could affect its rate of release from oil. After the maximum concentration of BTEX was reached, it is possible that evaporation from water to the atmosphere (Fingas et al., 2013) and/or photo-chemical weathering (Ward et al., 2018a&b) were the dominate physical and chemical processes.

The rate of monocyclics (BTEX) released was more rapid and peaked at shorter points in time for oils weathered under summer-time compared to cooler spring-time conditions. For the spring-time experiments, Access Western Blend (dilbit) and Western Canadian Select (dilsynbit) both contain condensate (as the diluent) in different amounts and displayed the highest averaged BTEX concentrations and for a longer period (up to 192 hours) than the other oils. In summer-time, the weathering of AWB displayed higher BTEX concentrations in water, than the other oils, which were detectable up to 144 hours upon returning to background levels. Nigeri et al. (2016) reported that during a spill of condensate on water, the monocyclics are dominant chemicals detected in the water column. So, for surface spills of bitumen blended with condensate as the diluent, one would expect the monocyclics to be dominant chemicals in the water column as well. BTEX quantities for the other oils declined rapidly within 48 hours. BTEX released in water was very low for both seasons during the weathering of Heidrun crude,. It may be

that the monocyclic aromatics are naturally part of the Heidrun crude oil and not an additive like the nonconventional bitumen blends. Another thought is that the chemical composition of Heidrun is quite different compared to the bitumen products (King et al., 2017a), where in proportion it contains less asphaltenes that could affect the rate of release of the monocyclics in water (Gary et al., 2014; Lee et al., 2015). This may explain the lower BTEX values in water during the weathering of Heidrun.

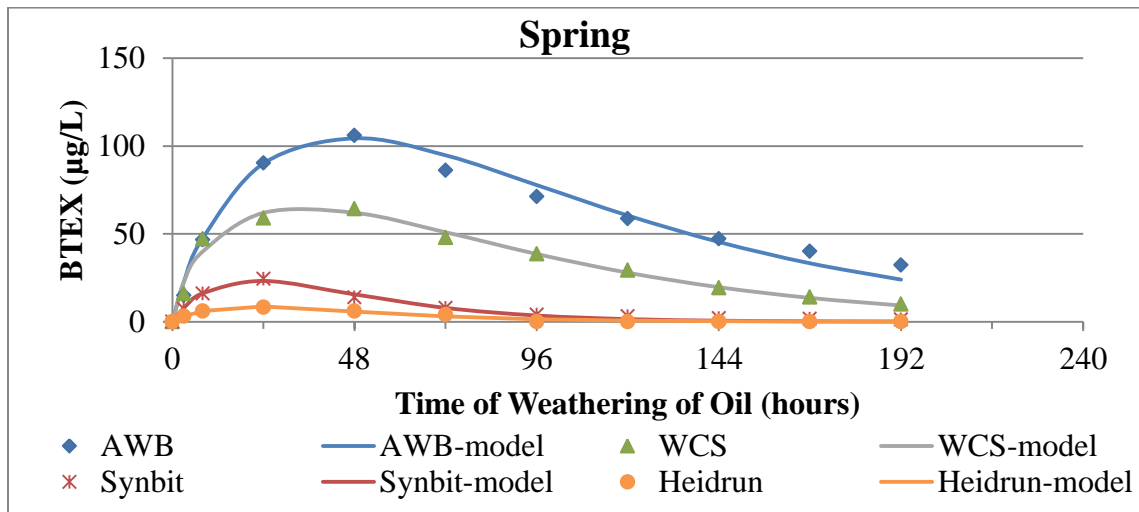


Figure 4.3: The Sum of BTEX Concentrations in the Water Column as a Function of Time of Weathering of Oil in Spring. The Data were Fitted to a Model (equation 4.5).

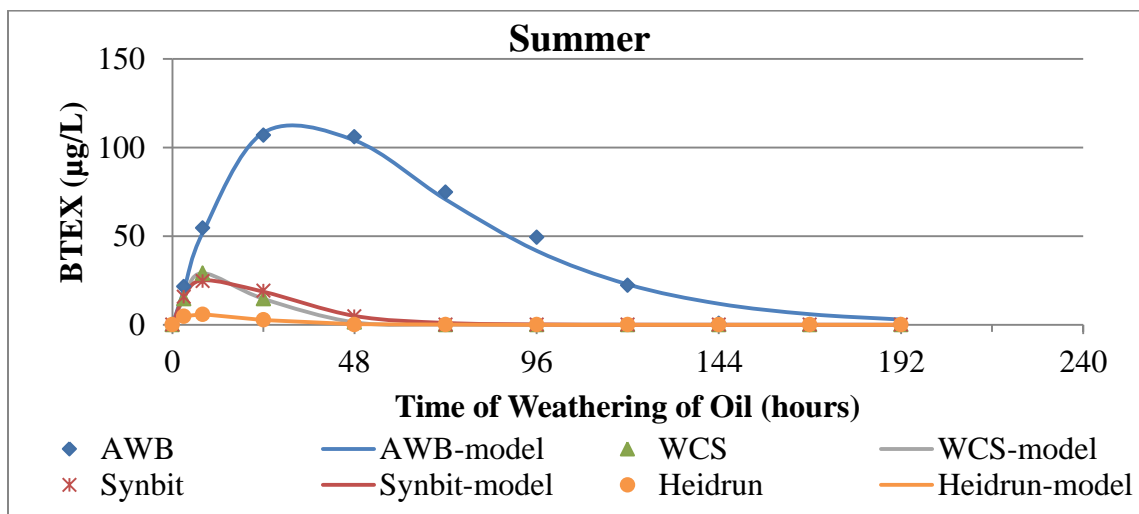


Figure 4.4: The Sum of BTEX Concentrations in the Water Column as a Function of the Weathering Time of Oil in Summer. The Data were Fitted to a Model (eq. 4.5).

4.2.2 Estimating Monocyclics Dissolution and Decay from Surface Spills of Oil

The solubility limit of BTEX in water varies for the individual oil components ranging from 130 mg/L for *p*-xylene (least soluble) to 1700 mg/L for benzene (most soluble) (Clark and McLeod, 1977). However, the ability of water to dissolve these volatiles decreases with the addition of electrolytes (potassium, sodium and chloride) that are present in saltwater environments. The movement of oil within each ring in the microcosm ensured uniform mixing of the oil components within the water column. As the area is constant with time, the release rate was constant with time until all the mass of the oil components was released from the oil. If the mass flow rate of release of a component is constant, the mass released into the water column increases linearly with time. Thus, the concentration in the water column for a given volume would increase linearly with time. Therefore, one could write:

$$[C]_{dissolution} = a \cdot t \quad (4.1)$$

where $C_{dissolution}$ is concentration as mass by volume, 'a' is the slope and 't' is time.

The evaporation of the dissolved oil component into the atmosphere depends on the concentration of the dissolved component into the water column via:

$$\frac{d[C]}{dt} = -b * [C] \quad (4.2)$$

which has the analytical solution:

$$[C]_t = [C]_0 \exp(-bt) \quad (4.3)$$

where C_0 is the initial dissolved oil concentration in the water column (at the beginning of the evaporation phase). Eq. 4.3 is the first order decay model, where 'b' is the slope and 't' is time. However, considering that dissolution in the experiments occurred quickly (within 8 to 48 hours, depending on season) and oil weathering occurred over 192 hours, it is reasonable to approximate $[C]_0$ by $[C]_{dissolution}$, and thus one obtains:

$$[C]_t = a. t \exp(-bt) \quad (4.4)$$

Fitting Eq. 3.4 to the data was satisfactory, but the fit was improved when the expression was allowed for a power law behavior, given by:

$$[C]_t = a. t^m \exp(-bt) \quad (4.5)$$

Fitting Eq. 4.5 to the data gave an 'm' value that varied from 0.69 to 1.4. The close proximity of 'm' equal to 1.0 (i.e. a linear increase with time) suggests that our model is reasonable. That is, the release of monocyclics into the water column is quasilinear with time, and it is followed by evaporation into the atmosphere. The deviation from the theoretical value of 1.0 could be due to variation with time of the oil water soluble concentrations within the oil, approximating $[C]_o$, an instantaneous value by an amount that varies over time (8 to 48 hours), and the speed of migration of the water solubles from the oil to the water column and subsequently to the atmosphere. Finally, the vapor pressure of the water solubles (also volatile) released from oil could not reach equilibrium, because the air space above the tank was well-ventilated to allow vapors to disperse into the atmosphere.

The model fit was generally significant, as one notes visually through the absence of any systematic bias (undershooting or overshooting), and the large coefficient of determination, R^2 ranging from 0.96 to 0.99. The developed functions in Table 4.1 can be used to show changes in the monocyclic aromatics released from blended bitumen products spilled under similar conditions in the aquatic environment. Also, the results can provide important information to those conducting environmental risk assessments on aquatic organisms exposed to the water soluble compounds released during a spill.

Table 4.1: Equations Fitted to BTEX Experimental Data for Various Oils Weathered Under Natural at Sea Conditions.

Oil (ST, T, Wspd)	Equation	a	b	m	R ²
AWB (4.0 mm, 5.5 °C, 16.4 km/hr)	$c(t) = a * (t^m) * \exp(-bt)$	9.40	0.0180	0.850	0.960
AWB (4.0 mm, 14 °C, 9.0 km/hr)	$c(t) = a * (t^m) * \exp(-bt)$	4.28	0.0364	1.200	0.983
WCS(4.0 mm, 6.3 °C, 24.7 km/hr)	$c(t) = a * (t^m) * \exp(-bt)$	11.2	0.0198	0.687	0.965
WCS (4.0 mm, 15 °C, 11.4 km/hr)	$c(t) = a * (t^m) * \exp(-bt)$	3.04	0.1390	1.400	0.999
Synbit (4.0 mm, 6.3 °C, 20.5 km/hr)	$c(t) = a * (t^m) * \exp(-bt)$	2.99	0.0451	0.986	0.974
Synbit (4.0 mm, 15 °C, 13.3 km/hr)	$c(t) = a * (t^m) * \exp(-bt)$	8.64	0.0813	0.914	0.998
Heidrun (4.2 mm, 6.7 °C, 13.6 km/hr)	$c(t) = a * (t^m) * \exp(-bt)$	1.20	0.0439	0.952	0.960
Heidrun (4.1 mm, 15 °C, 14.9 km/hr)	$c(t) = a * (t^m) * \exp(-bt)$	3.88	0.1030	0.762	0.996

All data for the climatic factors (sunlight intensity, salinity, rainfall, air and water temperature, and wind speed) measured during the experiments are found in Tables 4S.3 to 4S.6 and illustrated in Figures 4S.2 to 4S.9 (Supplementary Materials). The averaged water and air temperatures were higher in summer than spring. Average wind speeds varied from 11 to 25 km/hr the experiments. Salinities values were very similar (ranging from 29 to 31 part-per-thousand) and rainfall amounts were minimal for all experiments; thus, not affecting the salinity of the water. Sunlight exposure for each experiment varied with the higher values in direct sunlight and lower exposure during cloud cover and night time. The sunlight and water temperatures were taken hourly to the end of the experiments. The hourly values, for the climatic factors, were then averaged to the selected points in time, when water samples were collected. Correlation Analysis was conducted on the climatic factors and monocyclic aromatic values to determinations relationships among the variables (Appendix Tables 4S11a to 4S11d). To identify whether there were trends with the climatic factors and the dissolution of monocyclic

aromatics in water upon the weathering of oil, regression analysis was conducted on the data set. The results of the regression analysis (Pearson coefficient, 'R', ranging from 0.62 to 0.97) and Analysis of Variance (ANOVA) to test if the regression results are reliable are found in Table 4.2 and only those cases, where the trends were found to be significant ($p < 0.05$) are presented, except for spring-time results for Heidrun where p -values were slightly greater than 0.05 ($R^2 > 0.85$). However, only a limited number of data points could be used, so significant findings were assessed against literature results in the preceding paragraph.

Currently there is a debate in the literature, where Fingas (2003) reported that temperature and time were greater factors in oil evaporation than surface wind speed or oil slick thickness for a wide range of crude oils. In contrast, Gros et al. (2014) determined that wind speed strongly affected evaporation very early in an experimental spill of a Norwegian crude oil in the North Sea. In addition, a more recent lab study reported that both evaporation and photo-chemical oxidation resulted in increases in the physical properties of oil, but the increases were predominately larger for sunlight exposure (Ward et al., 2018a). One must note that all three of these studies involved the testing of conventional crude oil and not bitumen blends. Of the factors assessed in this study, air and water temperatures and sunlight had a significant effect on the dissolution of monocyclics in water for all oils. Therefore, water and air temperature (Fingas, 2003) and wind speeds (Gros et al., 2014) contributed to evaporation and solar energy to photolysis (Ward et al., 2018a&b) of the lighter components (in this case, monocyclic aromatics) of the oils weathered in summer than spring. The different proportions of chemicals (saturates, aromatics, resins and asphaltenes) present in the oils (Chapter 2)

could determine, which climatic factors influence the weathering of oil by type, which is discussed in the next few paragraphs.

Table 4.2: Regression Analysis Based on Correlation Analysis (Excel-Additional Information found in Appendix Tables 4S.11a to 4S.11d and 4S.12) of Climatic Factors with Monocyclic Aromatics Dissolution. Temperature-Tem, n-observations, R-pearson coefficient of determination, SE-Standard Error, MSE- Mean Square Error, *p*-value significant at <0.05.

Oil	Climatic	Regression			ANOVA (model fit)			
Type	Variable	n	R	SE	MSE	<i>p</i>-value	<i>Comment</i>	
Spring-Time								
AWB	<i>Sunlight</i>	4	0.96	14	4.8E+03	0.01	release	
	<i>Air Tem</i>	4	0.97	0.92	26	0.03	release	
	<i>Sunlight</i>	5	0.96	4.7E+02	8.7E+06	0.008	decay	
	Summer-Time							
	<i>Air Temp</i>	5	0.79	7.6	4.3E+03	0.03	decay	
	<i>Sunlight</i>	4	0.98	2.3E+03	5.0E+08	0.01	release	
Spring-Time								
WCS	<i>Sunlight</i>	4	0.99	0.87	1.4E+03	0.001	release	
	<i>Sunlight</i>	5	0.98	6.1	5.2E+02	0.003	decay	
	Summer-Time							
	<i>Sunlight</i>	5	0.95	5.4E+03	9.0E+08	0.01	decay	
Spring-Time								
Synbit	<i>Sunlight</i>	7	0.81	2.5	8.2E+01	0.03	release	
	<i>Wind Speed</i>	4	0.97	0.34	3.1E+02	0.03	release	
	<i>Water Tem</i>	7	0.78	0.19	0.3	0.04	decay	
	Summer-Time							
	<i>Air Tem</i>	4	0.93	0.68	11	0.04	decay	
	Spring-Time							
Heidrun	<i>Sunlight</i>	4	0.95	5.7E+02	5.6E+06	0.05	decay	
	<i>Water Tem</i>	4	0.94	0.34	1.7	0.06	release	
	Summer-Time							
	<i>Sunlight</i>	4	0.97	4.8E+03	8.7E+08	0.03	decay	

For these experiments, AWB weathered on water in spring-time conditions, air temperature and sunlight exposure had an effect on the rate of dissolution of monocyclics in water and only sunlight affected their rate of decay. For AWB study, the average

temperature of air was a few degrees higher than that of water; therefore could have affected the release of the monocyclics in water from the oil. The fact that sunlight exposure affected the rate of decay of monocyclics in water would suggest that photo-chemical weathering of these chemicals possible, but to far lesser degree than evaporation. The same factors were at work for AWB weathering on water under summer-time conditions. However, these two factors had an opposite effect. Sunlight affected the release of the monocyclics in water, where it most likely caused warming of the oil on the water surface. Whereas, the summer-time warmer air temperatures contributed to the rate of decay of monocyclics in water, most likely through evaporation. Sunlight energy affected the rate of release and decay of the monocyclics in water, the sun would encourage evaporation and photo-chemical weathering, to a lesser degree, during the weathering of WCS. Sunlight was at work in summer-time resulting in the photo-chemical decay of monocyclics in water released from the weathering of WCS. Both AWB and WCS are crude bitumen with condensate used as the diluent, but less so for WCS than AWB. Condensate is a very volatile liquid by-product of natural gas extraction from field separators, scrubbers, or inlets of natural gas processing plants. The chemical composition (primarily of low molecular weight aromatics and aliphatics in the range of n -C₅ to C₁₀) of condensate can vary depending on source or how it was processed (Environment and Climate Change Canada, 2016; Nigeri et al., 2016). As mentioned previously monocyclics are the dominate chemicals during a condensate spill and their concentrations in water were higher for the weathering of AWB and WCS.

Wind speed and solar energy affected the rate of dissolution of monocyclics in water from the weathering of Synbit in spring-time. Water temperature contributed to

their rate of decay. The wind most likely helped to increase current flow and movement of chemicals from the oil to the water column. In summer-time, air temperature affected the rate of release of monocyclics in water (warming the oil at the water surface) and air temperature affected their rate of decay through evaporation during the weathering of Synbit. Synbit contains the least amount of monocyclics than WCS and AWB (King et al., 2017b) and synthetic crude, as the diluent, contains a greater portion of chemicals including saturates in the range of C₁₇ to C₃₅ and alkylated polycyclic aromatics (Yang et al., 2011) that are less susceptible to natural attenuation by evaporation than condensate.

Water temperature, although cooler in spring-time, affected the rate of dissolution of monocyclics in water from the weathering of Heidrun crude. Heidrun is a medium crude oil with a lower viscosity (King et al., 2017b) so its release of monocyclics in water may be more affected by the cooler waters than the heavy more viscous bitumen blends. Sunlight affected their rate of decay, which suggests that photo-chemical weathering of the monocyclics was occurring. However, the climatic factors assessed for the spring-time data are not significant ($p > 0.05$) as mentioned previously. Sunlight affected the rate of decay of monocyclics in water when the oil was weathered under summer-time conditions. This suggests that both evaporation (warming of oil at the water surface) and photo-chemical weathering occurred.

Although biodegradation was not a main focus, since a recent review by Fayemiwo et al. (2017) stated that it is erroneous to assume that natural attenuation removes BTEX compounds from contaminated media. This may very well be due to the fact that BTEX is acutely toxic to marine organisms, including bacteria (Lee et al., 2015) and several factors, such as pollutant concentration, active biomass concentration,

temperature, pH, availability of inorganic nutrients and electron acceptors, and microbial adaptation; influence the rate and extent of biodegradation of BTEX (Singh and Celin, 2010). Also, that these chemicals are very volatile and are expected to evaporate rapidly early into the spill. While biodegradation could potentially play some role; evaporation and photo-chemical weathering are considered to be driving factors in the degradation of BTEX released from spills of oil.

Our initial assessment of the climatic effects on the dissolution of monocyclics in water from the weathering of oils indicated that temperature, wind speed and sunlight were the major contributing factors depending on oil type. ANOVA was conducted on the continuously measured monocyclic concentrations at the various points of time for spring and summer to determine if they were different. The results of the ANOVA are presented in Table 4.3 and a p -value <0.05 suggests that the outcomes are different and the season in which an oil spill occurs has an effect on the dissolution of monocyclics in water from the weathering of oil.

Table 4.3: ANOVA (Repeated Measures; Excel- See Appendix Table 4S.13 for more details) Comparing the Effects of Season on the Rate of Monocyclics Decayed in Water Released from Oils Weathered Under Simulated Natural Conditions. Half of the Samples (n -observations) were Based on Spring-Time (spr) and the Other Half on Summer-Time (sum). SRMSE-Square Root of the Mean Square Error, hr-hours, and p -value significant at <0.05 .

BTEX concentrations					
Oil Type	Source of Variation	n^*	SRMSE	p -value	Significant
AWB	Between Spr and Sum	10	56	0.02	Yes, $p<0.05$
WCS	Between Spr and Sum	14	59	0.001	Yes, $p<0.05$
Synbit	Between Spr and Sum	14	7.8	0.04	Yes, $p<0.05$
Heidrun	Between Spr and Sum	14	3.0	0.3	Not significant

* $n=n_1+n_2$

Season had a significant ($p<0.05$) effect on the rate of decay of monocyclics in water during the weathering of AWB, WCS and Synbit. The concentration of

monocyclics in water peaked at *ca.* 48 hr for AWB compared *ca.* 24 hours for Synbit and WCS, afterwards they started to decline. As mentioned early, AWB contained the highest w/w % of monocyclics than the other bitumen blends, which may account for the difference noted above. The seasonal effect was on the decay side of the curves (Figures 4.3 and 4.4) for the various bitumen blends. Also, the rate of decay of monocyclics in water was faster in summer than spring for these products. This effect was contributed to the difference in the climatic factors in spring than summer. Season did not affect the dissolution of monocyclics in water from the weathering of the conventional crude, Heidrun. The monocyclics in water peaked at *ca.* 24 hours for this crude oil. Further to this, statistical evaluation indicated that season did not have an effect on the rate of release of monocyclic in water for all four oils. For the bitumen blends, monocyclics are added to the oil through the diluent. They are naturally part of the Heidrun crude, which contains a lesser amount of asphaltenes than the other oils that could have an effect on the release rate of the monocyclics in water. Perhaps this explains why season had an effect on the dissolution of monocyclics in water for the bitumen blends and not Heidrun.

4.2.3 Percentages of BTEX Released Through Dissolution and Evaporation

Slick thickness and the quantities of oil added were controlled and the BTEX concentrations were measured for the crude oils. Therefore, we could determine the percentage of BTEX dissolution (based on maximum concentration) in water for the spring and summer experiments (Supporting Materials for example calculation). Percentage dissolution was highest for the bitumen blends ranging from 1.8 to 3.9 % over the two seasons evaluated (Table 4S.14, Supporting Materials). The percentage dissolution in water, for the oils, are comparable for both summer and spring, but the time

point where the maximum BTEX concentration occurred varied due most likely to the influence of water temperature and sunlight exposure. The progressive weathering of Heidrun (conventional crude) on water displayed the lowest % BTEX dissolution to the water column for both seasons and this was not expected, since it had the second highest amount of BTEX. Although as mentioned earlier this could be due to the fact that BTEX is naturally occurring in Heidrun and where its chemical composition contains much less of the asphaltenes that could affect the release of these compounds.

Assuming that 100% of the BTEX was released from the oil and noting that dissolution accounted for a small percentage (1.8 to 3.9 %) of the total mass of BTEX in these oils, subsequently >96% of BTEX was released to the atmosphere (Table 4S.14 in Supplementary Materials). This is considered to be a good estimate of BTEX to air based on the work by Kim et al. (2012) where they reported that the majority of BTEX evaporated in air occurred within 24 hours post spill. Fingas (1999) reported that evaporation is a very important process for most crude oil, where the rate of molecular diffusion for water is 10^5 slower than the maximum rate of evaporation. Also, it has been reported that evaporation (EVAP) accounts for a far greater mass loss (e.g. 10 to 100 times) of these chemicals than dissolution (Lee et al., 2015). The ratio of %EVAP in air to the %dissolved in water was calculated. The ratio varied by oil type and seasonal temperatures and sunlight intensity affected the time point, where the maximum aqueous phase concentration occurred (Table 4S.14, Supplementary Materials). For example, a ratio equal to 35 indicates that the % of BTEX lost to the atmosphere is 35 times that dissolved in the water column. Heidrun has the highest ratio of all oils tested, so most of the naturally occurring BTEX in the oil was most likely released in air. AWB has the

lowest ratio, where BTEX was an additive as part of the condensate blended with crude bitumen. Also, AWB oil had the highest concentration of BTEX compared to the other oils tested.

4.2.4 Risks Associated with the Exposure to Monocyclics Released from Bitumen Blend Spills on Water

Currently there is lack of information on the toxic effects of diluent released from bitumen blends on aquatic organisms (Dupius and Ucan-Marin, 2015). Toxic effects depend on the duration of exposure and the concentration of the oil components involved and can be lethal or sub-lethal affecting growth and reproduction (Rand et al., 1995). Toxic effects can be classified as either acute caused by short-term exposure to a high concentration of bioavailable chemicals or chronic caused by long-term exposure to a lower concentration.

There are many values for the acute toxicity (median lethal concentration, LC_{50}) of monocyclic aromatics in water and marine invertebrates and fish. LC_{50} represents a lethal concentration of BTEX in the water column that will kill 50% of the test organisms to a continuous period of exposure. LC_{50} over a 48 hour period was reported to be 10 to 50 mg/L for *Daphnia magna*, the water flea, 5 to 15 mg/L for *Artemia*, small brine shrimp, and 5 to 10 mg/L for rainbow trout larvae (National Research Council Committee, 2003). Based on these works, the low LC_{50} value is around 6 mg/L and the high value is around 25 mg/L. These values may change depending on the LC_{50} values generated for the species of concern. A more recent study (Ameh *et al.*, 2013) reported that typically water concentrations in excess of 1 mg/L are required to produce acute toxic effects in organisms such as algae, daphnids and fish. Pilibert et al. (2016) reported

that across all oil types (including bitumen blends); toxicity to Zebrafish was better explained by the BTEX content. Also, they concluded that future studies should focus on increasing the understanding of the toxicity of BTEX compounds to fish early life stages and the antagonistic and/or synergistic effects of complex mixtures containing BTEX and polycyclic aromatics. Many of the studies mentioned herein use a single-species approach to evaluate acute toxicity to fish from BTEX exposure and an ecosystem orientated approach should be considered as well in research studies to evaluate the pros and cons of both (Lindenmayer et al., 2007). Since sunlight exposure has a major influence on release and decay of monocyclics in water, then studies on oil toxicity to fish should be modified to more accurately reflect the role of sunlight exposure to oil spills in aquatic areas. This statement is supported by a recent study that found exposure to UV light increased the sensitivity of the coral reef larvae to the water accommodated fractions of condensate by *ca.* 43% (Nigeri et al., 2016). In addition, Ward et al (2018b) showed that photo-chemical oxidation was a dominant weathering process that oxidized more than half of the floating light oil, to reach the surface from the Deep Water Horizon spill, within hours to days.

It is known that thicker slicks weather more slowly than thinner ones (King et al., 2017b), and thus the slick thickness would influence the rate of BTEX dissolution and evaporation. Both can be influenced by the volume of oil released and whether it's a one-time or continuous rapid release and where conditions are unfavorable for rapid dilution, evaporation and biodegradation (Lee et al., 2015). In our study, if BTEX only dissolved in water, released from the oil, the concentration would reach mg/L (Table 4S-13, Supplementary Materials), high enough to induce acute biological effects. It has been calculated based on the data generated in this study that dissolution accounts for only a

small percentage (ca. 4%) of monocyclics (BTEX) released in salt water. As mentioned previously, the ability of water to dissolve these volatiles decreases with the addition of electrolytes (potassium, sodium and chloride) present in saltwater environments. Also, season (difference in temperature and solar energy) can influence the rate of release and decay of those chemicals during surface spills of bitumen blends. BTEX concentrations were recorded in part-per-billion (ppb), which was based on a one time release of oil (ca. 0.26 L) into a body of water (1310 L) producing an oil-to-water ratio of 1:5000 (v/v). The highest concentration of BTEX released to the water column was associated with surface spills of bitumen blended with all or some condensate (AWB and WCS, respectively) as the diluent. For BTEX concentrations to produce lethal effects, a larger ratio of oil to water is required to exceed the ppm levels mentioned previously for the single-species approach. The summer-time warm water results suggest that sunlight causes photo-chemical weathering as the monocyclics (BTEX) decay in the water column. Although not measured, the monocyclic metabolites are most likely present during this process and this statement is supported by the work of Ward et al. (2018a&b). The spring-time cold water results herein demonstrated that BTEX concentrations can be persistent up 192 hr (8 days) and exposure to it could potentially induce chronic biological effects; however, exposure studies are required to confirm this.

Since only approximately 4% (at maximum) was released to the water column, the majority (96%) of BTEX present in oil evaporated into air. The release of these chemicals in air can have a significant impact, through inhalation, on birds and mammals at the air/water boundary in the vicinity of the spill. Marine mammals are at acute risk of oil exposure through inhalation of volatile chemicals during their normal surface

behavior of breathing (Harris et al., 2011). In particular, killer whale populations that are listed as threatened or endangered (under the Species at Risk Act) are at great risk due to small population sizes, complex social structure, long lives, slow reproductive turnover, and the fact that they spend most of their time at the water surface (Rosenberger et al., 2017). Although other routes of exposure, such as oiling of feathers and ingestion, can greatly impact marine birds, they can inhale volatiles while feeding at the surface or through grooming when feathers are oiled (US Fish and Wildlife Services, 2010). Given these findings, a combination of indicator species and an ecosystem orientated approach to assess the impacts from monocyclic aromatics dissolved in sea water from the diluent released from surface spills of bitumen blends may be best to inform risk assessments. In addition, oil spill responders need to exercise caution when treating such spills to avoid inhalation of BTEX. Specifically workers closest to the freshly surfacing oil are most at risk of overexposure to monocyclic aromatics (Aven et al., 2011).

4.3 Conclusions

An empirical function was fitted to the BTEX data that can be used to show the rate of dissolution of monocyclic aromatics and their decay in water from surfaces spills of bitumen blends over two seasons. Of the climatic factors assessed, air and water temperatures and sunlight had a significant ($p < 0.05$) effect on all oils depending on oil type. Overall season had a significant ($p < 0.05$) influence on the dissolution of the monocyclics in water for all bitumen blends. In spring-time, the combination of colder water and air temperatures and reduced sunlight exposure slowed down the rate of decay of monocyclics in water. Whereas these factors (in particular light intensity) contributed to a higher rate of decay (photo-chemical weathering) of the monocyclics in water for oil

spilled in summer-time. Season did not have a major influence on the dissolution rate of monocyclics in water or their decay for the conventional crude oil, Heidrun. Heidrun contains a lesser amount of asphaltenes than the other oils, which could have an effect on the release rate of the monocyclics in water. These results aid to address the current debate over which climatic factors including temperature, wind speed and sunlight have the most influence on the weathering of oil, in particular the dissolution of monocyclics in water from oil. Our study suggests that all three factors are major contributors, but their influence on the weathering process is most likely driven by oil type (namely the proportion of chemicals that make up its composition) and the season in which a spill occurs. These findings were substantiated with results reported by others in the scientific literature on the influence of temperature, wind speed and sunlight exposure on oil spilled in aquatic areas. Also, the results indicate that the climatic factors could have influenced the fitting parameter values of the dissolution model applied to the various oil types and the season the spills occurred.

Dissolution only accounts for a small percentage of monocyclics released in water and the majority was evaporated to the atmosphere during simulated spills of oil in spring and summer. The study emphasizes that impact from the monocyclics released from the diluent of blended bitumen spills, would be greater at the air/water boundary and less so to the water column. Information from this study coupled with species sensitivity data suggests that marine species residing and feeding or grooming at the water surface in the vicinity of a spill are at a great risk from exposure to monocyclic aromatics. Also, studies on oil toxicity to fish should be modified to more accurately reflect the role of sunlight exposure to oil spills in aquatic areas. The simulated natural environment produced in

this study, provides concentrations that gradually increase and decrease over time, and may be more appropriate to assess impacts to representative indicator species or ecosystems exposed to monocyclics released in water and air from surface spills of bitumen blends in aquatic areas, where the rate of natural dilution and degradation are applicable.

Chapter 5: An Oil Spill Decision Matrix in Response to Surface Spills of Various Bitumen Blends

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5. Introduction

Alberta, Canada oil sands contain large deposits of bitumen or extremely heavy crude oil. Naturally-occurring bitumen is semi-solid at room temperature and is too viscous to transport via pipeline. The most common specification for pipeline inputs is a maximum density of 0.940 g/cm^3 and viscosity of 350 cSt (Fingas, 2015). Therefore, crude bitumen must be diluted with a lighter fluid (diluent) to adjust its physical properties to meet pipeline flow stipulations. There is a variety of diluents (e.g. condensate; condensate with added butane C_4 and/or pentane C_5 , synthetic crude; and synthetic naphtha) and the blending process is at the discretion of the producer, so a wide range of products of varying chemical composition are produced. The chemical composition of these blended bitumen products varies more widely than conventional crudes, because the characteristics of each blend depends on the source of bitumen, extraction method, type of diluent, and ratio of diluent to crude bitumen which varies with seasonal temperature during shipment. Oil sands heavy (e.g. bitumen blended with diluent or upgraded crude oil) represents ~2 million barrels per day (b/d) of the ~4 million b/d of crude oil produced and transported within Canada (CAPP, 2017).

In many of the new projects being contemplated (e.g. Northern Gateway and Energy East Pipelines), blended bitumen products would be transported by pipeline to coastal ports where they would be transferred to marine tankers for shipment to foreign markets. With so many new products and greater quantities exported, there is a greater risk of oil spills in brackish water (e.g. Saint Lawrence Seaway and Bay of Fundy,) near the coastal ports of eastern Canada where fresh water input from estuaries can lower the salinity of the marine waters (CAPP, 2017).

Three types of blended bitumen products were selected for this study: Access Western Blend (AWB), Cold Lake Blend (CLB), and Synthetic crude blended bitumen. The behaviour of blended bitumen spills have been considered to be comparable to those of lighter fuel oils in the early part of a spill, changing to the qualities of heavier fuel oils as weathering occurs (ENG, 2011). King et al. (2014) reported that AWB weathers rapidly, and its density is similar to that of heavy conventional oil within 24 hours after a surface release at sea. For this reason, Heidrun Crude (e.g. medium crude, lighter than bitumen blends) and IFO 180 (e.g. heavy fuel oil that is heavier than bitumen blends) were selected as comparative oil products for this study. It is necessary to determine how natural weathering increases the physical properties (e.g. density and viscosity) of blended bitumen over time, so that the information can be used to inform oil spill response plans. For instance, oil viscosity is critical in dispersant work because medium viscosity oils (<2,000 cSt) are readily dispersible, but heavy, highly-viscous oils (>10,000 cP) are not (National Research Council [NRC], 1989). Viscosity is also important when recovering oil with booms, and pumping it through skimmers and into reservoirs for off-site transport. *In situ* burning is another response option that has been successful in the

removal of oil, but the efficiency of burning decreases for heavy oils and weathered products (Fingas, 2015) and in open water situations it also requires booming or the use of herders to get the oil thick enough to sustain a burn. Density is important as it determines whether the oil will sink or float when spilled in water. If the oil density is less than that of water (1.0 g/cm^3 for fresh water, *ca.* 1.03 g/cm^3 for seawater), the oil floats, otherwise it sinks (GENIVAR, 2013). If the oil sinks, it is more challenging to track and monitor and oil spill response options become limited (Lee et al., 2015).

It has been argued that for a wide range of crude oils whose compositions consists mostly of hydrocarbons $>C_{10}$, temperature and time are the greatest factors affecting oil evaporation in comparison to other factors, such as wind speed and oil layer thickness (Fingas, 2004). In contrast, others have found that wind speed has the greatest influence on oil evaporation in the early stages of a spill (Gros et al., 2014). Despite this discrepancy, this information is based on conventional oil studies and not blended bitumen products (e.g. heavy oil). Research comparing the natural weathering of blended bitumen products to conventional oils is required to address these critical knowledge gaps. Besides gaps in modelling blended bitumen spills, challenges exist in how to use the models to more efficiently aid response decision-making (Lee et al., 2015). There is a requirement for rigorous science to support new Canadian regulations on the use of oil spill technologies (e.g. dispersants) and to improve the connection that science plays in decision-making to respond to spills.

Mesoscale (e.g. flume tank) research was conducted on five oil products to determine changes in the oils physical property due to natural processes reacting on spills in temperate brackish water. The flume tank used in the study is circular (Figure 4.1) with

a diameter of 1.5 m and a height of 1.0 m, and is capable of either flow-through or recirculating seawater. Water currents were generated at a velocity of 20 cm/s (e.g. 0.72 km/hr or 0.4 knots) sufficient to move a floating microcosm containing two oil products per experiment in a circular path on the water surface so as to permit the oils to be exposed to natural elements as would be the case in the event of an actual spill under similar conditions. A total of five oil products were tested at a slick thickness of *ca.* 4 mm to compare the natural weathering of the oil products spilled in temperate waters under similar conditions. In addition, three of the five were also tested at *ca.* 7 mm to determine the effect of oil slick thickness on changes in the heavy oil(s) physical properties as a function of time of weathering. The research aims to provide information for the development of models for the prediction of changes in the physical properties of blended bitumen products as they naturally weather on the surface of water over time. Final deliverables include the generation of a decision-making matrix for the treatment of bitumen blends that assimilates weathering and effectiveness of oil spill technologies. Analysis of the data and model results enable the forecasting of operational time windows, where oil spill response strategies are effective or not at treating weathered bitumen blends spilled in aquatic areas.

5.1 Materials and Methods

5.1.1 Circular Flume Tank

The details on the tank (Figure 4.1) are found in section 4.1.1.

5.1.2 Oil Products

The physical properties of the oils are found in Table 3.4. Based on calculated API values, the bitumen blends (e.g. Access Western Blend-winter [AWB]; Cold Lake

Blend-summer [CLB]; and Synthetic Bitumen Blend) and Fuel Oil 180 were classified as heavy oils, while Heidrun was classified as medium crude oil.

5.1.3 Floating Microcosm

Details on the floating microcosm (Figure 4.2) are found in section 4.1.3.

5.1.4 Flume Tank Studies: Sample Collection

Samples (~10 to 20 grams) were collected at the following time points (hours): 0, 3, 8, 24, 72, 96, 120, 192, 240, 288, and 336 and placed into pre-weighed scintillation vials using a scoopula to remove as much oil as possible. Time points varied slightly depending on work hours and climatic conditions (e.g. heavy rain). Time zero represents a sample of the unweathered oil. Salinity and temperature readings were taken prior to sample collection.

5.1.5 Analyses of Oil Samples Procured During Flume Tank Studies

All oil samples were analysed using an Anton Paar SVM 3000 Viscometer/Densimeter to obtain viscosity and density measurements using ASTM D7042 and D5002 methods respectively (Supporting Materials; Tables 5S.1 to 5S.8).

5.2 Results and Discussion

5.2.1 Measurements Taken During Natural Weathering of Oils in a Flume Tank

The design of the outdoor flume system permitted the oils to be weathered under mild (e.g. current flow of 20 cm/s or 0.4 knots) at sea conditions (e.g. exposure to rain, wind, sun, etc.) in the summer (August to September) of 2016. The water (Bedford Basin seawater) was filtered prior to oil application, so that suspended particles were < 5µm in the water column and not expected to contribute to changes in the physical properties of the oil over time.

The time-series physical measurements of the weathered oil products, collected during flume tank studies, are recorded in Tables 5S.9 to 5S.12 (Supporting Materials). For the first three experiments, the average recordings for water and air temperatures, salinity and wind speeds were comparable. The fourth experiment (Table 5S.12) conducted in late summer showed a decrease in average air and water temperatures compared to the first three experiments; however, the physical properties measurements (e.g. conducted in triplicate) of the oils, for all experiments, were taken at 15 °C to permit comparison of all oils tested at a slick thickness of *ca.* 4 mm (Figures 5.1 and 5.2).

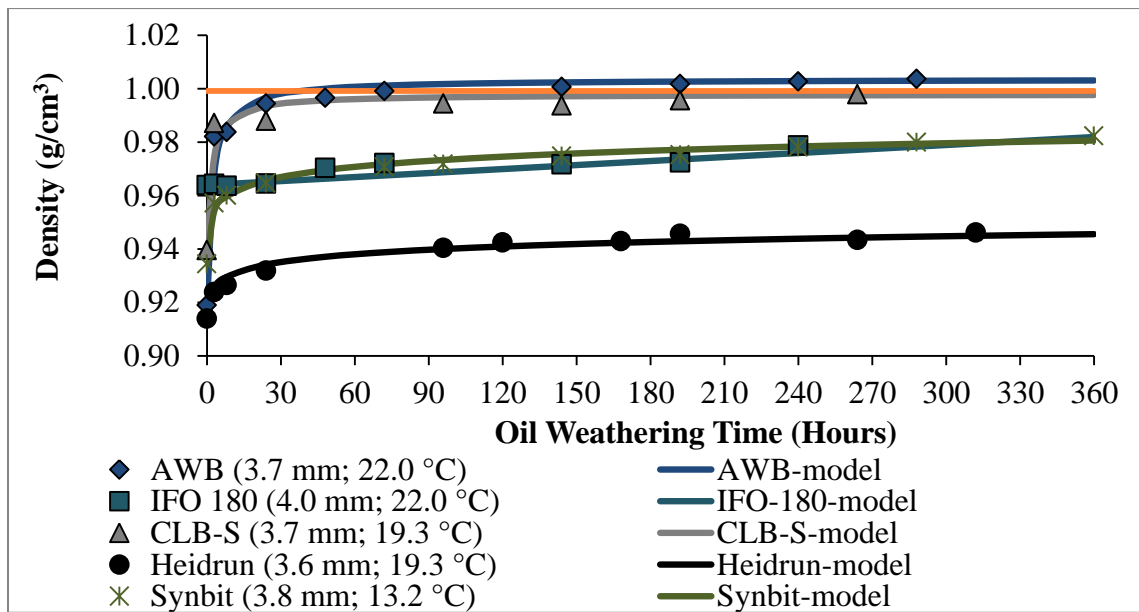


Figure 5.1: Oil Density Variation as Function of Time of Weathering Oil at a Slick Thickness *ca.* 4 mm.

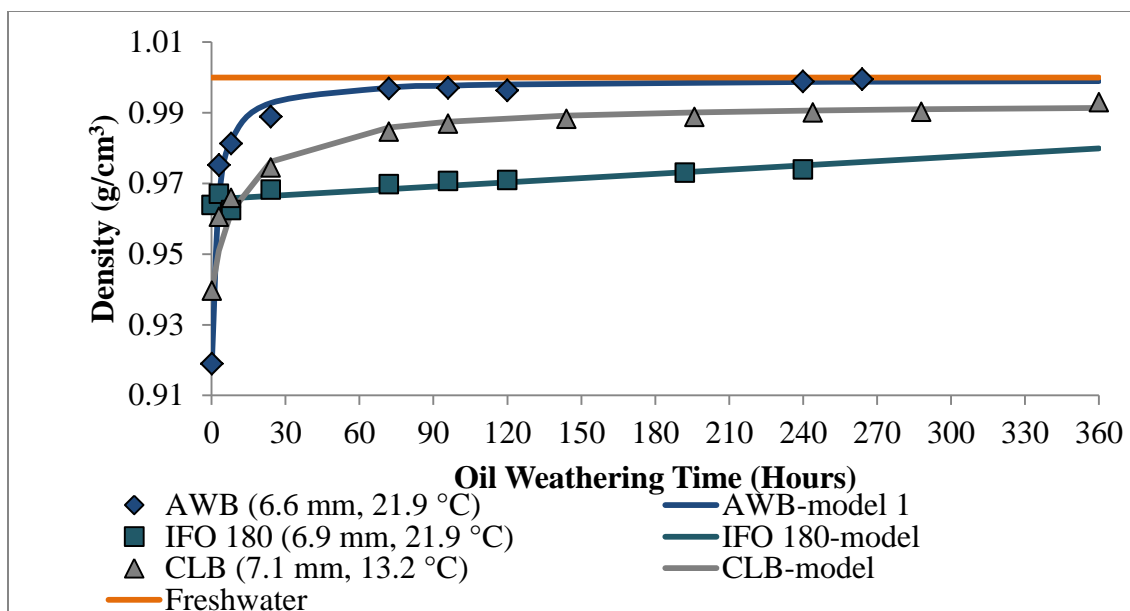


Figure 5.2: Oil Density Variation as Function of Time of Weathering Oil at a Slick Thickness *ca.* 7 mm.

5.2.2 Density to Predict Oil Buoyancy and Sinking in Aquatic Environments

All tested oils, including the bitumen blends, had an initial density at 15 °C less than fresh water (i.e., ~1.00 g/cm³ at 15 °C). The lighter chemicals (e.g. volatiles and water solubles) associated with the oil were lost during natural weathering, causing an increase in the density of the oil. Figure 5.1 reports the density of the five tested oils for a slick thickness of 4.0 mm. It shows that only AWB exceeded the density of fresh water, and it occurred within 48 hours of weathering. An earlier study by King et al. (2014) showed that AWB exceeded the density of fresh water six days after natural weathering; however, the oil slick in that case was thicker and the study was conducted under quiescent sea conditions whereas the water used in the current study was initially filtered and the setup was outdoors in low hydrodynamic (20 cm/s current velocity) conditions.

The 7.0 mm slick thickness oil density results (Figure 5.2) indicate that the increase in density was much smaller than the 4.0 mm slick thickness (for the available

data). In particular, the AWB density remained lower than 1.0, which is unlike the 4.0 mm slick thickness (Figure 5.1).

In general, the AWB and CLB showed a rapid increase in their density within the first 48 hours and slowly approached the density of fresh water near the end of the study (Figures 5.1 and 5.2). These condensate blended bitumen products are expected to contribute to ecological impacts similar to and perhaps greater than lighter crude oil; however the probability of these products adhering to suspended sediments and sinking elevates the risk for benthic impacts in aquatic environments (Dew et al., 2015). Density values for the other oils remained well below those of fresh water for the duration the studies. This is most likely due to the fact that the diluent for synbit has more of the high molecular chemicals (e.g. $>C_{10}$) than condensate or other lighter solvents (Dew et al., 2015) and thus does not evaporate as fast to cause an increase in the density of the remaining oil product. As mentioned previously, the Bedford Basin seawater used in these studies was filtered prior to oil application, so that particles present in the water would not contribute to changes in the physical properties of oils as they weathered. The raw data for all physical measurements, conducted in triplicate, are found in the Supporting Materials, Tables 5S.12 to 5S.15.

Figure 5.3 shows changes in the viscosity of the oil products as a function of time for a slick thickness of 4.0 mm. The viscosity of the bitumen/condensate blends (AWB and CLB) changed rapidly, exceeding 10,000 cSt within three hours, and 100,000 cSt within 48 hours. Synbit produced a different oil weathering profile, exhibiting a much slower increase; it took 144 hours or 6 days for its viscosity to approach 10,000 cSt. Heidrun's viscosity remained lower than 1,000 cSt throughout the duration. The changes

in viscosity of IFO 180 are somewhat similar to Synbit in terms of the gradual increase, and exceeded 10,000 cSt in 144 hours or 6 days.

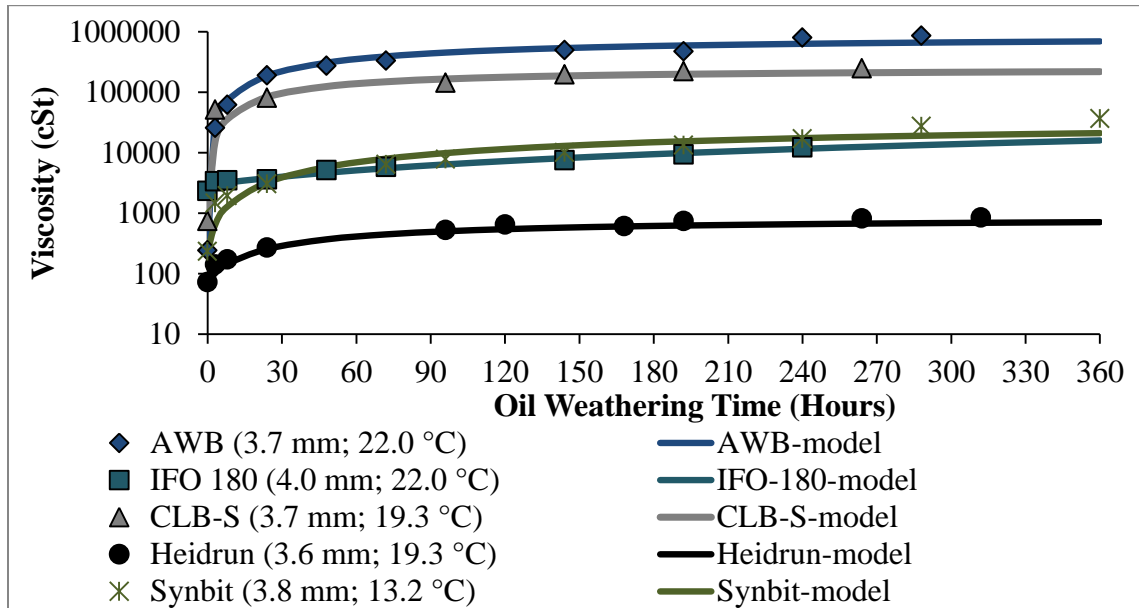


Figure 5.3: Variation of the Oil Viscosity as Function of the Time of Weathering of Oil at a Slick Thickness *ca.* 4 mm. Note the Logarithmic Scale of the Viscosity Axis.

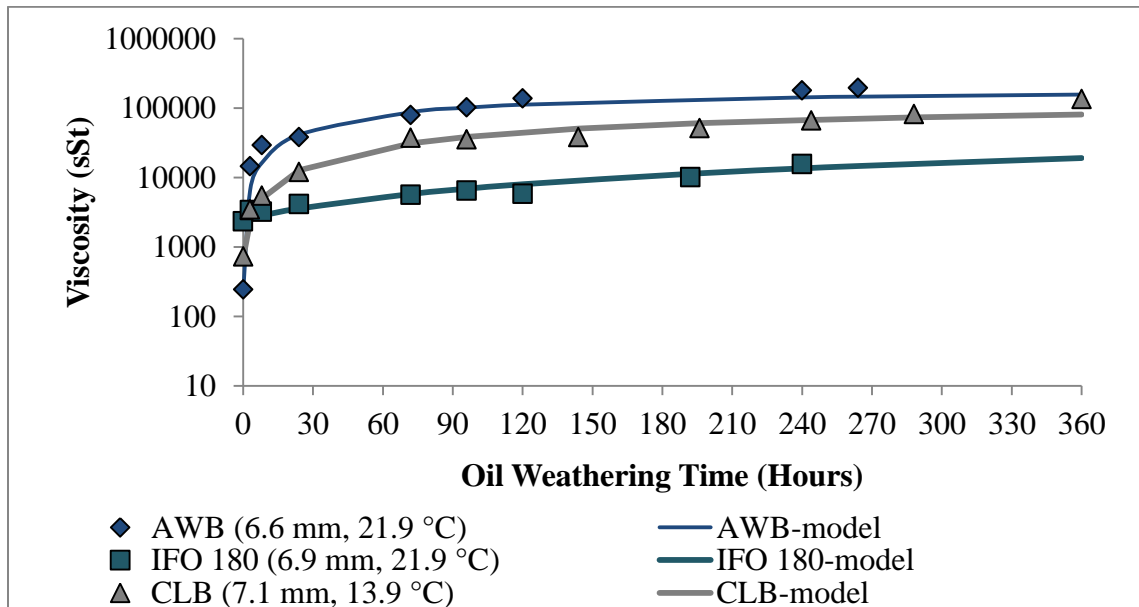


Figure 5.4: Variation of the Oil Viscosity as a Function of the Time of Weathering of Oil at a Slick Thickness *ca.* 7 mm. Note the Logarithmic Scale of the Viscosity Axis.

Figure 5.4 shows that increasing the oil thickness to 7.0 mm strongly reduced the weathering of the oil; for AWB, it took around four days for the viscosity to exceed 100,000 cSt, while it took less than one day to reach that value when the oil thickness was 4.0 mm (Figure 5.3). In Figure 5.4, the 7.0 mm thick CLB barely reached 100,000 cSt after 360 hours (15 days), while it exceeded that value within two days (Figure 5.3, oil thickness *ca.* 4.0 mm). The IFO viscosity seemed to be independent of the oil thickness, as it exhibited the same behaviour in both Figures 5.3 and 5.4.

For the AWB and IFO experiments, average wind speeds varied from 12.9 to 13.3 km/hr and surface water temperatures were 21.9 to 22.0 °C, so these factors were considered to be very similar. Therefore, variation in oil slick thickness (Figures 5.1 to 5.4) was considered to be the major factor affecting the rate at which these oils weathered. It is important to note that in the case of the CLB experiments there was a variation of around 6 °C in average water temperature during the experiments. Also, the average wind speeds varied from 14.9 to 17.6 km/hr. However, it appears that oil slick thickness was the greater factor contributing to the rate at which the CLB weathered and was therefore used in the statistical evaluations.

A modified Monod-type (or hyperbolic) model was fitted to the density (equation 5.1) and viscosity (equation 5.2) data in Figures 5.1 through 5.4. The formulae are as follows:

$$\rho = \rho_0 + (\rho_f - \rho_0) \left(\frac{t}{T + t} \right)^n \quad (5.1)$$

$$\nu = \nu_0 + (\nu_f - \nu_0) \left(\frac{t}{T + t} \right)^n \quad (5.2)$$

where ρ and ν represents density and viscosity, respectively, power “ n ” controls the rate at which the early values (ρ_0 or ν_0) approach the final values (ρ_f or ν_f) and then for a plateau, if needed, through the incorporation of the value ‘ T ’. ‘ T ’ is the "half-velocity constant"; the value of t when either p/p_{\max} or $\nu/\nu_{\max} = 0.5$. The fits were generally good, as one notes visually through the absence of any systematic bias (undershooting or overshooting), and the large coefficient of determination, $R^2 > 0.86$. The developed functions listed in Table 5.1 can be used to predict changes in the physical properties (e.g. density and viscosity) of blended bitumen products spilled under similar conditions in the aquatic environment.

A statistical t-test (Microsoft Excel’s paired two-sample for means) was applied to determine if oil slick thickness had an effect on the physical properties of the heavy oils as they weathered over time. The t-test results are found in Table 5.2. Oil slick thickness had a significant ($p < 0.05$) effect on changes in the density of all three oils weathered under similar environmental conditions. Slick thickness has a significant ($p < 0.05$) effect on changes in the viscosity of bitumen/condensate blends (e.g. AWB and CLB) weathered over time on brackish water; however, this was more apparent in the later stages (e.g. > 10 hr) of the weathering of the heavy oils. This was not the case for IFO 180, where the oil slick thickness did not have an influence on changes in viscosity as the oil weathered, but did have an effect on changes in oil density.

Table 5.1: Statistic Data to Support Equations Fitted to Density and Viscosity Experimental Data for Various Oils Weathered under Natural at Sea Conditions.

Oil (ST, T, Wspd)*	Equation	T	n	R ²
Density				
AWB-W (4 mm, 22.0 °C, 13.3 km/hr)	$\rho = \rho_0 + (\rho_f - \rho_0) \left(\frac{t}{T+t} \right)^n$ $\rho_0 = 0.9189; \rho_f = 1.0036$	57	0.11	0.99
IFO 180 (4 mm, 22.0 °C, 13.3 km/hr)	$\rho_0 = 0.9639; \rho_f = 1.034$	2300	0.71	0.86
CLB-S (4 mm, 19.3 °C, 14.9 km/hr)	$\rho_0 = 0.9396; \rho_f = 0.9929$	31	0.39	0.98
Heidrun (4 mm, 19.3 °C, 14.9 km/hr)	$\rho_0 = 0.9139; \rho_f = 0.9461$	40	0.50	0.98
Synbit (4 mm, 13.2 °C, 17.6 km/hr)	$\rho_0 = 0.9344; \rho_f = 0.9823$	190	0.19	0.98
AWB-W (7 mm, 21.9 °C, 12.9 km/hr)	$\rho_0 = 0.9189; \rho_f = 0.9994$	54	0.12	0.99
IFO 180 (7 mm, 21.9 °C, 12.9 km/hr)	$\rho_0 = 0.9639; \rho_f = 1.352$	6.3×10 ⁵	0.46	0.83
CLB-S (7 mm, 13.2 °C, 17.6 km/hr)	$\rho_0 = 0.9396; \rho_f = 0.9949$	47	0.053	0.98
Viscosity				
AWB-W (4 mm, 22.0 °C, 13.3 km/hr)	$\nu = \nu_0 + (\nu_f - \nu_0) \left(\frac{t}{T+t} \right)^n$ $\nu_0 = 244; \nu_f = 863,606$	110	0.97	0.98
IFO 180 (4 mm, 22.0 °C, 13.3 km/hr)	$\nu_0 = 2342; \nu_f = 6.952 \times 10^5$	1.5×10 ⁵	0.66	0.94
CLB-S (4 mm, 19.3 °C, 14.9km/hr)	$\nu_0 = 730; \nu_f = 134,735$	440	0.82	0.94
Heidrun (4 mm, 19.3 °C, 14.9 km/hr)	$\nu_0 = 73; \nu_f = 853$	74	0.88	0.98
Synbit (4 mm, 13.2 °C, 17.6 km/hr)	$\nu_0 = 234; \nu_f = 36,620$	690	0.69	0.93
AWB-W (7 mm, 21.9 °C, 12.9 km/hr)	$\nu_0 = 244; \nu_f = 195,221$	180	0.65	0.95
IFO 180 (7 mm, 21.9 °C, 12.9 km/hr)	$\nu_0 = 2342; \nu_f = 8.047 \times 10^5$	1.5×10 ⁴	1.0	0.86
CLB-S (7 mm, 13.2 °C, 17.6 km/hr)	$\nu_0 = 730; \nu_f = 309,489$	228.9	0.61	0.91

*(ST-Oil slick thickness, T-water temperature, Wspd-wind speed)

Table 5.2: Statistical t-Test (Paired Two-sample for Means, Two-Tail-Further Details Found in Appendix Table 5S.16) Comparing the Effects of Oil Slick Thickness on the Density and Viscosity of Oil Weathered under Natural at Sea Conditions. Half of the Samples (n-obs.) had the 4.0 mm Thickness and the Other Half had the 7.0 mm Thickness. $p < 0.05$ is significant.

Oil (Thickness)	*n-observations	T-statistical	T-critical	[^] df	<i>p-value</i>
Density					
AWB-W	24	2.4	2.1	22	0.01
CLB-S	20	3.5	2.1	18	0.001
IFO 180	28	2.6	2.1	26	0.008
Viscosity					
AWB-W	24	4.1	2.1	22	0.0001
CLB-S	20	3.8	2.1	18	0.0004
IFO 180	28	0.85	2.1	26	0.20

$n = n_1 + n_2$, [^]df-degrees of freedom ($n_1 + n_2 - 2$)

The impact of slick thickness suggests that, for these oils, the mass transfer limitation for evaporation is within the oil and not the atmosphere above it as observed for water evaporation (Sutton, 1934; Brustaert, 1982). This agrees with the findings of Fingas (2011 & 2013), where their experiments suggested that the evaporation of oils did not increase markedly with the wind speed, and thus concluded correctly that the evaporation of oil is not limited by the air boundary layer, but rather by the diffusion of oil components to the interface between the oil and the atmosphere. However, Fingas's (2011 & 2013) evaporation studies were based on light crude oils and petroleum products, and heavy oils including bitumen blends were not considered. In an earlier study, Fingas (2014) reported that temperature and time were greater factors in the evaporation for a wide range oil types rather than thickness of the slick and wind speed velocity, where the bulk of the oils' hydrocarbons are $>C_{10}$. For the IFO 180, it is possible that the

evaporation from it is small due to the small percentage of low molecular weight compounds within it, which confirms Fingas's study (2014). However, the fate and behaviour of bitumen blends, unlike conventional heavy oils, are driven by the lighter diluent blended with the crude bitumen. The exception is when synthetic crude is used as the diluent mixed with crude bitumen, which produces an evaporation profile that is closer to a heavy oil product such as IFO 180.

5.2.3 Viscosity Limitations on Oil Spill Response Options

The empirical data developed herein can be used to aid in the decision-making process on the selection of oil spill countermeasures to treat bitumen blend spills on water. If sinking of oil occurred within 48 hours after an actual spill, recovery and remediation of the submerged oil would be a challenge, especially when oil particle aggregates (OPA) form (Zhao et al., 2016). To put this into perspective, the Enbridge line 6B pipeline rupture released an estimated 840,000 gallons of blended bitumen product into the Talmadge Creek and flowed into the Kalamazoo River Marshall Michigan, USA in 2010 (US EPA, 2016). After five days, the lighter components of the oil evaporated causing the denser weathered oil mixed with suspended sediments to sink, resulting in a more extensive, lengthy and expensive recovery of oil from the river (US EPA, 2016).

As oil products naturally weather, their density and viscosity increase, which can affect decisions on the appropriate response option to consider. Natural attenuation (i.e. natural recovery) can permit the removal of as much as 40% of medium crude and 10% for heavy oil product through natural processes within days (Fingas, 1999). Condensate bitumen blends can lose 15 to 18% of their total mass after weathering for two week on seawater under static conditions (King et al., 2014). Other response options, such as

chemical dispersant effectiveness, decreases with increasing oil viscosity (Zhao et al., 2014). Most dispersants have low effectiveness as the oil viscosity exceeds 2,000 cSt, and practically zero effectiveness as the oil viscosity approaches 10,000 cSt (National Research Council, 1989; GENIVAR, 2013). Li et al. (2010) demonstrated that IFO 180 (2,574 cSt) treated with the chemical dispersant COREXIT®EC9500A was effectively dispersed (95%) in temperate waters (15.6 °C); however, as the viscosity increased (9,179 cSt) with decreasing water temperature (9.8 °C) dispersant effectiveness declined rapidly (12.9%). King et al. (2015) showed that chemical dispersant was only moderately effective (59%) in treating CLB (winter blend, viscosity 1,067 cSt) in temperate waters (17 °C on average) and the effectiveness declined (45%) with decreasing water temperature (<8.5 °C on average) where the oil viscosity increased (2,340 cSt). The time to reach the desired dispersion or a given dispersion effectiveness is also of importance. A recent lab experiment by Pan et al. (2017) indicated that the dispersant increased the dispersion of CLB significantly, from less than 10% to around 60%, but for the latter longer mixing times and greater mixing energy were required to produce findings consistent with those found in a wave tank by King et al. (2015).

Information on the use of chemical dispersant to treat other bitumen blends (e.g. synbit and dilsynbit) is currently not available in the scientific literature. In addition, oils with a viscosity >100,000 cSt can impede oil recovery operations when booms and skimmers are deployed (International Tanker Owner Federation Ltd, 2012), and under calm sea conditions the mechanical process only typically achieves 10 to 15 % recovery of spilled oil on water (Wadsworth, 1995; International Tanker Owner Federation Ltd, 2012). This clean up technique is also limited by storage and disposal of recovered oily

water at sea. *In situ* burning is another response option that has been successful in the removal of oil (e.g. depending on oil type) from the water surface and can be quite effective (e.g. 90 to 99%) in the first 96 hours following an oil spill (National Academies, 2015). It should be noted, however, that the oil slick must be >2 mm thick in order for it to ignite, and the efficiency of burning decreases for heavy oils and weathered products (Fingas, 2014). Furthermore, most of the oil components that ignite tend to evaporate when the spill occurs, and thus burning the remaining oil is not easy, and could require the addition of fuel to start the burn and booming, or the use of herders to increase the thickness of the oil to enable a sustained burn. Controlled burning could achieve 50 to 75% removal of condensate bitumen blends provided the weathering of the oil is limited to a day (National Academies, 2015). Both mechanical and *in situ* burning techniques require calm sea states and containment of sufficient quantities of oil to be effective. The use of *in situ* burning and dispersant can be very contentious, as *in situ* burning can cause air pollution due to the incomplete combustion of hydrocarbons, and dispersants make the oil more bioavailable to aquatic species. Lack of information to support decision-making on the selection of response options can narrow the “window of opportunity” to initiate a pro-active response, thus limiting the use of some tactics. The information on oil spill response options is presented in Table 5.3.

The viscosity modelling data (based on oil weathering of the approximately 4 mm slick thickness) and the literature information on response options were used to produce an oil spill response decision-making matrix for bitumen blends compared to the other tested oil products (Table 5.4). Note that the matrix applies only to oil spills on temperate water, and factors the conditions under which the respective response options are optimal

(at best). Synthetic bitumen and IFO 180 have very similar viscosity changes as a function of time of weathering of oil, so the two were paired in the matrix. The matrix shows that treatment and recovery of condensate bitumen blends would be challenging and limited to *in situ* burning in the first two days of a spill provided that conditions are favorable (e.g. sufficient containment of oil products can only be achieved in calm seas, whereas containment and *in situ* burning are not feasible in rough seas) and it is feasible to do so (i.e. oil thickness is sufficient for a sustained burn). Under ideal conditions, an integrated approach using natural attenuation, dispersant, and *in situ* burning may be feasible to treat a Heidrun crude oil spill at sea. A combination of dispersant and *in situ* burning may prove effective in treating spills of synthetic bitumen and IFO 180 depending on sea conditions.

Table 5.3: Effectiveness of Oil Spill Countermeasures for Conventional Oils Compared to Bitumen Blends Spills on Water.

		Medium Crude Heidrun	Heavy Crude IFO 180	Condensate Bitumen blends	Synthetic Bitumen Blend
* Oil Spill Countermeasure	No response	~40 % lost to natural processes within days ^(Fingas, 1999)	~10% lost to natural processes within days ^(Fingas, 1999)	~20% of diluent lost to natural processes within weeks ^(King et al., 2014)	expected to be similar to IFO 180
	Mechanical	10 to 15% ^(Wadsworth, 2012)	10 to 15% ^(Wadsworth, 2012)	10 to 15% (based on IFO 180)	expected to be similar to IFO 180
	Dispersant	>75% up to 2 weeks ^(NRC, 1989)	90% at 24 hr ^(Liet al., 2010)	50 to 60% at 3 hr, 0% thereafter ^(King et al., 2015a)	expected to be similar to IFO 180
	<i>In situ</i> burning (assuming oil slick thickness is >2 mm)	99% at 96 hr ^(NAS, 2016)	90% at 96hr ^(NAS, 2016)	50 to 75% at 24 hr ^(NAS, 2016)	expected to be similar to IFO 180
Effectiveness is based on ideal environmental conditions suited to the response option					

*Information in the table has been summarized from the literature and cited in the text

Table 5.4: An Oil Spill Response Decision-Making Matrix for Bitumen Blends and Other Oils Products Spilled On Seawater. Based on the Effectiveness of Countermeasures: Effectiveness >50%=Green; Effectiveness between 30 and 50%=yellow; below 30%=red.

		Condensate Bitumen Blends (based on AWB)			
		Response time (Days)			
		<0.5	>0.5 to 2	>2 to 10	>10 to 15
Viscosity (cSt)→		<65000	>65000 to 150000	>150,000 to 580,000	>580,000 to 650,000
Density (g/cm)→		< 0.990	>0.990 to 0.996	>0.996 to 1.002	>1.002
Oil Spill Countermeasure	No response				Extremely weathered
	Mechanical	Calm Sea	Calm Sea	Potential to Sink	Extremely weathered
	Dispersant	Rough Sea	Rough Sea	Potential to Sink	Extremely Weathered
	<i>In situ</i> burning	Calm Sea	Calm Sea	Potential to Sink	Extremely Weathered
		Heidrun (medium crude)			
Viscosity (cSt)→		<200	>200 to <400	>400 to 660	>660 to 720
Density (g/cm)→		< 0.930	>0.930 to 0.937	>0.937 to 0.944	>0.944 to 0.946
Oil Spill Countermeasure	No response				
	Mechanical	Calm Sea	Calm Sea	Calm Sea	Calm Sea
	Dispersant	Rough Sea	Rough Sea	Rough Sea	Rough Sea
	<i>In situ</i> burning	Calm Sea	Calm Sea	Calm Sea	Calm Sea
		Synthetic Bitumen Blend and IFO 180			
Viscosity (cSt)→		<2400	>2400 to <3100	>3100 to 17000	>17000 to 21000
Density (g/cm)→		<0.965	>0.965 to 0.970	>0.970 to 0.978	>0.978 to 0.982
Oil Spill Countermeasure	No response				
	Mechanical	Calm Sea	Calm Sea	Calm Sea	Calm Sea
	Dispersant	Rough Sea	Rough Sea	Rough Sea	Rough Sea
	<i>In situ</i> burning	Calm Sea	Calm Sea	Calm Sea	Calm Sea

5.3 Conclusions

The condensate bitumen blends are more susceptible to reaching a density either very close to or exceeding fresh water (e.g. 1.000 g/cm³ at 15 °C) as they weather overtime on temperate water; thus, challenging oil spill response. The same products were also vulnerable to rapid changes in their viscosities. The synthetic bitumen blend, IFO 180 and Heidrun crude, showed more gradual changes in their viscosities and densities as function of time of weathering of oil. Their densities remained well below that of fresh water and viscosities were below 22,000 cSt after approximately two week of weathering on water. The oil slick thickness had a statistically significant effect on changes in the physical properties of AWB and CLB, but not much on IFO180, which is probably due to the initially high viscosity of that oil which contains less volatile chemicals.

Modelling data of viscosity changes over time based on the 4 mm oil slick thickness were integrated with information on the effectiveness of various oil spill response options to produce Table 4.8, an oil spill response decision-making matrix for bitumen blend spills that occur in aquatic environments. The matrix provides time windows where a response option is effective or limited based on the oils evaporative model results (and based on the sea conditions most suited to the type of response method). The matrix re-emphasizes that as bitumen blends naturally weather on water, changes in viscosity over time can limit the selection of oil spill response options. In particular, the response to condensate bitumen blend spills is limited to *in situ* burning within 48 hours after a spill, and these blends are more challenging to cleanup beyond that point. However, containment of the oil prior to *in situ* burning is also problematic

due to the low amount of oil that is captured by containment. Dispersants are applicable within the first 48 hrs of an IFO 180 or synthetic bitumen spill; however, *in situ* burning, if conditions are favorable and response capabilities are in place, may prove to be most effective. In comparison, medium crude spills (e.g. Heidrun) are more receptive to a number of response options (e.g. natural attenuation, dispersant and *in situ* burning) provided environmental conditions and response capacities are favorable. The decision-making matrix offers to strengthen critical elements that are often missing in contingency plans and effective response. In particular, it incorporates information on the evolution of physical properties of bitumen blends over time.

Chapter 6: Seasonal Climatic Factors that Affect Changes in the Density and Viscosity of Bitumen Blends Naturally Weathered on Water

The predicted changes in oils' viscosities data from the viscosity hyperbolic function on oil weathering for spring and summer were published along with a version of Chapter 7 in the Journal of Marine Science and Engineering, 6 (4); 128; <https://doi.org/10.3390/jmse6040128> (open access: <https://www.mdpi.com/about/openaccess>).

6. Introduction

Crude oil continues to play a critical role in meeting global energy demands. Oil exploration and production will continue until alternative energy sources reduce our dependence on fossil fuels. Canada holds an estimated 168 billion barrels of oil in reserves (National Resources Canada, 2017) and produces more oil than it uses; thus, most of its crude products are transported to other countries with the majority to the US (National Energy Board, 2017). Heavy crude oil represents approximately half of the estimated four million barrels/day (b/d) of crude oil produced and transported within Canada (CAPP, 2015). Currently there are several pipelines located in western Canada that transport heavy oil products from Alberta Oil sands into the United States. Pipelines transporting these products are mostly located onshore near aquatic areas and nearshore close to marine ports where oil products are eventually shipped by tankers to global markets. Although spills from tankers have significantly decreased over the past decade (Lee et al., 2015), they are of major concern in Canada since ship traffic will increase significantly with increased production of heavy oil from the Alberta oil sands. Major oil spills can have devastating economic, social and environmental impacts on affected communities. Spills of heavy oil products are a controversial issue, since there is limited

literature available to understand the fate and behaviour of such spills in diverse environments, and therefore information is needed to prepare response plans and actions (National Academies of Sciences, 2016).

Currently there are many oil spill cleanup options available, including containment and skimming to recover oil, *in situ* burning to consume it, shoreline cleaning agent to aid in removal, and natural attenuation (no treatment). In Canada, oil spills near coastal areas are recovered through mechanical means and/or left to natural attenuation. Changes to Canadian regulations may make it feasible to employ other oil spill response options, including shoreline cleaning agents and *in situ* burning. The use of any oil spill response options is limited by oil type, seasonal climatic factors, site conditions, and the degree of natural weathering. Viscosity is important when recovering oil with skimmers and transferring it with pumps. If the oil is too viscous much less of it can be removed resulting in long term damage to aquatic areas. Density is important as it determines whether the oil will eventually sink or float when spilled on water. Sub-surface oil within the water column and sunken oil entrained with sediments is challenging to track, monitor and treat effectively with traditional oil spill response options designed for use on the water surface. Both of these physical properties aid in assessing the degree of weathering of oil spilled in aquatic areas.

For this study three subtype blended bitumen products were selected: Access Western Blend (dilbit), which is a mixture of 30% condensate with crude bitumen, Western Canadian Select (dilsynbit), which is a mixture of 50% condensate/synthetic crude blended with crude bitumen, and Synthetic bitumen (synbit), which is 50% synthetic crude mixed with crude product. These selected products represent the bulk

unconventional oils (including blended bitumen products) that are transported throughout North America (CAPP, 2015). In addition, for a comparison to nonconventional crude, data were also collected for Heidrun crude oil. Heidrun is a conventional crude oil and was selected since its physical properties (density and viscosity) are as close as we could find to those of the nonconventional diluted bitumen blends used in these experiments.

When oil is spilled in the environment numerous physical, chemical and biological processes reduce, eliminate, or transform the toxic chemicals associated with the released oil. Collectively these processes are referred to as weathering. The chemical and physical processes account for a portion of oil degradation and include evaporation, dissolution, dispersion, photo-chemical oxidation, and sedimentation; which can lead to sinking after the adsorption of oil onto suspended sediment particles in the water column. The most important of these physical processes is evaporation, which in the first few days after a spill can account for a 5 to 75% of the mass of the spilled oil depending on the oil type and environmental conditions (Fingas, 1999). A more recent study has shown that exposure of oil to sunlight can cause photo-chemical weathering of oil, thus causing significant changes in the chemical composition of light crude oil within a few days (Ward et al., 2018a). The eventual fate (months to years) of the remaining oil (depending on type) is influenced by biological processes (Prince et al., 2015) involving microorganisms (e.g. heterotrophic bacteria and fungi) and is considered to be critical in the remediation of the non-volatile, water insoluble fraction of crude oil, if ecological conditions are favorable. A recent study provided a model to illustrate the changes in density and viscosity of various bitumen blends weathered in temperate waters (King et al., 2017b) and could be applied to illustrate changes in those same physical properties

affected by the season in which an oil spill occurs. With so many new heavy oil products produced from Alberta oil sands and greater quantities expected to be transported during the next decade by various means, there is a need to enhance our understanding of those seasonal climatic factors that influence changes in the physical properties of oil over time by natural attenuation to provide information to support contingency plans to deal with heavy oil spills on a variety of aquatic coastal ecosystems. To simulate the conditions, which could be encountered, the experimental oil spills were exposed to natural outdoor elements (e.g. sun, wind, rain, and varying air and water temperatures). Attempts are made to address gaps in knowledge by 1) evaluating the seasonal climatic factors (air and water temperature, wind speeds, rainfall amounts, salinity, and sunlight exposure) to identify those that influence changes in the physical properties of the oils as they weather; and 2) determining if the season in which a spill occurs has an effect on the natural attenuation of oil spilled in the aquatic environment to better inform oil spill response planning.

6.1 Materials and Methods

6.1.1 Circular Flume Tank

Further details on the tank (Figure 4.1) are found in section 4.1.1.

6.1.2 Oil Products

The physical properties of the oils are found in Table 3.4. The blended bitumen products have similar densities and viscosities, since they are engineered to meet pipeline specifications. Heavy crudes have an American Petroleum Institute (API) gravity value greater than 22.3° and medium crudes fall in the range of 22.3 to 31.1° (Petroleum.co.uk, 2015). Based on API gravity values, the bitumen blends are classed as heavy oils.

Heidrun is a conventional crude oil with a density that is similar to the bitumen blend products, but its viscosity is approximately three times less at 15 °C. With an API value of 23.3°, it is classified as medium crude oil.

6.1.3 Floating Microcosm

Further details on the floating microcosm (Figure 4.2) are found in section 4.1.3 and King et al. (2017a). The floating microcosm was placed into the circular flume tank under static (e.g. no flow) conditions. Then, sufficient oil was placed into 20 of the numbered containment rings to achieve the desired slick thickness. Following distribution of the individual oil samples, the circulating pump was turned on, which generated the currents at an average speed of 20.7 ± 0.4 cm/s (n=10) or ~0.4 knots. Each of the oil weathering studies was run for approximately 192 hours in duplicate during the spring and summer of 2017.

When an oil spill occurs it can take up to 48 hours, depending on environmental conditions, to respond to it. A time window of 192 hours (8 days) was selected for this study to provide enough information on those seasonal climatic factors the influence changes in the physical properties oil by natural attenuation.

6.1.4 Flume Tank Studies: Sample Collection

Duplicate oil samples were recovered at the following time points (hours): 0, 3, 8, 24, 48, 72, 96, 120, 144, 168, and 192 during the experiments. Time zero represents a sample of the unweathered oil. The oil was removed from the water surface using a spatula. Sufficient quantities of oil are collected to measure density and viscosity at various points in time. The oil's initial mass was recorded, but the final mass at time of collection was not, since the sample now contained some water. During each sampling

period, salinity, air and water temperatures, rainfall amounts, sunlight intensity and wind speed data were collected.

6.1.5 Measurements Taken During Natural Weathering of Oils in a Flume Tank

The design of the outdoor flume system allowed the oils to be weathered under mild (e.g. current flow of 20 cm/s or 0.4 knots) at-sea conditions (e.g. exposure to rain, wind, sun, etc.) in the spring and summer of 2017 using water from the Bedford Basin, Nova Scotia, Canada. The water was filtered, prior to oil application, to remove particles $>5\mu\text{m}$ to minimize the effect of suspended particles on the physical properties of the oil over time.

Environmental conditions (water temperature, salinity, air temperature, light energy, rainfall amounts and wind speeds) recorded during the flume tank studies are given in Supporting Materials (Tables 6S.3 to 6S.6 and Figure 6S.1 to 6S.16). The air temperature, rainfall amounts and wind speeds were recorded by a weather station located near the tank. The salinity and water temperature measurements were made using a hand held meter (YSI model #30-1-FT; Yellow Springs, USA) at each time point. Light intensity and water temperature was measured using a HOBO Pendant Data Logger made by ITM Instruments Inc. Sunlight intensity and water temperature was measured 24 hours per day (sunlight, night time and cloud cover) for the 8 day study.

Each oil experiment was run in duplicate and the oil thickness was controlled at *ca.* 4 mm. Although oil slick thickness could have an effect on the rate of weathering of oil (King et al., 2017b), the focus of the study is to evaluate the climatic factors that influence the weathering process. Controlling the oil slick thickness in separate oil containment rings provided a convenient way to sample the oil at various points in time.

Also, it represents, to a certain degree, the heavy oil slicks that may pool near coastal areas after a spill or those occurring inland affecting aquatic areas.

6.1.6 Analyses of Oil Samples and Data

The viscosity and the density of each oil sample were conducted in triplicate measurements using an Anton Paar SVM 3000 Viscometer/Densitometer following ASTM D7042 and D5002, respectively. All readings are found in the Supporting Materials (Tables 6S.1 to 6S.2). Regression Analysis (Excel, linear fit) was used to identify trends that may exist with the climatic factors and physical properties (density and viscosity) of the oils and Analysis of Variance (ANOVA, Excel) to assess goodness of curve fit. Also, ANOVA (single factor test) was applied to determine if season, in which a spill occurred, had an effect on the averaged changes in the physical properties of the oils weathered at various points in time.

6.2 Results and Discussion

6.2.1 Seasonal Effects on the Physical Properties of Oil Weathered in Aquatic Areas

As in King et al. (2017b), a modified Monod-type (or hyperbolic) model was fitted to the density (equation 6.1) and viscosity (equation 6.2) data presented in Figures 6.1 and 6.2. The formulae are as follows:

$$\rho = \rho_0 + (\rho_f - \rho_0) \left(\frac{t}{T + t} \right)^n \quad (6.1)$$

$$\nu = \nu_0 + (\nu_f - \nu_0) \left(\frac{t}{T + t} \right)^n \quad (6.2)$$

where ρ and ν represents density and viscosity, respectively. Time is represented by ‘ t ’. The power ‘ n ’ controls the rate at which the early values (ρ_0 or ν_0) approach the final values (ρ_f or ν_f). To model plateaus in the data, the fitting coefficient ‘ T ’ is incorporated,

where a large value of ' T ' is considerably offset by a relatively smaller accompanying value of n . ' T ' is the "half-velocity constant"; the value of ' t ' when either p/p_{\max} or $v/v_{\max} = 0.5$. The fits were generally significant, as noted through the absence of any systematic bias (undershooting or overshooting), and the large coefficients of determination, which ranged from $R^2 > 0.86$ to 0.99 (Table 6.1). The value of ' T ' was larger for oils weathered in summer than spring. For all oils, the final averaged density and viscosity values were higher in summer than spring. This suggests that the higher temperatures in summer most likely influenced the weathering of the oils. The results show that the function chosen was applicable to illustrate changes in the density and viscosity of oils weathered in the two seasons (spring and summer) selected for the study. A more robust discussion on how the climatic factors affect the weathering of oil is provided later.

Figure 6.1 (A and B) illustrates the averaged changes in densities and viscosities of the four oils weathered in spring and summer conditions. For comparison purposes, all density and viscosity measurements were taken at 15 °C to separate the effects of the exposure conditions from the inherent effect of temperature at the time of measurement on density and viscosity. Knowing the oil density aids in understanding the buoyancy of the oil when it is released on water. None of the oil products had densities exceeding that of fresh water (1.0 g/cm³) over the two seasonal water averaged temperatures, 6 °C in spring and 15 °C in summer. An earlier study by King et al (2017b) recorded that AWB's density exceeded that of fresh water, when it was weathered at the same oil thickness on water with an average water temperature of 22 °C. This later study suggests that the warmer water temperatures experienced in late summer can affect the rate of weathering of AWB. However, the presence of suspended particles in aquatic areas could affect these

results. For example, it has been reported that oil-particle-aggregate (OPAs) formation can occur in the presence of fine suspended particles ($<20 \mu\text{m}$) at a sediment concentration of $50 \text{ mg}\cdot\text{L}^{-1}$ or higher (Khelifa et al., 2008) although it should be noted that concentrations as low as $10 \text{ mg}\cdot\text{L}^{-1}$ have been shown to produce OPAs in laboratory experiments (Ajijolaiya et al., 2006). Winter and Haddad (2014) concluded that diluted bitumen has a greater propensity to sink than do conventional oils. One study has shown that approximately 20% of conventional heavy oil spills result in a significant portion of the products sinking or being submerged in the water column (NRC, 1999). In the first few hours or days, evaporation and photo-chemical weathering of the diluent increases the oil density, enhancing the probability that the residual oil will submerge or sink. Weathered bitumen blends are likely to interact with suspended sediments to form OPAs, because so little of the bitumen itself will evaporate or biodegrade, further increasing the probability of sedimentation. This suggests that further investigations should be conducted to examine the interaction of weathered bitumen blends with suspended particles in aquatic settings, to observe OPA formation and to study their potential to sink.

For this study, the averaged viscosity data showed a trend similar to that observed for the density results. While water temperature contributed to increases in the viscosity (greater changes in summer than spring) as oil weathered; at higher temperatures (as noted from a previous study by King et al., 2017a) the rate of diluent release increased significantly causing a much larger (an order of magnitude) increase in AWB's viscosity. As identify from that same study, the thickness of the oil slick can influence the rate of weathering of oil, especially in an open sea environment. Viscosity is important when

recovering oil by mechanical techniques. If the oil is too viscous much less of it can be removed with skimmers or be transferred with pumps resulting in long term damage to aquatic areas. For this study, the most significant changes were observed for AWB (dilbit) and the least for Heidrun crude oil for spring and summer data. AWB, WCS, and Synbit all had very similar densities and viscosities (engineered for pipeline specifications) prior to weathering, so the difference in the final physical property values is contributed to the rate of weathering of the diluent portion of blended products.

For the spring and summer studies, the higher percentage (%) difference in density and viscosity occurred in the order of AWB (dilbit), WCS (dilsynbit), synbit, and Heidrun (Tables 6S.1 to 6S.2 in the Supporting Materials). This order was expected for the bitumen blends, since condensate contain more of low-molecular weight volatiles (primarily aromatics and aliphatics in the range of C_5 to C_{15}) as the diluent (Environment and Climate Change Canada, 2016) than synthetic crude. The lighter chemicals, of the diluent, are expected to be lost by evaporation (Fingas, 2015) and more recently reported, photo-chemical weathering (Ward et al., 2018). The conventional crude, Heidrun, showed the least % difference change in density (2.2% in the spring and 3.0% in the summer; Table 6S1 of the Supporting Materials). This occurred even though its initial value was similar to the other crudes tested; however, it is a lighter crude oil based on its API gravity value. Although Heidrun contains many of the same chemicals found in bitumen blends, it has a greater proportion of saturates (C_{10} to C_{35}) and alkylated polycyclic aromatic hydrocarbons (PAHs), which degrade more slowly over time (King et al., 2017b). In particular, alkylated PAHs have slower biodegradation rates than other hydrocarbons (Oberoi and Philip, 2016). Also, bitumen blends contain more of the

recalcitrant high-molecular weight resins and asphaltenes that would affect the long-term fate of the products spilled in aquatic areas (King et al., 2017b).

Climatic factors, including rainfall amounts, wind speeds, air and water temperatures, and sunlight exposure for the two seasons were recorded (data are found in Tables 6S.3 to 6S.6 and illustrated in Figures 6S.1 to 6S.16 in Supporting Materials). Sunlight exposure was greater during sunlight hours and least for cloud cover and night time. The averaged water temperatures were *ca.* 6 °C in spring and *ca.* 15 °C in summer. For both seasons, salinities ranged, on average, from 28.7 to 31.0 parts-per-thousand (ppth). Averaged wind speeds varied from 11.4 to 24.7 km/hr over the two seasons. To identify whether there were trends with the measured climatic factors (rainfall, sunlight, wind speed, salinity, and air and water temperatures) and changes in the physical properties (density and viscosity) of the oils as they weathered on water, regression analysis was conducted on the data set. The results of the regression analysis (R^2 ranging from 0.65 to 0.88) and Analysis of Variance (ANOVA) to assess if the results are reliable are found in Tables 6.3 (density) and 6.4 (viscosity) and only those cases, where the trends were found to be significant ($p < 0.05$) are presented. A significant trend would suggest that the climatic factors have an influence on oil weathering, in particular the density and viscosity of the oils. Of the factors assessed, air and water temperatures and sunlight exposure had a significant effect on all bitumen blends. In addition, wind speed had an effect on the changes in density and viscosity of Synbit weathered on water over both seasons and as well for AWB, but only in the summer. The weathering of Heidrun crude resulted in changes in its physical properties that were mostly affected by sunlight exposure. Sunlight, in most cases, appeared to affect the weathering of all oils. A

previous report suggested that temperature and time were greater factors in oil evaporation than surface wind speed or oil slick thickness for a wide range of crude oils (Fingas, 2004). In contrast, Gros et al. (2014) determined that wind speed strongly affected evaporation very early in an experimental spill of a Norwegian crude in the North Sea. Our study suggests that temperature and wind speeds are contributing factors in the weathering of bitumen blends (non-conventional oils) but sunlight had a significant influence on all four oils. Since the tested oils have different proportions of saturates, aromatic, resins and asphaltenes (King et al., 2017b) the discussions to follow are separated based on oil type.

For weathering of AWB on water in spring-time conditions, water temperature and sunlight had an effect on the changes in the density and viscosity of the oil. This would suggest that evaporation and photo-chemical weathering of the oil occurred. For this study, the averaged air temperature was a few degrees higher than the water temperature; therefore, could have affected the rate of evaporation of volatile chemicals from the oil by warming it at the water surface. Sunlight and wind speed were the major factors affecting the changes in density of the oil weathered in summer-time. Wind speed would contribute to evaporation and sunlight would induce photo-chemical weathering of the oil. This process would in itself contribute to the changes in the density of the oil, as its chemical composition changes, where aromatics oxidize to water soluble forms leaving high molecular weight resins and asphaltenes behind (Prince et al., 2003). This was substantiated by a more recent study (Aeppli et al., 2012) that suggested photo-chemical weathering produces oxidized chemicals (compounds with a C=O group such as carboxylic acids, aldehydes, alcohols, amides, etc.) that might persist in the environment

and thus can be carried by water flow (Chapella, 2001). In one set of laboratory experiments, the photo-chemical oxidation of crude oil in fresh water under direct ultraviolet irradiation showed oxidation of 5% of the branched alkanes, 9% of the *n*-alkanes, and 37% of the aromatics (NAS, 2016). If similar effects were to occur in marine waters, and there is no reason to assume otherwise, then oxidized chemicals produced from the weathering of oil could have a major impact on aquatic species where dilution of such chemicals is minimal; thus, providing implications for oil spill response.

The changes in the viscosity of the AWB weathered in summer-time were contributed to air temperature and wind speed. Both of these climatic factors would cause evaporation; thus, resulting in thicker more viscous oil slicks. A recent lab study (Ward et al., 2018) reported that both evaporation and photo-chemical oxidation resulted in increases in the physical properties of oil, but the increases were predominately larger for sunlight exposure. However, AWB contains condensate as the diluent and changes in the physical properties of the oil are most likely due to evaporative weathering and biodegradation of the condensate portion of the product. Condensate is very volatile liquid by-product of natural gas extraction from field separators, scrubbers, or inlets of natural gas processing plants. The chemical composition (primarily of low molecular weight aromatics and aliphatics in the range of *n*-C₅ to C₁₀) of condensate can vary depending on source or how it was processed (Environment and Climate Change Canada, 2016).

Air temperature was the only climatic factor associated with changes in the density of weathered WCS in spring conditions. Sunlight exposure affected changes in the oil's viscosity. Temperature and solar energy affected changes in the density and

viscosity of WCS weathered on water during summer. The results suggest that evaporation (i.e. volatiles), biodegradation and photo-chemical oxidation contributed to the weathering of WCS in spring and summer. Similar to AWB, WCS contains condensate, but in lesser amounts as the diluent, which is more susceptible to weathering than the crude bitumen.

Wind speed and sunlight affected the density of Synbit weathered on water in spring-time. These same climatic factors affected changes in viscosity of the oil as well. They also affected both the viscosity of Synbit weathered in summer-time. Air temperature and sunlight affected the density of the oil in spring. Therefore, evaporation and photo-chemical oxidation were active in weathering the oil over both seasons. Also, averaged wind speeds recorded for the experiments were similar to or less than the other oil experiments. Perhaps the unique chemical composition of synthetic crude, used as the diluent, was more sensitive to air flow above the oil slick to induce evaporation. However, its composition contains a greater portion of chemicals including saturates in the range of C₁₇ to C₃₅ and alkylated polycyclic aromatics (Yang et al., 2011) that are less susceptible to natural attenuation by evaporation than condensate. For the 8 day study, saturates are susceptible to biodegradation (Garneau et al., 2011) and aromatics to photo-chemical weathering (Radović et al., 2014; Ward et al., 2018). Therefore, we considered that although some evaporation occurred, photo-chemical oxidation would play a major role in the weathering of Synbit, since the non-volatile portion of its chemical composition is susceptible to this weathering process.

Sunlight was the only climatic factor associated with changes in the density and viscosity of Heidrun weathered on water over the two seasons. This suggests that photo-

chemical oxidation was a major contributor to the weathering of the conventional crude, Heidrun. The results for Heidrun are consistent with those of Ward et al. (2018) where photo-chemical weathering had a major influence on changes in the physical properties of a light conventional crude oil. Another explanation points to the chemical composition of Heidrun, where it contains a higher percentage of aromatics (King et al., 2017b) that may make it more susceptible to photo-chemical weathering than the other oils.

Although biodegradation was not assessed in this study, it was not expected to affect the already highly degraded bitumen portion of the bitumen blends over the 196 hour experiments. The diluent (condensate and synthetic crude) portions of the products are readily susceptible to microbial degradation. Tremblay et al. (2017) reported that the *n*-alkanes portion (C₁₅ and shorter) of gas condensate was rapidly degraded in cold winter and warm summer waters. All four oils used in the study contain aromatics with 2 to 6 ring structures, their alkylated homologues, and straight chain saturates (C₁₀ to C₃₅), but in different portions (King et al., 2017b). It has been documented in literature reviews (Adams et al., 2015; Bombach et al., 2010) that crude oil products were rapidly degraded in temperate waters, but more slowly under frigid conditions, after the addition of treating agents and nutrients. The *n*-alkane fraction of oil was the most rapidly degraded and oil type affected the process (Garneau et al., 2011; Scheibye et al., 2017; Zhuang et al., 2015; McFarlin et al., 2014). The biodegradation rates of aromatics decrease as the number of fused aromatic rings increase, so 4 to 6 ring PAHs and their alkylated homologues are more environmentally persistent than 2 to 3 ring PAHs. Heterocyclic aromatics (e.g. dibenzothiophene and naphthobenzothiophene) and their alkyl homologues were present in the oils (King et al., 2017a) and are thought to be more toxic (Madison et

al., 2015) and have slower biodegradation rates compared to other hydrocarbons (Oberoi and Philip, 2016). In general PAHs with more than three-rings are very poorly soluble in water (MacKay et al., 2006) and hence less available for microbial degradation. Also, it has been demonstrated that heavy oil such as blended bitumen products can be biodegraded in fresh water settings and water temperature can greatly affect the rate of degradation (Deshpande et al., 2017). Still, it must be noted that a large fraction of the components (resins and asphaltenes) within diluted bitumen products (King et al., 2017a) are likely to be highly recalcitrant to biodegradation.

Our initial assessment of the climatic effects on the changes in density and viscosity as the oil weathered on water indicated that temperature, sunlight and wind speed were the major contributing factors for the bitumen blends. Sunlight was the major contributing factor that affected the weathering of the conventional crude, Heidrun and as mentioned earlier its chemical composition may contribute to its slower rate of weathering for this 8 day study. Temperature (air and water) and sunlight energy values were lower in spring than summer. Analysis of Variance (ANOVA repeated measures, Excel) was used to investigate changes in the physical properties of the oils weathered over time for the two seasons. The oils were assessed separately for density and viscosity. Season had a significant ($p < 0.01$) effect on changes in the mean density and viscosity of the oils as they weathered on water (Table 6.5); with the greater difference reported for the oil's physical properties when weathered in summer than spring. There was no significant difference in the changes in physical properties of the oils weathered up to 96 hours over the two seasons. The difference in the later points in time suggests that biodegradation and photo-chemical weathering would be more prevalent in the warmer

summer waters as evaporation is expected to occur more so in the first 48 hours (where the most rapid changes in physical properties occur) post spill. The results suggest that temperature, wind speed, and sunlight exposure are major climatic factors in the natural attenuation of oil, but their influence on the weathering of oil is possibly driven by oil type and the season in which a spill occurs.

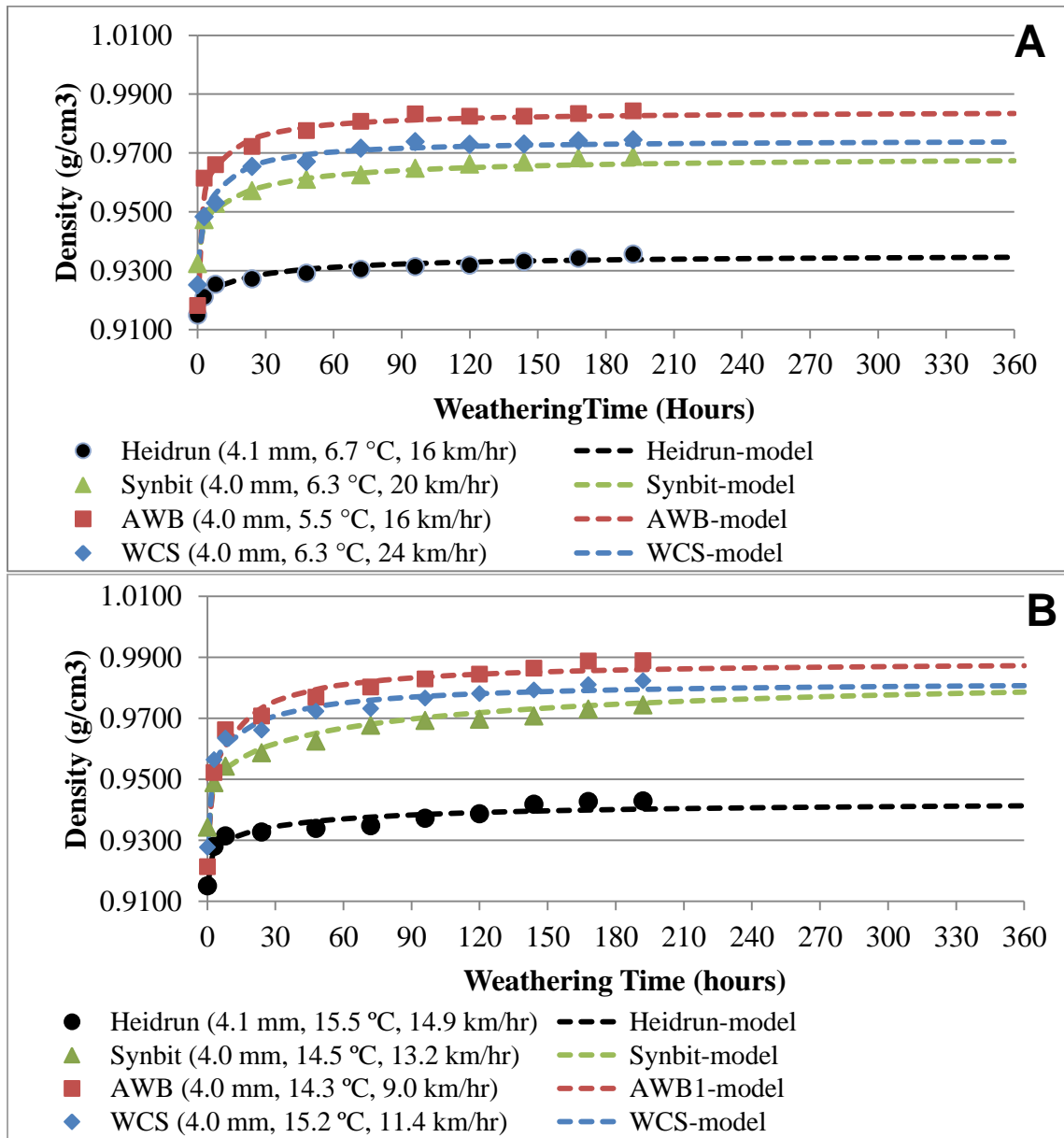


Figure 6.1: Oil Density (measured at 15 °C) as a Function of Time of Weathering: A) Spring-Time Conditions and B) Summer-time Conditions.

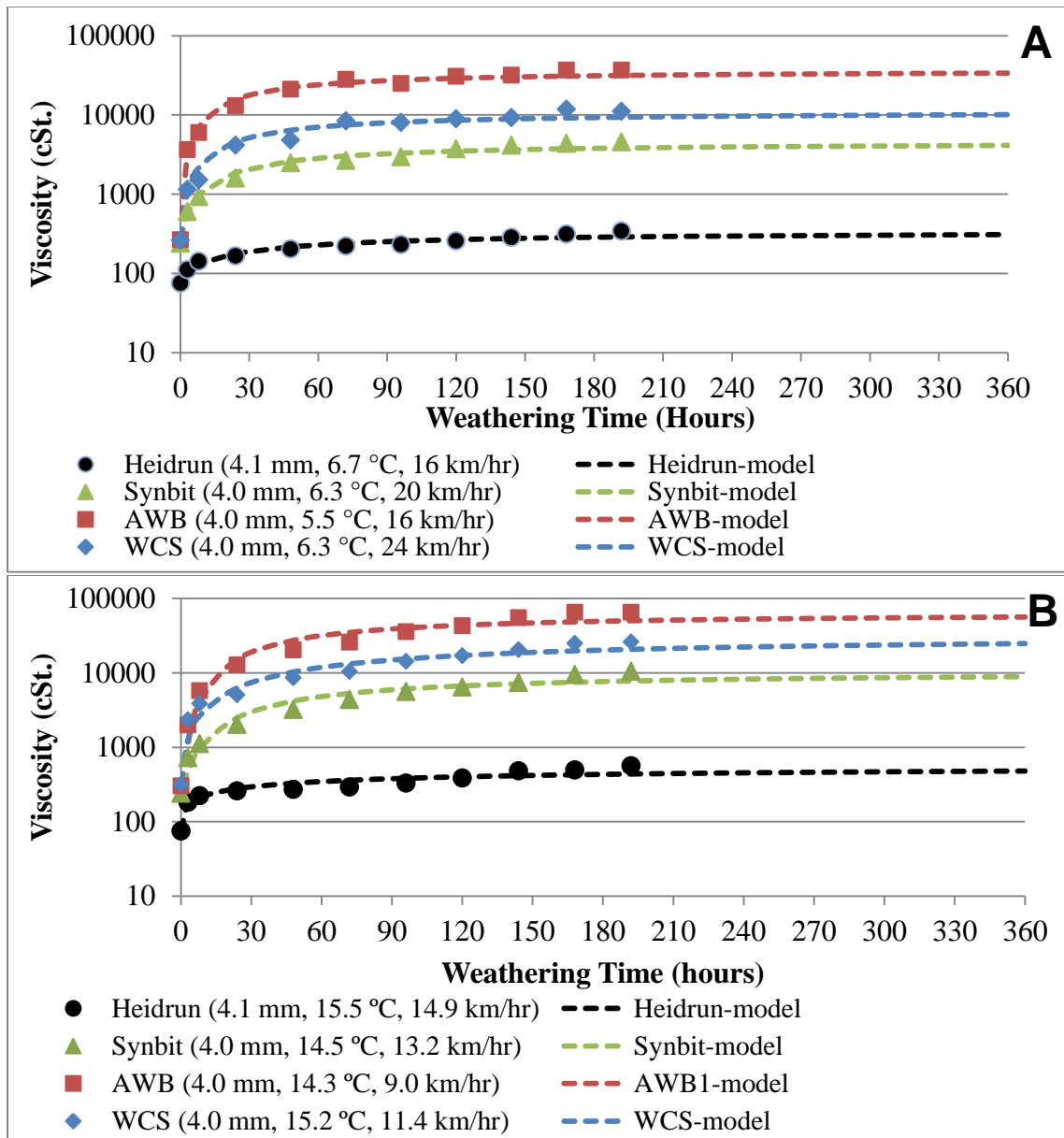


Figure 6.2: Oil Viscosity (measured at 15 °C) as a Function of Time of Weathering: A) Spring-Time Conditions and B) Summer-Time Conditions. Note Logarithmic scale for viscosity.

Table 6.1: Statistical Data Analysis of Density and Viscosity Experimental Data for Various Oils Weathered on Seawater in Spring and Summer. ST-Oil slick thickness, T-water temperature, and Wspd-wind speed.

Oil (ST, T, Wspd)*	Equation	T	n	R ²
Density (average of duplicate)				
AWB (4.0 mm, 5.5 °C, 16.4 km/hr) <i>Spring</i>	$\rho = \rho_0 + (\rho_f - \rho_0) \left(\frac{t}{T+t} \right)^n$ $\rho_0=0.9181; \rho_f=0.9843$	16	0.33	0.99
AWB (4.1 mm, 14.3 °C, 9.0 km/hr) <i>Summer</i>	$\rho_0=0.9214; \rho_f=0.9888$	21	0.42	0.98
WCS (4.1 mm, 6.3 °C, 24.7 km/hr) <i>Spring</i>	$\rho_0=0.9252; \rho_f=0.9745$	11	0.55	0.96
WCS (4.0 mm, 15.2 °C, 11.8 km/hr) <i>Summer</i>	$\rho_0=0.9277; \rho_f=0.9839$	41	0.28	0.98
Synbit (4.0 mm, 6.3 °C, 20.5 km/hr) <i>Spring</i>	$\rho_0=0.9324; \rho_f=0.9688$	40	0.38	0.98
Synbit (4.0 mm, 14.5 °C, 13.2 km/hr) <i>Summer</i>	$\rho_0=0.9386; \rho_f=0.9853$	220	0.29	0.96
Heidrun (4.2 mm, 6.7 °C, 13.6 km/hr) <i>Spring</i>	$\rho_0=0.9212; \rho_f=0.9356$	48	0.41	0.97
Heidrun (4.1 mm, 15.5 °C, 14.9 km/hr) <i>Summer</i>	$\rho_0=0.9151; \rho_f=0.9429$	95	0.25	0.94
Viscosity (average of duplicate)				
AWB (4.0 mm, 5.5 °C, 16.4 km/hr) <i>Spring</i>	$v = v_0 + (v_f - v_0) \left(\frac{t}{T+t} \right)^n$ $v_0 = 265; v_f = 36646$	28	1.1	0.95
AWB (4.1 mm, 14.3 °C, 9.0 km/hr) <i>Summer</i>	$v_0 = 299; v_f = 69309$	29	1.8	0.86
WCS (4.1 mm, 6.3 °C, 24.7 km/hr) <i>Spring</i>	$v_0 = 260; v_f = 11053$	34	1.1	0.92
WCS (4.0 mm, 15.2 °C, 11.8 km/hr) <i>Summer</i>	$v_0 = 308; v_f = 25073$	110	0.97	0.90
Synbit (4.0 mm, 6.3 °C, 20.5 km/hr) <i>Spring</i>	$v_0 = 240; v_f = 4580$	40	0.98	0.93
Synbit (4.0 mm, 14.5 °C, 13.2 km/hr) <i>Summer</i>	$v_0 = 242; v_f = 10924$	52	1.3	0.87
Heidrun (4.2 mm, 6.7 °C, 13.6 km/hr) <i>Spring</i>	$v_0 = 75; v_f = 345$	80	0.64	0.93
Heidrun (4.1 mm, 15.5 °C, 14.9 km/hr) <i>Summer</i>	$v_0 = 75; v_f = 695$	250	0.36	0.83

Table 6.2: Regression Analysis of the Correlation (Excel- for additional information see Appendix Tables 6S.7a to 6S.7d) of Climatic Factors with Density of Oil Weathered on Water in Spring and Summer. Temperature-Temp, set of n-points, R²-R squared is the coefficient of determination, SE-Standard Error, MSE-Mean Square Error, p-value <0.05 is significant.

		Density					
Oil	Climatic	Regression			ANOVA (model fit)		
Type	Variable	n	R ²	SE	MSE	p-value	Significant
AWB	Spring-Time						
	Sunlight	10	0.92	4.3E+03	7.8E+08	0.0002	<0.05
	Water Temp	10	0.74	1.3	56	0.0005	<0.05
	Summer-Time						
	Sunlight	10	0.86	4.9E+03	5.4E+08	0.001	<0.05
	Wind Spd	10	0.77	1.7	98	0.0006	<0.05
WCS	Spring-Time						
	Water Temp	10	0.61	0.04	8.6E-04	0.04	<0.05
	Summer-Time						
	Water Temp	10	0.84	2.4	1.1E+02	0.002	<0.05
	Sunlight	10	0.85	1.0E+04	2.9E+09	0.002	<0.05
Synbit	Spring-Time						
	Sunlight	10	0.88	5.5E+03	8.3E+08	0.0005	<0.05
	Wind Spd	10	0.87	3.9	3.7E+02	0.001	<0.05
	Summer-Time						
	Sunlight	8	0.96	9.3E-04	1.4E-04	0.0001	<0.05
Heidrun	Spring-Time						
	Sunlight	8	0.92	2.2E+03	1.7E+08	0.001	<0.05
	Summer-Time						
	Sunlight	10	0.69	9.2E+05	2.2E+09	0.03	<0.05

Table 6.3: Regression Analysis of the Correlations (Excel- for additional information see Appendix Tables 6S.7a to 6S.7d) of climatic Factors with the Viscosity of Oil Weathered on Water in Spring and Summer. Temperature-Temp, n-observations, R²-R squared is the coefficient of determination, SE-Standard Error, MSE-Mean Square Error, *p*-value <0.05 is significant.

		Viscosity					
Oil	Climatic	Regression			ANOVA (model fit)		
Type	Variable	n	R ²	SE	MSE	<i>p</i> -value	Significant
AWB	Spring-Time						
	Sunlight	8	0.79	5700	6.4E+08	0.004	<0.05
	Water Temp	8	0.88	1.5	52	0.002	<0.05
	Summer-Time						
	Air Temp	8	0.86	1.1	29	0.006	<0.05
WCS	Spring-Time						
	Sunlight	10	0.64	1.5E+03	2.9E+07	0.04	<0.05
	Air Temp	10	0.67	0.32	1.4	0.03	<0.05
	Summer-Time						
	Water Temp	8	0.83	1.8	94	0.01	<0.05
	Sunlight	8	0.74	1.1E+04	1.9E+09	0.04	<0.05
Synbit	Spring-Time						
	Sunlight	9	0.82	1.5E+03	2.0E+07	0.01	<0.05
	Wind Speed	9	0.79	3.0	1.9E+02	0.01	<0.05
	Summer-Time						
	Sunlight	9	0.81	1.6E+03	1.1E+08	0.008	<0.05
Heidrun	Spring-Time						
	Sunlight	8	0.93	2.2E+03	1.7E+08	0.0006	<0.05
	Summer-Time						
	Sunlight	8	0.87	165E+04	4.3E+09	0.005	<0.05

Table 6.4: ANOVA (repeated measures; Excel-additional information is found in the Appendix Table 6S.8) Comparing the Effects of Season on the Changes in Density and Viscosity of Oils Weathered under Natural at Sea Conditions. Half of the Samples (n-observations) were based on Spring-Time (spr) and the Other Half on Summer-Time (sum). SRMS-Square Root of the Mean Square Sum, *p*-value significant at <0.01.

Oil Type	Source of Variation	*n	SRMS	P-value
Density				
AWB	Between Spr and Sum	10	0.005	0.009
WCS	Between Spr and Sum	10	0.01	0.008
Synbit	Between Spr and Sum	10	0.005	0.008
Heidrun	Between Spr and Sum	10	0.01	0.001
Viscosity				
AWB	Between Spr and Sum	10	35000	0.009
WCS	Between Spr and Sum	10	16000	0.003
Synbit	Between Spr and Sum	10	6500	0.005
Heidrun	Between Spr and Sum	10	260	0.004

* $n=n1+n2$

6.3 Conclusions

Experimental oil spills of three blended bitumen products and Heidrun crude oil on water were monitored during exposure to natural climatic factors (e.g. sun, wind, rain, and varying air and water temperatures) over two seasons. A previously developed hyperbolic model was fitted to the empirical density and viscosity data with a coefficient of determination, ranging from $R^2 > 0.86$ to 0.99. The densities of all three bitumen blends weathered on water at two temperatures, 6 °C (spring) and 15 °C (summer), were less than the density of fresh water (1.0 g/cm³). This suggests that after 8 days of weathering, under similar conditions, the products would remain floating on the water. However, earlier work (King et al., 2017a) had shown that AWB would sink after 24 hours when weathered on water with temperatures at 22 °C. It should be noted that under those test conditions, the AWB density exceeded that of fresh water, but did not reach the

density of marine saltwater. The model results may be affected, if conditions are favorable for OPA formation (which could increase the propensity for oil to sink). Therefore, further studies should be conducted to examine the interaction of weathered bitumen blends with suspended particles in aquatic settings to observe OPA formation and its effects on the buoyance of the products. Also, there would be limitations on the model when applied to open seas, where oil would spread into much thinner slicks; thus affecting the rate of weathering of oil.

For spring and summer seasons, AWB (dilbit) compared to the other test oils (WCS [dilsynbit], synbit, and conventional crude) showed the higher % difference in its physical properties as it weathered on seawater. This suggests that condensate, added as the diluent, greatly affects the rate of weathering of the original product when it is spilled in aquatic areas which, in turn, put greater constraints on oil spill response efforts. Synthetic crude is a better choice for use as a diluent than condensate, as the different proportions of chemicals that make up its composition are less susceptible to natural attenuation up to 192 hours (8 days) on water over the two seasonal conditions evaluated.

Regression analysis revealed that significant ($p < 0.05$) trends exist with the seasonal climatic factors and changes in the density and viscosity of the oils weathered on water. The study aids to address the current debates over whether temperature or wind speed is the major contributing factor affecting the weathering of oil. Temperature, wind speed, and sunlight exposure were all contributing factors in the weathering process. However, sunlight was the only factor significantly affecting the weathering of the conventional crude oil, Heidrun. Also, the results indicate that the climatic factors could

have influenced the fitting parameter values of the density and viscosity models applied to the various oil types and the season the spills occurred.

Repeated measures ANOVA showed that season (different conditions) had a significant ($p < 0.01$) effect on changes in the densities and viscosities of all the tested oils weathered on water between 96 to 192 hours (over different times). However, season had no significant effect on the weathering of the oils up to 96 hours on water. The difference in the later stages of weathering of the oils was greater in summer than spring. This suggests that the warmer temperatures and higher amounts of sunlight exposure in summer contributed to the difference. Also, evaporation takes place within the first 24 hours (shown as a steep rise in the slope of the changes in density and viscosity) of an oil spill, so the difference at these later points in time suggest photo-chemical weathering and biodegradation are most likely greater in warm summer waters.

Natural attenuation will always play a role in oil spill response operations as there is no other clean-up strategy that is 100% effective. This study has shown that evaporation and photo-chemical weathering could play a critical role in the natural attenuation of oil. The major contributing factors to this process were temperature, wind speed and sunlight exposure for the weathering of bitumen blend spills. Their influence on the weathering of oil is probably driven by oil type (or in the case of bitumen blends by diluent type) and the season in which a spill occurs. The production of oxidized chemicals from the photo-chemical weathering process could provide implications for oil spill response planning, if natural dilution and mixing are minimal post spill. While biodegradation processes will play a role in the weathering of oil; the recalcitrant (e.g. resins and asphaltenes) nature of bitumen will always pose a challenge. Also, weathered

bitumen blends are likely to interact with suspended sediments to form OPAs in coastal areas, increasing the probability of sedimentation.

Chapter 7: Estimating the Usefulness of Chemical Dispersant to Treat Surface Spills of Oil Sands Products

A version of this chapter has been published along with part of Chapter 6 in the Journal of Marine Science and Engineering, 6 (4); 128; <https://doi.org/10.3390/jmse6040128> (open access: <https://www.mdpi.com/about/openaccess>).

7. Introduction

Crude bitumen, produced in Alberta, Canada, is a highly viscous, semi-solid crude oil at room temperature. There are insufficient oil refinement capabilities in Alberta, so the majority of the oil produced is shipped via pipeline and railcars outside the province. In order to meet conventional oil pipeline specifications, the crude bitumen is diluted with a lighter hydrocarbon oil to reduce its viscosity and subsequently improve flow. The blending process for crude bitumen is at the discretion of the oil producer, so a wide variety of products of varying chemical composition are produced (King et al., 2017a). Heavy oil sands oil, which is crude bitumen blended with diluent (lighter hydrocarbon fluid) represents roughly two million barrels per day (b/d) of the four million b/d of crude oil produced and transported in Canada (CAPP, 2017). From pipelines, some of these oil products are transferred to tankers and shipped to global markets. Canada's production, transport, and sale of these products (e.g. Access Western Blend or dilbit, 30% condensate with crude bitumen; Western Canadian Select or dilsynbit, 50% condensate/synthetic crude with crude bitumen; and Synthetic bitumen or synbit, 50% synthetic crude with crude bitumen) are expected to increase by a million barrels per day in the next decade (CAPP, 2017), and with the anticipated growth in oil

production and transport there is increased risk of oil spills in aquatic areas, placing greater demands on oil spill transport routes and capabilities to respond to spills.

In July of 2016, Environment and Climate Change Canada released new regulations and a list of approved oil spill treating agents that included COREXIT®EC9500A to be used as an alternative measure, in addition to recovery operations, to remediate oil spills that occur in waters offshore Canada (Canada Gazette, 2016). The purpose of using a spill treating agent in offshore areas, by the responding parties, is to reduce damage to shoreline areas that are costly to clean. The application of conventional oil spill cleanup techniques, such as spill treating agents, are limited to studies showing significant, but incomplete effectiveness of COREXIT®EC9500A on a Cold Lake bitumen blend (e.g. Cold Lake crude bitumen blend with 30% condensate, dilbit) spilled under different environmental conditions (King et al., 2015a&b). However, there is no information in the literature to support the use of chemical dispersant to treat surface spills of various other oil sands products that have weathered after their initial release at sea. In addition, a science-based tool to estimate the window of opportunity to treat such spills is highly desirable. According to a Royal Society of Canada report on the behaviour and environmental impacts of crude oil released into aquatic environments (Lee et al., 2015), more research is required on the natural and chemically enhanced dispersion of bitumen blends under a variety of oceanographic conditions. Chemical dispersants have been shown to be effective in treating heavy fuel oil, but water temperature can be a limiting factor (Srinivasan et al., 2007; Li et al., 2010). Therefore, seasonal temperature variations were considered in this study, since the blended bitumen products are classified as heavy oils. Also, weathering of oil can increase its viscosity,

which reduces the effectiveness of chemical dispersant to treat spills (King et al., 2017a). The chemical dispersant, COREXIT®EC9500A (as the only listed dispersant for offshore use in Canada), was tested at a dispersant-to-oil ratio (DOR) of 1:20 (manufacturer's recommended dose) to determine its effectiveness at treating surface spills of bitumen blends and readily dispersible conventional oil spilled on seawater in a flow-through wave tank during the spring and summer of 2016 and 2017 in Atlantic Canada.

Attempts are made to address these gaps in knowledge by 1) evaluating dispersant effectiveness by oil type, including fresh and weathered products and seasonal effects (i.e. water temperature) to generate a new dispersant model based on empirical data, and 2) a previously generated viscosity weathering model of the same oils (King et al., 2017b; Chapters 4) was integrated with the newly generated dispersion effectiveness model to provide a means to estimate the effectiveness of dispersant to treat weathered oil. The information generated will aid oil spill responders and decision-makers on the appropriate conditions, where dispersant might be applicable to treat oil spills that have weathered at sea.

7.1 Materials and Methods

7.1.1 Lab Analyses to Characterize the Chemical Composition of the Oil Products

Further details on the chemical composition of the oil products can be found in Chapter 3.

7.1.2 Wave Tank Facility

The wave tank facility is located at the Bedford Institute of Oceanography (BIO) in Dartmouth, Nova Scotia, Canada. Tank dimensions are 30 m long, 0.6 m wide and 2.0 m high (Figure 7.1). The tank is equipped with a series of manifolds to generate a more or less uniform current along the wave propagation direction; hence, the label flow-

through system has been used to evaluate dispersant effectiveness of fresh and weathered crude oils. The current speed is only around 0.5 cm/s (around 350m/day), but it allows the dilution and flushing of applied chemicals, which cannot be achieved in standard wave tanks. Additional details on the wave tank can be found in King et al. (2015a&b).

7.1.3 Oil and Dispersant Application during Wave Tank Tests

Access Western Blend (a dilbit comprised of crude bitumen blended at 30% with condensate), synthetic bitumen (a synbit made up of 50% synthetic crude oil blended with crude bitumen) and Western Canadian Select (a dilsynbit consisting of 50% synthetic crude oil/condensate blended with crude bitumen) were selected for this study because they represent the highest volume of oil sands products transported throughout Canada. Heidrun was also selected as the reference conventional crude, since its physical properties are reasonably close to the blended bitumen products. Similar to the technique used by Li et al. (2009a), the bitumen oil products were artificially weathered by purging them with nitrogen for 48 hours at ~20 °C. The mass of the product was recorded prior to and after weathering. Weathering the products prior to placing them in the tank for dispersion effectiveness testing is a key step, as weathering is a natural process expected during any real oil spill; it generally increases oil viscosity and is likely to limit chemical dispersant effectiveness.

The experimental and sampling procedures were consistent with the crude oil dispersant efficacy testing in the flow-through wave tank reported previously (King et al., 2015a). Briefly, for each experiment, quiescent conditions were achieved in the tank (i.e., no waves). Next, *ca.* 240 g of oil product was gently poured onto the filtered seawater surface within a 40 cm diameter ring located 10 m downstream from the wave maker, and

ca. 12 g of the dispersant COREXIT®EC9500A was gently sprayed (using a nozzle pressurized at 60 psi, 0.635 mm i.d.) onto the oil slick. This resulted in a dispersant-to-oil ratio (DOR) of 1:20. The wave maker was started and produced a sequence of waves, and the ring was promptly lifted immediately prior to the arrival of the first breaking wave at the location of the ring. The sequence of waves generated a 0.4 m high plunging breaker (where the water curls and re-enters the water surface downstream) every 40 seconds at the same location (where the ring was initially placed) using the dispersive focusing technique (Botrus et al., 2008). In this study, only breaking waves were investigated with the use of chemical dispersant to treat oil spills, since an earlier study (Government of Canada, 2013) revealed that spill treating agents were ineffective in the dispersion of condensate bitumen blends when no breaking wave occurs. Breaking waves can be generated in the wave tank to simulate various energy dissipation rates in the field. The various wave types generated in the wave tank were characterized in prior works (Venosa et al., 2008; Wickley-Olsen et al., 2008). Each experiment was conducted for one hour during which each wave cycle (four breakers) lasted for 15 seconds followed by a quiescence period that lasted for 25 seconds. Therefore, there were four breaking waves every 40 seconds in the test tank producing a total of 360 breakers during a one hour oil spill experiment.

The tank is equipped with a series of manifolds to recirculate the water, generating a relatively uniform current along the wave propagation direction; hence, the term ‘flow-through system’ has been used to describe the method used to evaluate dispersant effectiveness of fresh and weathered crude oils. The current speed is approximately 0.5 cm/s (around 350 m/day), and allows for the dilution and flushing of

applied chemicals which cannot be achieved in standard wave tanks. The wave tank system has been used to test dispersant effectiveness (DE) in seawater along with the oil concentration in dissolved and dispersed (i.e., droplets) forms (Li et al., 2008; Li et al., 2009a, 2009b, 2009c; Li et al., 2010; King et al., 2015a).

7.1.4 Wave Tank In Situ Measuring Devices

Two Laser In Situ Scattering and Transmissometry (LISST-100X, Sequoia Scientific, Inc.) particle size counters were employed during the experiments, one at 1.2 m and another at 12 m downstream of the oil release point and both at a depth of 0.45 m (Figure 7.1). Particle size (2 to 500 μ m) distributions were recorded at 2.0 s intervals for one hour per experiment (Li et al., 2009a; King et al., 2015a).

7.1.5 Lab Analysis of Seawater Samples from Wave Tank Studies

Four water sampling devices were deployed, one at 2.0 m upstream from the oil release point and the other three downstream at 2.0 m, 8.0 m and 12 m from the oil release point (Figure 6.1). Each of the four samplers collects water (*ca.* 100 mL) at three depths (0.5, 0.75 and 1.4 m) in the tank at the time points, and samples were taken at 5, 15, 30, 45, and 60 minutes. In addition, effluent samples (from the end of the tank opposite to the wave maker) were taken (Figure 7.1). Four time-zero samples (prior to oil release, to check background levels) were selected at arbitrary sampling locations.

The collected water samples were extracted and analysed for total petroleum hydrocarbons (TPH) using a gas chromatograph equipped with flame ionization detection (GC-FID) (Cole et al., 2007; King et al., 2015a). The method is a modified version of EPA 3500C, whereby the sample container is the extraction vessel. Briefly, 12 mL of dichloromethane (DCM) were added to a 125 mL amber glass sample bottle containing

ca. 80 mL of seawater collected during the experiments. Next, the sample was placed on a Wheaton R₂P roller (VWR, Canada) for 18 hours. The roller has been modified to accommodate a 3 inch (ID) PVC pipe into each roller slot. This modification allows sample containers of different sizes to be used in the apparatus. Once extraction was complete, the sample bottles were removed and the DCM was recovered. The recovered DCM was placed in a pre-weighed 15 mL centrifuge tube, and the solvent was removed using a nitrogen evaporator until the final volume reached 1.0 mL graduation on the centrifuge tube. The extracts were then analysed by GC-FID. Calibration standards prepared from the test oils were used to develop calibration curves for evaluating the oil concentration in the seawater extracts. The method detection limit is <0.5mg/L. The benefit of this procedure is that 240 samples can be extracted simultaneously; thus increasing productivity with acceptable accuracy and precision.

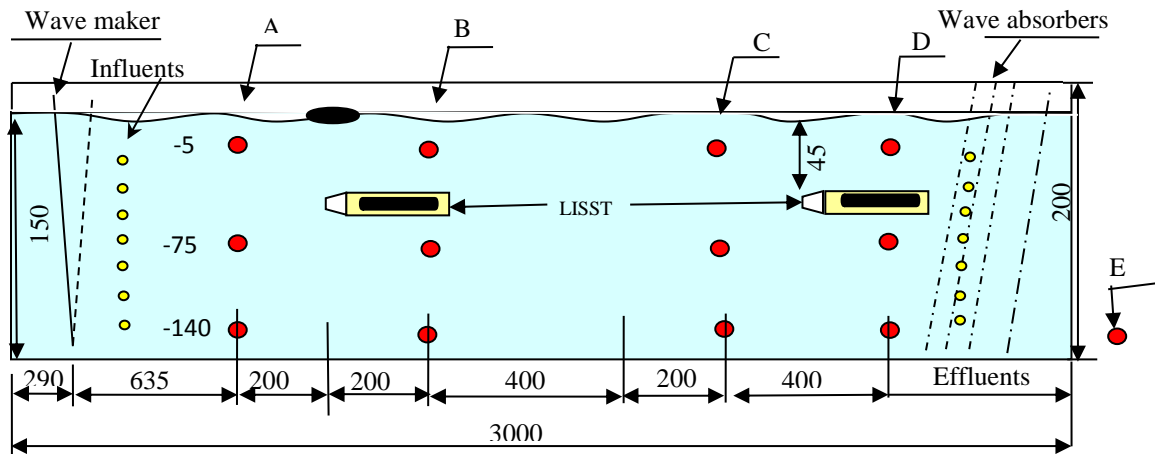


Figure 7.1: Schematic Diagram (Not to Scale, all Units in Centimeters) Showing the Location of the Oil Source (Black Ellipse Between A and B), LISST Particle Counters, Sampling Locations at A, B, C, D (3 depths), and the Effluent Port E. LISST#1 is at Location B (1.2 m) and LISST#2 is at Location D (12 m) Downstream of Oil Release.

7.2 Results and Discussion

7.2.1 Composition and Physical Properties of Test Oils

In their unweathered state, bitumen blends have viscosities of >200 cSt at 15 °C and are classified as heavy oils (Chapter 3). The bitumen blends contain a greater percentage of resin and asphaltenes compared to Heidrun crude oil, which is the medium conventional crude. Depending on the rate of diluent released and seawater temperatures during a spill, these high molecular weight (>500 atomic mass units) chemicals can greatly affect the physical properties (e.g. density and viscosity) of the oils that are relevant to the choice of methods used for responding to spills. The source of these chemicals in blended bitumen products is most likely from the crude bitumen. Oil Sands products are expected to significantly weather within a few hours post-spill; thus, significantly altering their viscosities, which would limit chemical dispersant effectiveness (King et al., 2017a). Heidrun is not expected to weather to the extent that limits its treatment with chemical dispersant after a spill. The viscosities and densities of the four oils, at the recorded experimental seawater temperatures are found in Supporting Materials (Table 7S.1), where one notes a viscosity range varying from 60 up to 10,000 cSt.

7.2.2 Test Conditions during Wave Tank Studies

To assess the effect of water temperature on the chemical dispersion of the test oil products, experiments were conducted consecutively during early spring and late summer of 2016 and 2017, and the physical measurements of the seawater obtained are recorded in Table 7S.1 of the Supporting Materials. The water was obtained directly from the Bedford Basin in Dartmouth, Nova Scotia, and water temperature ranged from 3.7 to 19.7

°C, over the duration of the study. Water temperature can affect dispersant effectiveness when treating heavy conventional oils such as IFO 180 (Li et al., 2010). Salinity is also an important factor to consider, since it can affect the efficacy of oil spill dispersants applied to conventional oils, in particular those like COREXITEC®9500A that are formulated for saltwater environments (Chandrasekar et al., 2006). In our experiments, the salinity over the spring and summer months ranged from 25.5 to 30.4 part-per-thousand (ppt). The small difference between these values suggests that salinity variation would not make a measureable impact on the behavior of the test oils during the experiments.

7.2.3 Total Petroleum Hydrocarbons in the Water Column

Averaged total petroleum hydrocarbon (TPH) concentrations at all depths (0.5 to 1.4 m) for location D (12 m from oil release point; Figure 7.1.) in the test tank are plotted in Figure 7.2 as a function of time for the four oils under natural and chemically enhanced dispersion conditions. Low TPH concentrations were observed under natural dispersion conditions. The concentration during the summer was slightly higher than spring (warmer temperatures decrease the viscosity thus affecting dispersion), but remained an order of magnitude smaller than the chemically dispersed TPH for both seasons.

The increased oil concentration in the water column is controversial, since it makes the oil more bioavailable to aquatic species but reduces the amount of oil reaching sensitive habitats in shorelines. Through natural dilution and transport the TPH concentrations in the water column dropped to near background levels. Sufficient mixing and water currents to transport dispersed oil are critical components when assessing not

only dispersant effectiveness to treat oil products, but the rate of dilution and transport to ensure minimal impacts to aquatic species and their habitats.

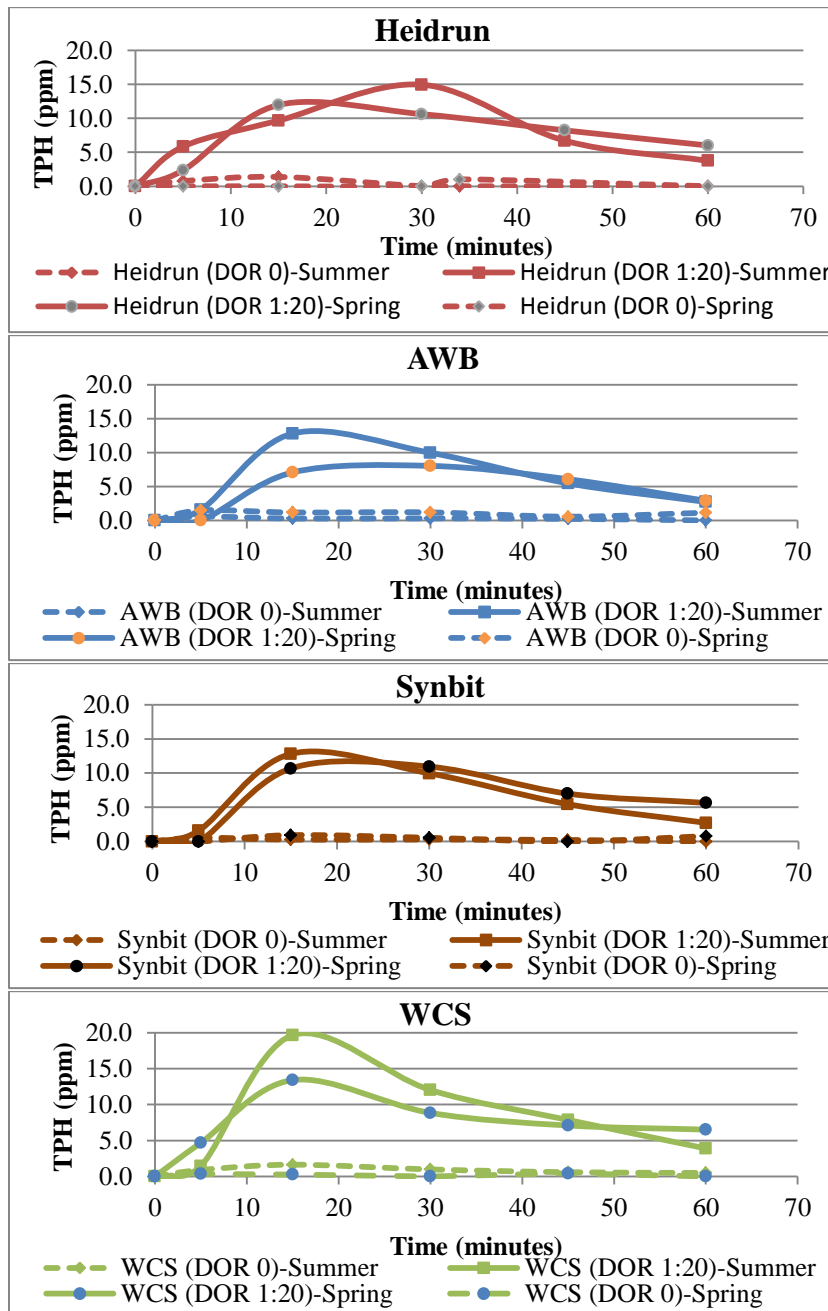


Figure 7.2: TPH Concentrations in the Water Column Over a Depth of 0.05 to 1.4 m Located 12 m Downstream from the Oil Release Point for Treated and Untreated Oils.

7.2.4 *In situ LISST*

Previous wave tank studies have shown through the use of LISST particle size analyzers that surface oil that becomes dispersed and driven into the water column under breaking waves in the presence of chemical dispersant has oil droplet sizes in the range of 2.5 to 50 μm in a distinctive, bimodal or multimodal droplet size distribution (Li et al., 2009c). These oil droplets remain dispersed and do not coalesce. Oil droplets that have been produced by breaking waves in the absence of dispersant are typically larger than 50 μm , have a unimodal distribution, and tend to rise to the surface where they coalesce. The use of the LISSTs is suitable at differentiating between chemically enhanced and naturally dispersed oil. However, a recent study by Zhao et al. (2018) expressed major concerns associated with using the instrument that include the impact of high concentrations and/or out-of-range particle (droplet) sizes on the LISST reading. The study reported that when high particle concentration reduced the optical transmission to below 30%, the measured peak value tended to underestimate the true peak value, and the accuracy of the LISST decreased by ~8% to ~28%. The out-of-range sizes of particles affected the LISST measurements when the sizes were close to the LISST measurement range. The large out-of-range particles slightly changed the size distribution of the in-range particles, but their concentration was preserved.

Figure 7.3 reports contour plots of data obtained from the LISST-100X (12 m from the oil application) for the natural dispersion case as a function of time. The vertical axis (y-axis) represents particle or oil droplet size (μm) and the colour gradient (z-axis) represents the volume concentration ($\mu\text{L/L}$). Additional information on particle sizes, volume concentrations and sauter values can be found in Figures 7S.1 to 7S.5

(Supplementary Materials). Without any treatment, the four oils showed poor natural dispersion under spring and summer conditions, where very little oil (in dispersed form or as small droplets) was in the water column. Only the largest size ($>100\ \mu\text{m}$) droplets had a non-negligible concentration, but it was still low. Information collected from the first LISST (1.2 m from oil release) was placed in Figures 7S.1 to 7S.5 (Supporting Materials).

The chemically enhanced dispersed oil detected by the first LISST 1.2 m from oil release (Supplementary Materials) remained dispersed in the water column and was detected by the second LISST. Figure 7.4 shows that the LISST, located 12 m from oil release, recorded higher volume concentrations and smaller particle sizes ($<50\ \mu\text{m}$) in the water column compared to natural dispersion (without dispersant) of all oil types for spring and summer conditions. In general for all oils, higher concentrations of small particles ($<50\ \mu\text{m}$) were detected when surface spills of the oils were treated in summer conditions. The chemical dispersion of Heidrun and synbit (both in spring and summer) produced large concentrations of very small droplets ($<10\ \mu\text{m}$). This occurred also for the chemical dispersion of WCS, but only in summer conditions.

7.2.5 Dispersant Effectiveness (DE)

The averaged TPH concentrations for all depths at each sampling location (A, B, C, D, and E) were used to generate DE (%) values, which were obtained over the duration of the entire experiment by computing the fraction of dispersed oil in the effluent from the wave tank and the residual dispersed oil in the water column at the end of each experiment. Details on calculating DE (%) values during wave tank studies can be found in King et al. (2015a&b).

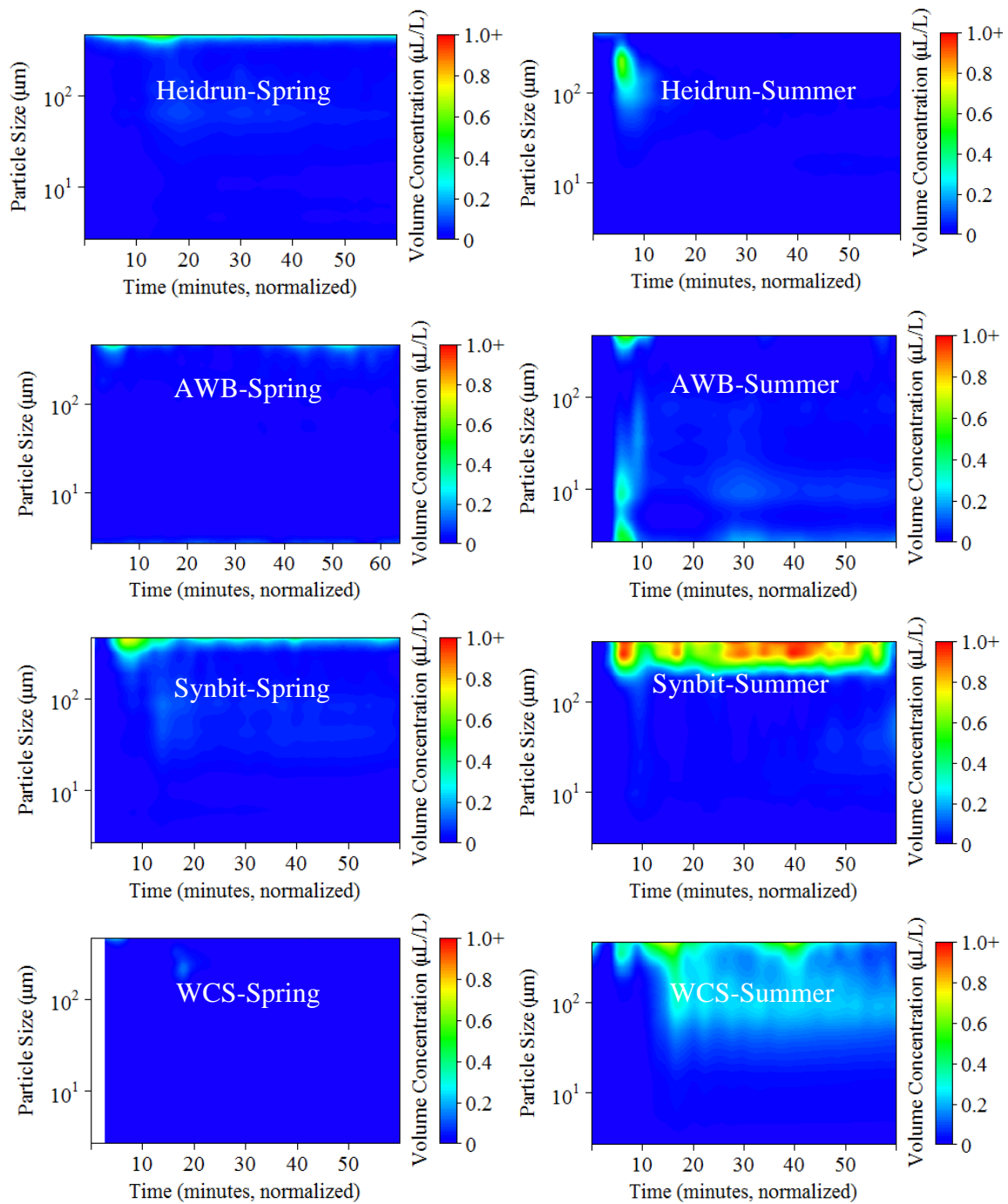


Figure 7.3: Contour Plots (LISST data, 12 m from oil release) Showing Seasonal Effects on the Concentration of Oil Particle Size Simulated in the Wave Tank for the Natural Dispersion of Four Oil Types.

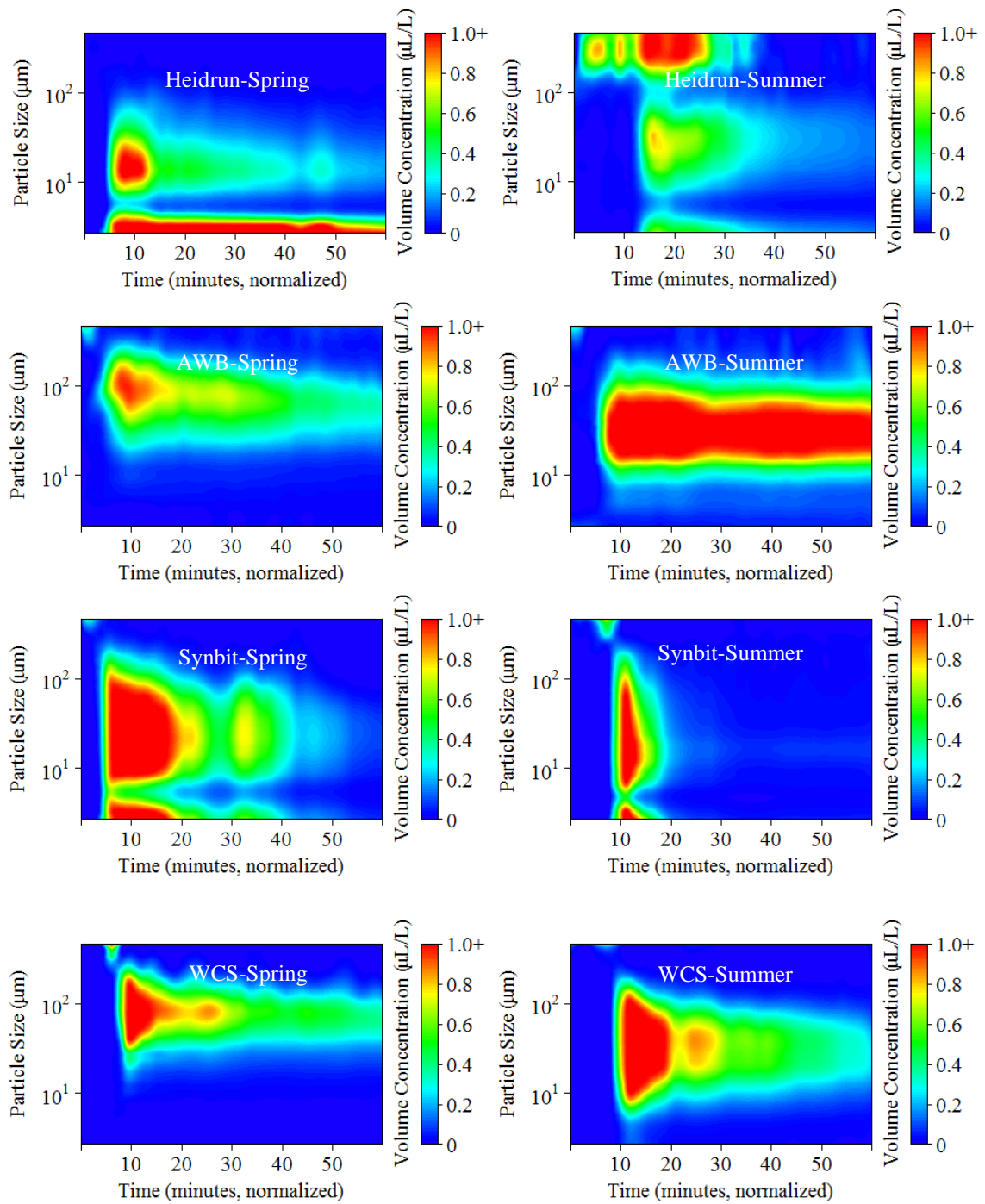


Figure 7.4: Contour Plots (data from LISST, 12 m from Oil Release) Illustrating Seasonal Effects on the Concentration of Oil Particle Size for Chemically Enhanced Dispersion of Four Oils.

Table 7S.1 (Supporting Materials) shows the natural and chemically enhanced dispersion of the four oils under breaking waves and spring and summer environmental conditions. For each untreated and treated oil type, DE testing was performed in triplicate covering a range of seawater temperatures over two seasons. Natural dispersion effectiveness ranged from 0 to 7% for all four oils based on the study conditions. The application of a chemical dispersant had a significant ($p < 0.05$) effect on dispersion of all oil types (Table 7.1). Heidrun crude oil was readily dispersible when treated with chemical dispersant over the entire temperature range with DE values $>70\%$ for both spring (7.1 ± 0.8 °C) and summer (16.8 ± 1.6 °C) conditions. With this medium crude oil, the reported seawater temperature range did not have a significant ($p = 0.28$) influence on the effectiveness of the chemical dispersant (Table 7.2). In the discussions to follow reference is made to viscosities in units of centipoise (cP) when taken from the literature. To get viscosity in cSt, divide cP by the density of the oil. Oil viscosity is critical in studying dispersants because thin, medium viscosity ($<2,000$ cp) oils are readily dispersible, but heavy, highly-viscous ($>10,000$ cP) oils are not (National Research Council, 1989; GENIVAR, 2013). Lewis (2004) reported that a less viscous (2,000 cP) oil treated with COREXIT®EC9500A dispersed quickly and completely, but a more viscous (7,000 cP) fuel oil did not. This implies that viscosity has an effect on dispersion of oil; however in that study the time window of opportunity to treat weathered oil is not considered. Since, Heidrun's viscosity is <2000 cSt even with seasonal temperature factored in, the performance of the chemical dispersant was not affected when treating it. For the bitumen blends (e.g. AWB, synbit and WCS), DE was notably lower (~ 20 to 30% less) most likely due to the fact that these products are more viscous, in their pre-

weathered state, than the fresh Heidrun crude oil. As mentioned previously cSt is calculated from cP, by dividing it by the density of oil. In this case, cSt values would be approximately 10% higher than cP. Also, the dispersant had an effectiveness of 40 to 50% and low as 30% for bitumen blends with viscosities of 4000 and near 10,000 cSt, respectively. Also, significantly ($p < 0.05$) higher DE values were recorded during summer than spring conditions, since temperature affects the viscosity of these heavy oil products. This is consistent with a study on heavy conventional oil products such as IFO 180 which was effectively dispersed with a DE of 90 % at high temperature (16 °C) and had low DE (<10%) at low temperatures (<10 °C) using the same test facility (Li et al., 2010). Also, laboratory studies showed a 20% difference in DE of heavy oils between 16 and 5 °C (Srinivasan et al., 2007). The seasonal effects (% difference) on DE for the bitumen blends were greatest (22.3%) for AWB (dilbit) and the least (10.8%) for synbit (Table 7.2). This is most likely due to the fact that synthetic crude as the diluent portion of synbit is less volatile than the condensate in AWB (dilbit). Both diluents (condensate and synthetic crude) are present in WCS (dilsynbit), so the seasonal effect (% difference) on DE falls between the other two blends. Also, one notes that the oils prior to treatment have different viscosities, since they were weathered prior to testing.

These data were supported by the LISST particle size distribution data (Figures 7 and 8; Supplementary Materials), where the majority of the particles produced were <50 μm in size when the chemical dispersant (COREXITEC®9500A) was applied to the oils. Under summer-time conditions, dispersant application removed more of the oil from the water surface compared to spring-time.

Table 7.1: ANOVA Analysis (single factor-Excel, Additional Information Found in the Appendix Table 7S.2) Show the Dispersion Effectiveness (DE) of Dispersant to the Natural Dispersion of Four Oils Under Breaking Waves. A p -value <0.01 is significant, indicating that treatment with dispersant is more effective than natural dispersion. Average \pm Standard Deviation (Ave \pm std).

Treatment	n^*	Spring			Summer		
		Value (%) (Ave \pm std)	Diff. (%)	p	Value (%) (Ave \pm std)	Diff. (%)	p
No Treatment-AWB	6	1.7 \pm 1.6	-	-	1.8 \pm 1.1	-	-
Corexit/AWB	6	30.6 \pm 2.8	-29	1.0E-04	53.2 \pm 3.3	-51	1.0E-05
No Treatment-Heidrun	6	2.7 \pm 1.2	-	-	1.8 \pm 1.1	-	-
COREXIT/Heidrun	6	70.6 \pm 1.7	-68	5.0E-07	76.0 \pm 7.4	-74	7.9E-05
No Treatment-Synbit	6	4.2 \pm 3.0	-	-	4.0 \pm 1.6	-	-
COREXIT/Synbit	6	48.4 \pm 4.8	-44	1.7E-04	59.2 \pm 2.9	-55	9.0E-06
No Treatment-WCS	6	2.7 \pm 1.6	-	-	3.5 \pm 1.0	-	-
COREXIT/WCS	6	41.3 \pm 4.2	-39	1.2E-04	53.5 \pm 4.0	-50	3.1E-05

* $n = n_1 + n_2$ observations

Table 7.2: ANOVA Analysis (single factor-Excel, Additional information found in the Appendix Table 7S.3) Show the Dispersant Effectiveness (DE) of Oils Affected by Seasonal Water Temperatures Under Breaking Waves. The p -value <0.01 is significant, indicating that difference in temperature (spring versus summer) had an effect on the performance of the dispersant. The Average \pm Standard Deviation (Ave \pm std).

Treatment	n^*	The Effect of Seasonal Water Temperature on DE		
		Value (%) Ave \pm std	Diff. %	p
COREXIT/AWB-Spring	6	30.6 \pm 2.8	-	-
COREXIT/AWB-Summer	6	53.2 \pm 3.3	-23	0.00088
COREXIT/Heidrun-Spring	6	70.6 \pm 1.7	-	-
COREXIT/Heidrun-Summer	6	76.0 \pm 7.4	-5.4	0.28
COREXIT/Synbit-Spring	6	48.4 \pm 4.8	-	-
COREXIT/Synbit-Summer	6	59.2 \pm 2.9	-11	0.029
COREXIT/WCS-Spring	6	41.3 \pm 4.2	-	-
COREXIT/WCS-Summer	6	53.5 \pm 4.0	-12	0.023

* $n = n_1 + n_2$ observations

7.2.6 Modelling Dispersion Effectiveness

The four different oil types, consisting of fresh and artificially weathered products, selected for this study cover a broad range of viscosities (*ca.* 60 to 10,000 cSt) over two seasons, with measured DE values (Supporting Materials; Table 7S.1). The untreated (naturally dispersed) oil DE values were plotted as a function of oil viscosity (Figure 7.5). The plot revealed that natural DE was very similar or changes were minimal for all four oils dispersed under spring and summer conditions. Figure 7.6 reports the DE as function of the viscosity for the chemically enhanced dispersion. A linear model was fitted to the plot of chemical DE as a function of the log of the viscosity of oil (Figure .6). Therefore one would write the equation 7.1:

$$DE = m \ln(v) + b \quad (7.1)$$

where ‘*m*’ is the slope, ‘*v*’ is the viscosity of the oil and ‘*b*’ is the y-intercept.

The fit was generally good, as one notes visually through the absence of any systematic bias (undershooting or overshooting), and the large coefficient of determination, $R^2 > 0.86$. If the viscosity of oil at a specific water temperature is known or can be computed after the initial release, then the model can be used to estimate the chemically enhanced DE (%) of spilled oil provided the conditions are similar to this study.

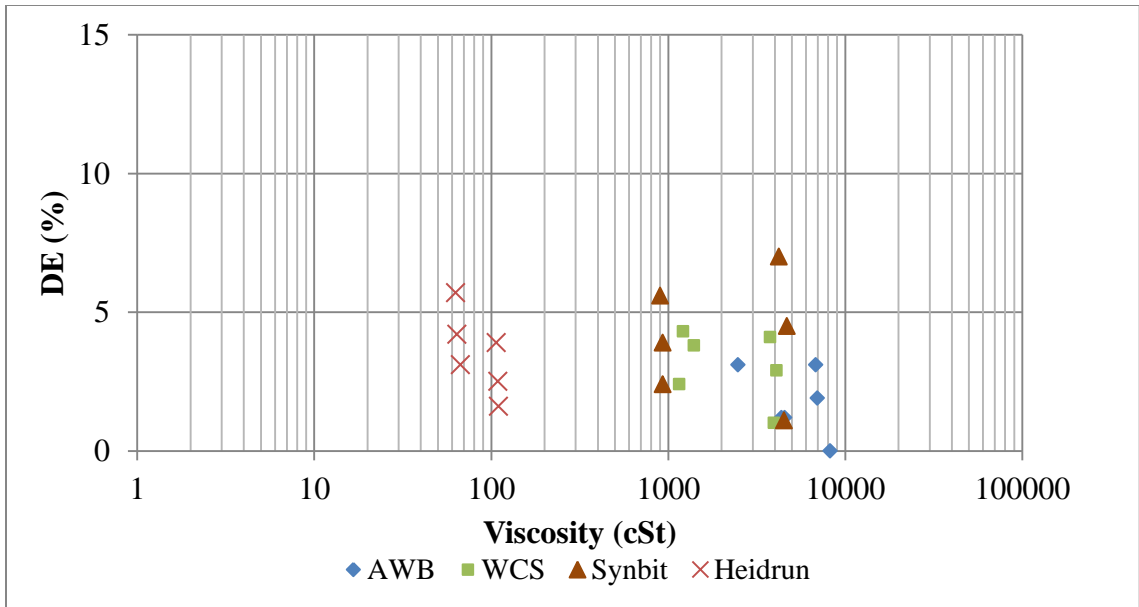


Figure 7.5: A plot of Effectiveness of Natural Dispersion as a Function of Oil Viscosity. Experiments were Conducted in Spring and Summer (Table 7S.1).

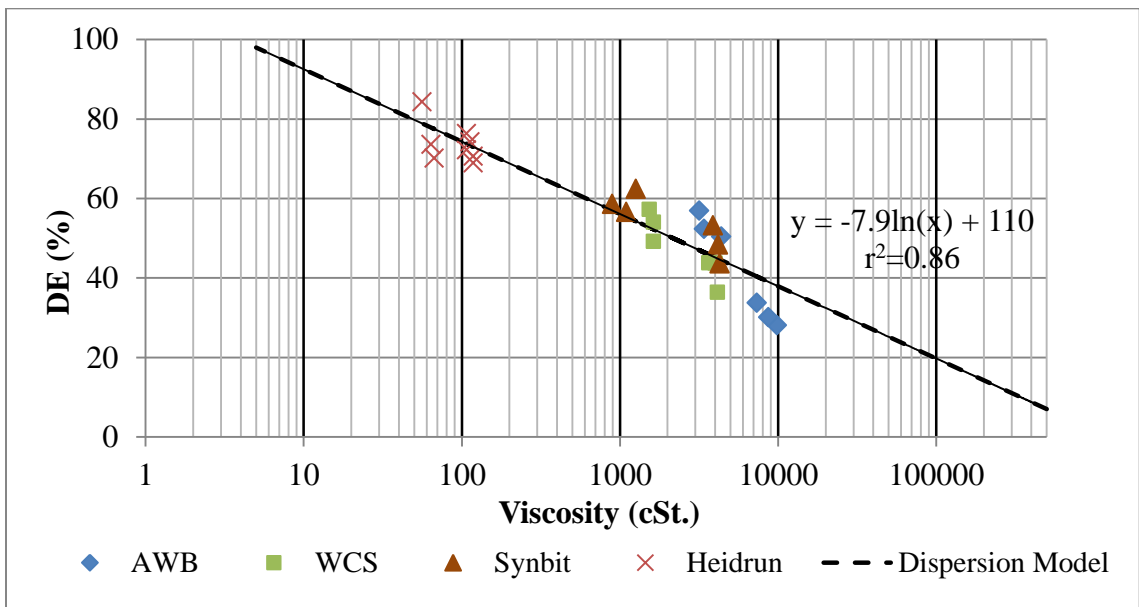


Figure 7.6: A Plot of Effectiveness of Chemically Enhanced Dispersion as a Function of Oil Viscosity. Experiments were Conducted in Spring and Summer with Fresh and Weathered oils (Table 7S.1). A Dispersion Model was Fitted to the Data Points that Represent Four Different Oil Types.

7.2.7 Combining DE and Viscosity Functions to Estimate the Window of Opportunity to Treat Surface Spills of Oil after the Initial Release

In previous experiments, AWB, WCS, synbit and Heidrun crude were naturally weathered under mild conditions in the spring and summer in flume tank to examine changes in their physical properties. The empirical data from each experiment were fitted to a hyperbolic function with their coefficients of determination, R^2 , ranging from 0.86 to 0.99 (Chapter 6). The viscosity model (equation 7.2) was previously validated by King et al. (2017a) to illustrate changes in the viscosity of the oils weathered on water:

$$v_{predict} = (v_0 + (v_f - v_0) \left(\frac{t}{T+t} \right)^n) \quad (7.2)$$

where v represents the logarithm of viscosity (cSt) of weathered oil, v_0 and v_f are the initial and final oil viscosities, respectively, and ‘ t ’ represents time in hours. The advantage of Eq. 7.2 is that it allows for the rapid increase in the early hours, and then for the plateaus in the data, the fitting coefficient ‘ T ’ is incorporated, where a large value of ‘ T ’ is considerably offset by a relatively smaller accompanying value of n . The power ‘ n ’ controls the rate at which the early values approach the final value (v_f). This Eq. 7.2 was generated when the oil was weathered under calm conditions.

Equation 7.2 can be substituted for v in Eq. 7.1 to determine DE as function of v with time of weathering of oils, used in this study:

$$DE = a \ln(v_{predict}) + b \quad (7.3)$$

In order to substitute equation 7.2 to produce equation 7.3, the oil must first weather under calm conditions and then change to an energetic state where dispersant is applicable. Equation 7.3 could be used to estimate DE values for all four oils weathered in the spring and summer (Table 7S.4, Supporting Materials) for Chapters 5 and 6. A

previous report (Fingas, 2013) suggested that temperature and time were greater factors in oil evaporation than surface wind speed or oil slick thickness for a wide range of crude oils. In contrast, Gros et al. (2014) determined that wind speed strongly affected the thickness of the oil slick and thus evaporation very early in an experimental spill of Norwegian crude in the North Sea. As previously mentioned in Chapter 6 the thickness of the oil slick can affect the rate of weathering of condensate bitumen blends, so there may be limitations on the use of equation 7.3. However, the results of that study showed a 4 mm thick slick of AWB's viscosity exceeded 10,000 cSt within three hours of weathering on temperate water. In cooler temperatures the rate of weathering of oil is slower (Chapter 6); however, AWB's (dilbit) viscosity exceeded 10,000 cSt in 24 hours. It took longer for both WCS and synbit to reach a similar viscosity. This would suggest that under similar conditions that there is a wider window of opportunity to use dispersant to treat spills of these later blends spilled in cooler waters. However, the data is based on an oil slick thickness of 4 mm and one must note that oil slickness affects the rate of weathering of oil (Chapter 5) and thus the window of opportunity could be shorter for thinner slicks of oil weathered under similar conditions. The function proposed here may be applicable to other oil types with the limitations mentioned above. Also, if the oil's viscosity can be computed, then equation 7.1 could be useful to estimate chemical DE of dispersant to treat oil spills that have weathering on water over time.

7.3 Conclusions

Natural dispersion effectiveness (DE) was $\leq 7\%$ for the bitumen blends and conventional oil under breaking waves in test conditions for spring and summer simulated in the wave tank. The droplet size distribution resulting from dispersant

produced a higher concentration of oil droplet sizes ranging from 2.5 to 50 μm compared to natural dispersion of the oils. The application of the chemical dispersant (COREXITEC®9500A) had a significant ($p < 0.05$) effect on dispersion of all oil types with a DE increasing by an order of magnitude over that observed for natural dispersion. Seasonal effects (namely water temperature) had a significant ($p < 0.05$) effect on chemical DE for all oils, except the conventional crude, Heidrun. Heidrun's viscosity is at least an order of magnitude lower than the bitumen blends in this study. The change in temperature due to season has a small effect on the viscosity of Heidrun; therefore, it is readily dispersible. The application of dispersant to treat an oil spill would need to produce a net environment benefit over natural attenuation or other alternative oil spill response methods.

In this study, there was a semi-log linear relationship between chemical DE and oil viscosity taking into account oil type, including fresh and weathered products, over two seasons to evaluate the effect of water temperature. If the viscosity can be computed any time after the initial oil spill, the function may be used to estimate a DE value to assess the potential to use chemical dispersant to treat spills. In addition, chemical dispersant still showed some effectiveness when the oil's viscosity exceeded 2000 cSt, which is contrary to the literature.

In this study, a viscosity hyperbolic function was combined with the newly developed dispersion model from this study to potentially estimate DE values for dispersant to treat weathered oil. The application of it implies that the oil was initially weathered under calm prior to energetic conditions, where dispersant might be applicable. Previous studies (Chapter 5) showed that AWB's viscosity exceeded 10,000

cst within three hours of weathering on water at a temperature of 22 °C. This would suggest that the window of opportunity to treat such spills would be extremely short and dispersant would not be considered a viable response option under such conditions. In cooler temperatures the rate of weathering of oil is slower (Chapter 6); however, AWB's (dilbit) viscosity exceeded 10,000 cSt in 24 hours. It took longer for both WCS and synbit to reach a similar viscosity. This would suggest that under similar conditions that there is a wider window of opportunity to use dispersant to treat spills of these later blends spilled in cooler waters. However, the data is based on an oil slick thickness of 4 mm and one must note that oil thickness affects the rate of weathering of oil (Chapter 5) and thus the window of opportunity could be shorter for thinner slicks of oil weathered under similar conditions. In conclusion, the results suggest that the window of opportunity is very narrow ranging from a few hours to a couple of days (at best) where dispersant would provide moderate effectiveness at treating spills of various bitumen blends after the initial release. Although there are limitations with application of the dispersant model, the approach may offer some insight for future work on dispersant to treat weathered oil.

Chapter 8: Conclusions and Contributions

8.1 The Main Findings of this Dissertation

The main findings are chapter-specific and conclusions are provided within the relevant empirical chapters. This section integrates the experimental findings to address the study's objectives.

- *To characterize various bitumen blends and comparative conventional oils to provide information pertinent to spill response and ecological impacts.*

Oil sands products (bitumen blends) contain monocyclic aromatics (e.g. benzene, toluene, ethylbenzene and xylenes) and straight-chain saturates, but in different proportions compared to conventional oil products. The groups of chemicals present depend on the diluent used to produce the products, and they are expected to readily degrade after the initial release. Bitumen blends also contain polycyclic and heterocyclic aromatics and their alkylated homologues in different proportions compared to the conventional oils. The presence of these chemicals is most likely derived from the crude bitumen, and is of environmental importance, since they are more toxic and carcinogenic than the saturate hydrocarbons. Oil sands products (non-conventional oils) contain many of the same chemicals (e.g. saturates, aromatics, resins and asphaltenes) present in conventional oils. The relative amount of these chemicals varies compared to conventional oils, in particular, the high-molecular weight resins and asphaltenes. These recalcitrant chemicals can greatly affect the oils' physical properties (e.g. density and viscosity) that are relevant to spill response as the oil products weather when spilled at sea. Unweathered bitumen blends have similar physical properties, since they are engineered to meet pipeline specifications. Final examination of these products lead into

further study to address the subsequent objectives, regarding how natural weathering transforms the oil into substances with physical and chemical characteristics that vary from the original source material spilled at sea, and how changes affect spill response and impacts to aquatic areas.

- *To develop an empirical model to show dissolution of monocyclic aromatics in water released from the diluent of surface spills of bitumen blends and evaluate the effect of season (spring and summer) and the associated climatic factors on the dissolution of monocyclics in water, so that the information can be used in the preparation of environmental risk assessments.*

This study was limited to only two seasons (spring and summer) and not the more extreme conditions of Canadian winters or aquatic areas that become influenced by the presence of ice. The system used would require major modifications to prevent plumping from damage due to freezing temperatures. Fall was not considered. In early fall, temperatures can be similar to spring and in mid to late fall, freezing temperatures create operational problems. A newly developed model was fitted to the monocyclic aromatics empirical data that can be used to show the rate of dissolution and decay of monocyclic aromatics in water from surfaces spills of bitumen blends over two seasons. The monocyclic aromatics were selected, since they were expected to be the major components of the water soluble chemicals released from condensate used as a diluent in bitumen production. Of the climatic factors assessed: wind speed, temperature (air and water) and sunlight had a significant ($p < 0.05$) effect on the dissolution of monocyclics in water from the weathering of oils. In summer-time, sunlight exposure had a major influence on the rate of decay of these chemicals in the water column. Overall season had a significant ($p < 0.05$) influence on the dissolution of monocyclics in water for the

weathering of WCS, AWB and Synbit. In spring-time, the combination of colder temperature and reduced sunlight exposure caused a slower rate of decay of the monocyclics in water. Whereas these factors (in particular light intensity) contributed to a higher rate of decay (photo-chemical weathering) of the monocyclics in water from oil spilled in summer-time. These results aid to address the current debate over which climatic factors including temperature, wind speed and sunlight have the most influence on the weathering of oil; in particular dissolution of monocyclic aromatics in water. Our study suggests that all three factors are major contributors, but their influence on the weathering process is most likely driven by oil type and the season in which a spill occurs.

The rate of dissolution of monocyclic aromatics in water was <5%. Through mass different, the evaporation of the same chemicals in air accounted for a significant portion (>95%) of the acutely toxic chemical fraction of the diluent released from the oil spills. This suggests that the diluent released from surface spills of oil sands products would have a greater impact on oil spill responders, birds and mammals at the air/water boundary in the vicinity of the spill and to a lesser extent to species residing in the water column. However, oil type, volume released, rate of dilution with transport, and whether the spill is a one time or continuous release are factors that must be considered. The dissolution data from the study can be combined with species sensitivity data that are site specific to prepare environmental risk assessments for oil spill response planning in coastal waters.

- *To develop empirical models for the time evolution of oil physical properties and integrate it with information on the effectiveness of various oil spill response options to produce a decision-making matrix to aid spill response.*

It was found that there was a major difference in the time evolution of oil properties (density and viscosity), raising doubt on the accuracy of weathering models that do not consider the thickness of the oil slick especially when applied to condensate bitumen blends. The new hyperbolic model estimates (Chapter 5) of oils' physical properties (density and viscosity) were incorporated with data on oil spill response options from the literature to create a decision matrix that indicated that most response options, including chemical dispersants, work much more effectively within 48 hours of the initiation of weathering of surface spills of bitumen blends. After that window of opportunity closes, natural attenuation or *in situ* burning are the only options remaining, but containment of oil is a limiting factor for *in situ* burning. However in this case, rapid changes in the physical properties of the bitumen blend at a thickness of 4 mm considerably limits the choice of oil spill countermeasures, so one would assume that if thinner oil slicks weather even more quickly the conclusions may not be that different. Also, the information generated from the study was only applicable to surface spills in temperate waters.

- *To evaluate seasonal climatic effects on the changes in density and viscosity of oils weathered on water.*

This study was limited to only two seasons (spring and summer) and not the more extreme conditions of Canadian winters or aquatic areas that become influenced by the presence of ice. The system used would require major modifications to prevent plumping from damage due to freezing temperatures. Fall was not considered. In early fall, temperatures can be similar to spring and in mid to late fall, freezing temperatures create operational problems. Experimental oil spills of three blended bitumen products and Heidrun crude oil on water were monitored during exposure to natural climatic

factors (e.g. sun, wind, rain, and varying air and water temperatures) over two seasons (Chapter 6). Regardless of the season (spring and summer), AWB (dilbit) compared to the other test oils (WCS (dilsynbit), synbit, and conventional crude) showed the greatest % difference in its physical properties as it weathered on seawater. This suggests that condensate, added as a diluent, greatly affects the rate of evaporative weathering of the original product when it is spilled in aquatic areas; this, in turn, puts great constraints on oil spill response efforts. Synthetic crude is a better choice for use as a diluent than condensate, as the different proportions of chemicals that make up its composition are less susceptible to evaporative natural attenuation over the two seasons evaluated.

A previously developed hyperbolic model (Chapter 5) was fitted to the empirical density and viscosity data with a coefficient of determination, ranging from $R^2 > 0.86$ to 0.99. Regression analysis revealed that significant ($p < 0.05$) trends exist with the seasonal climatic factors and changes in the density and viscosity of the oils weathered on water. The study aids to address the current debates over whether temperature or wind speed is the major contributing factor affecting the weathering of oil. Temperature, wind speed, and sunlight exposure were all contributing factors in the weathering process for this study. However, sunlight was the only factor significantly affecting the weathering of the conventional crude oil, Heidrun. This oil contains a greater portion of aromatics that are more susceptible to photo-chemical weathering. This would suggest that different proportions of the major chemicals (saturates, aromatics, resins and asphaltenes) present in oil could affect which climatic factors influence the weathering of oil.

Season had a significant ($p < 0.01$) effect on changes in the densities and viscosities of all the tested oils weathered on water between 96 to 192 hours. However, it

had no significant effect on the weathering of the oils up to 96 hours on water. The difference in the later stages of weathering of the oils was greater in summer than spring. This would suggest that the warmer temperatures and possible higher amounts of sunlight exposure in summer contributed to the difference. Also, most of the evaporation of oil takes place within the first 24 hours of a spill, so the difference at these later points in time suggest photo-chemical weathering and biodegradation are most likely greater in warm summer waters for the tested oils.

Natural attenuation will always play a role in oil spill response operations as there is no other clean-up strategy that is 100% effective. This study suggests that the major contributing factors were temperature, wind speed and sunlight exposure that influenced the weathering of bitumen blend spills. Therefore, evaporation and photo-chemical weathering could play a critical role in the natural weathering of these oils. The production of oxidized chemicals from photo-chemical weathering could have implications for oil spill response planning, if natural dilution and mixing are minimal. Also, while biodegradation processes play a role in the weathering of oil, the recalcitrant (e.g. resins and asphaltenes) nature of bitumen will always pose a challenge.

Whether oil will float or sink depends on its density and the density of the liquid it is placed in. At 15 °C, saltwater has a density ranging from 1.020 g/cm³ (brackish near coastal areas where there is fresh receiving water) to 1.030 g/cm³ (marine), whereas fresh water has a density of 1.000 g/cm³. Bitumen blends are new oil products produced by blending crude bitumen with a lighter hydrocarbon, often referred to as diluent (e.g. condensate, synthetic crude, combination of both, etc.) to reduce viscosity to a range required for transport by rail, pipelines and tankers. These products have a density that is

less than fresh water and will float in the initial stages of a spill. Thus, “fresh” blended bitumen that is being transported within a pipeline will float when spilled onto fresh and marine waters. However, as with conventional crude oils, density and viscosity will begin to change following its release into the open environment due to natural weathering processes such as evaporation, biodegradation, dissolution, photo oxidation, etc. It is important to note that for dilbit, the low molecular wt. diluent (condensate) may be lost quite rapidly. The length of time bitumen blends will remain floating will depend on their chemical composition, oil slick thickness, and the season the spill occurs including the climatic factors acting on it (Chapter 6). In more temperate (22 °C) water conditions (Chapter 5) experienced during late summer, the natural weathering of Access Western Blend (dilbit; condensate mixed with crude bitumen) caused the oil to exceed the density of fresh water within 24 hours. Based on experimental studies and actual field observations, weathered condensate/bitumen blends (AWB) may remain floating from 24 hours to days. In the case of the Enbridge Kalamazoo River oil spill, the sinking of dilbit was attributed to a combination of high temperature conditions and high energy mixing (from flood waters) that facilitated an interaction between sediments suspended within the water column and the bitumen blend. Laboratory studies (Government of Canada, 2013; section 8.3) have shown that this phenomenon may also occur in some coastal waters that contain high concentrations of suspended particles. It is important to note that weathered heavy conventional crude oils and refined products (e.g. Bunker C fuel oil) may also sink under similar natural environmental conditions. Therefore, further studies should be conducted to examine the interaction of weathered bitumen blends with

suspended particles in aquatic settings to observe OPA formation and its effects on the buoyancy of the products.

- *To develop empirical models to estimate the ‘window of opportunity’ and limitations of COREXIT®EC9500A to treat spills of weathered oil.*

Experiments were conducted over two seasons in 2017 to assess the impact of seasonal water temperatures on oil dispersion in the tank with breaking waves at a height of 0.4 m (Chapter 7). Results showed that the dispersion effectiveness (DE) without the use of chemical dispersant was <7%, whereas the application of dispersant increased the DE by an order of magnitude to a significant ($p<0.05$) degree. In addition, chemical dispersant still showed some effectiveness when the oil’s viscosity exceeded 2000 cSt; which is contrary to some of the results in the literature. For this study, various oil types including fresh and weathered oils, and seasonal temperature effects produced a broad range of oil viscosities with measured chemical DE values that were fitted to a linear regression model. If viscosity of the oil can be computed after release, then the model could be used to estimate a DE value for dispersant to treat the spill.

Previous studies (Chapter 6) documented that there was a seasonal effect on the rate of change in viscosities of the four oils and a hyperbolic model (Chapter 5) was fitted to the empirical data. That model was combined with the newly developed dispersion model from this study to estimate DE values for viscosities at various times after the oil spill, if conditions change from calm to more energetic (sufficient mixing energy in the form of waves) sea states. The findings suggest that dispersant effectiveness declines as the viscosity of the oil increases with time of weathering and lower seasonal water temperatures, but dispersant effectiveness is predicted to be better than natural dispersion

based on the study conditions. AWB's viscosity reached 10,000 cSt within three hours of weathering on water at an average temperature of 22 °C (Chapter 5). This would suggest that the window of opportunity to treat such spills would be extremely short and dispersant would not be considered a viable response option under such conditions. In cooler temperatures the rate of weathering of oil is slower (Chapter 6); however, AWB's (dilbit) viscosity exceeded 10,000 cSt in 24 hours. It took longer for both WCS and synbit to reach this viscosity value. This would suggest that under similar conditions, there is a wider window of opportunity to use dispersant to treat spills of these later blends spilled in cooler waters. However, the data is based on an oil slick thickness of 4 mm and one must note that oil thickness affects the rate of weathering of oil (Chapter 5) and thus the window of opportunity could be shorter for thinner slicks of oil weathered under similar conditions. In conclusion, the results suggest that the window of opportunity is very narrow ranging from a few hours to a couple of days (at best) where dispersant would provide moderate effectiveness at treating spills of various bitumen blends after the initial release. Although there are limitations with the application of the combined viscosity hyperbolic and dispersant function, the approach may offer some insight for future work on dispersant to treat weathered oil.

8.2 Contributions of the Research

8.2.1 Theoretical Contributions

The theoretical contributions of this dissertation are in the knowledge or value added to applied theory of the natural weathering of oil and how changes in the physical properties of oil over time could affect spill response and risk assessment. This research introduced an empirical expression for the evolution of oil density to illustrate those

conditions, where oil sands products have the potential to sink in aquatic areas. A second function to show changes in viscosity of oil naturally weathered on water, and estimates the time window of opportunity to deploy various oil spill response options that are affected by the viscosity of oil spilled in aquatic systems. Also, an empirical expression to show the rate of release and decay of monocyclic aromatic in water released from the oil weathered over time. Of the climatic factors assessed: temperature, wind speed and sunlight could have an influence on the fitting parameters (i.e. slope of the curves) of the developed empirical functions.

An empirical expression was developed to show viscosity limitations on the chemical dispersion effectiveness (DE) that included different oil types, fresh and weathered products, and seasonal (temperature) effect data. The newly developed DE function was combined with the previously developed empirical expression for the time evolution of viscosity to estimate DE of chemical dispersant to treat surface spills of oil sands products long after the initial release, if conditions change from calm to more energetic seas.

Hence this thesis may become a suitable reference for oil spill responders and decision-making when dealing with blended bitumen spills in aquatic areas.

8.2.2 Practical Contributions

This research introduced the development of empirical expressions for the evolution of density and viscosity of oil naturally weathered on water. A spill on water at a temperature of 22 °C caused rapid weathering of a condensate bitumen blend (AWB) where the product approached physical properties close to the crude bitumen. Under these conditions, the oil's density exceeded that of freshwater. The intermolecular forces

(e.g. *London dispersion*- boiling point increases with increasing molecular size, *dipole-dipole*- positive and negative charge attraction between molecules, and *hydrogen bonding*- attraction of positively charged hydrogen with electronegative atoms such as fluorine, oxygen and nitrogen) of attraction in liquids (in this case oil) determine the rate of evaporation. The weaker the intermolecular forces in a liquid the more rapid the evaporation. At higher temperatures (>15 °C), the intermolecular forces of attraction in a liquid are weaker; thus increasing the rate of evaporation. The viscosity hyperbolic model predictions were incorporated with data on oil spill response options from the literature to create a decision matrix. The decision-making matrix offers to strengthen critical elements that are often missing in contingency plans and effective response. In particular, it incorporated information on the evolution of physical properties of bitumen blends over time into decision making. There was a major difference in the time evolution of oil properties (density and viscosity), raising doubts on the utility of weathering models that do not consider the thickness of oil. The impact of slick thickness suggests that, for these oils, the mass transfer limitation for evaporation is within the oil and not the atmosphere above it as observed for water evaporation (Sutton, 1934; Brustaert, 1982). This agrees with the findings of Fingas (2011 & 2013), where their experiments suggested that the evaporation of oils did not increase markedly with the wind speed, and thus concluded correctly that the evaporation of oil is not limited by the air boundary layer, but rather by the diffusion of oil components to the interface between the oil and the atmosphere. However, Fingas's (2011 & 2013) evaporation studies were based on light crude oils and petroleum products, and heavy oils including bitumen blends were not considered. In an earlier study, Fingas (2014) reported that temperature

and time were greater factors in the evaporation for a wide range oil types rather than thickness of the slick and wind speed velocity, where the bulk of the oils' hydrocarbons are $>C_{10}$. For the IFO 180, it is possible that the evaporation from it is small due to the small percentage of low molecular weight compounds within it, which confirms Fingas's study (2014). However, the fate and behaviour of bitumen blends, unlike conventional heavy oils, are driven by the lighter diluent blended with the crude bitumen. The exception is when synthetic crude is used as the diluent mixed with crude bitumen, which produces an evaporation profile that is closer to a heavy oil product such as IFO 180.

Exposure to sunlight can affect the rate of decay of monocyclic aromatics in water and plays a significant role in changes in the density and viscosity of oil weathered on water; critical information that suggests photo-chemical weathering contributes to the natural attenuation of oil to aid oil spill contingency plans. Temperature and wind speed can influence the rate of evaporation during the weathering of oil. Also, the season in which the spill occurred can significantly ($p < 0.05$) affect the rate of weathering of oil on water under calm conditions at sea. Although temperature, wind speed, and sunlight exposure are major climatic factors in the natural attenuation of oil, their influence on the weathering process is most likely driven by oil type and the season in which a spill occurs.

The project has provided insight into the risk associated with the dissolution of monocyclic aromatics in water from the diluent released post-spill of bitumen blends. Dissolution accounts for approximately 4 % removal of monocyclics to water and the remainder to air from oil spilled on water. This is considered to be a good estimate of monocyclics to air based on the work by Kim et al. (2012) where they reported that the

majority of BTEX evaporated in air, occurred within 24 hours after an oil spill. Fingas (1999) reported that evaporation is a very important process for most crude oils, where the rate of molecular diffusion for water is 10^5 slower than the maximum rate of evaporation. Also, it has been reported that evaporation accounts for a far greater mass loss (e.g. 10 to 100 times) of these chemicals than dissolution (Lee et al., 2015). The findings emphasize that impact from those chemicals released from oils would be greater at the air/oil boundary and less so to the water column. Whales, seals, turtles, and birds are at high risk due to inhalation of monocyclic aromatics through feeding and oiling of body surfaces in the vicinity of a spill. Also, responders would be at risk of inhaling vapours when combating the spill. Studies to assess the impacts to aquatic life from oil spills should consider the oxidized chemicals produced from the photo-chemical weathering of oil on water.

If the viscosity of the weathered oil can be computed, then the new dispersion model can be used to estimate the DE of chemical dispersant to treat spills. For the combined model that integrates the dispersion model with the viscosity hyperbolic function, viscosity is unknown and is predicted using the viscosity hyperbolic function (Chapter 5). However, the thickness of the oil slick and season in which an oil spill occurs could limit the application of the viscosity hyperbolic function and; therefore, its application to estimate DE for chemical dispersant to treat weathered oil at sea.

The empirical expressions for dissolution, physical properties (density and viscosity) and dispersion are being considered for implementation into Environment and Climate Change Canada (ECCC) Emergency Response's newly developed Canadian Oil

Spill Modelling Suite (COSMoS) which would allow the verification of the science-based oil spill models against historical cases or field measurement campaigns.

The circular flume tank developed under this project provides a controlled environment to evaluate the toxic, water soluble hydrocarbons released from surface spills of oil sands products that are readily available to aquatic species, as well as the physical property changes of oil as it naturally weathers over time.

8.3 Related Studies

In addition to this project, numerous collaborations have been established to address other priority research problems. These are outlined below.

8.3.1 The Effects of Mixing Time and Energy on Dispersion Effectiveness

This study is linked to Chapter 7, where dispersant is used to treat surface spills of various bitumen blends in a wave tank facility. Dispersion of oil occurred under continuous plunger breaker waves at a height of 0.4 m for one hour, where longer mixing times and greater wave energies were not considered. A controlled lab study was conducted to investigate the impact of mixing time and energy on the effectiveness of dispersion and droplets size distribution of oil by Pan et al. (2017). The results showed that Cold Lake Blend (CLB dilbit), compared to the low viscosity conventional oil, Alaskan North Slope, had a higher sensitivity to the mixing energy where the dispersion effectiveness increased considerably between 0.02 and 4.05 W/kg (energy dissipation rate), thus producing smaller oil droplet sizes with increasing mixing energy. The findings indicate that chemical dispersant may be more effective at dispersing dilbit products spilled in rougher (more energetic breaking wave) conditions at sea.

8.3.2 Dilbit-Sediment-Particle Aggregation

This study is linked to Chapter 5 that reports models for the time evolution of the density of various bitumen blends to determine under what conditions bitumen products will sink. Chapter 5 takes into consideration that oil can interact with suspended sediments thus increasing its propensity to sink. A series of lab and wave tank experiments were conducted to study the fate and behaviour of oil particles and the influence of chemical dispersant (COREXIT®EC 9500A) on the natural process of sedimentation (O’Laughlin et al., 2016; O’Laughlin et al., 2017). Results from this preliminary investigation suggest that in colder water (<10 °C) and at low sediment concentration (15 mg·L⁻¹), the formation of oil-particle-aggregates (OPAs) in the wave tank was unsuccessful. The application of chemical dispersant increased the concentration of oil particles into the water column at a depth of 0.35 m under breaking wave conditions. *In situ* flocculation camera images showed some effectiveness of chemical dispersant to remove diluted bitumen from the water surface, but showed no OPAs under the above-mentioned conditions (O’Laughlin et al., 2016; O’Laughlin et al., 2017). However, lab studies demonstrated that OPA’s derived from diluted bitumen formed using a similar sediment concentration, but longer mixing times and greater mixing energy were required. In contrast, the wave tank studies were based on a settling time of two hours that appeared to be too short, or the suspended sediment concentration might have needed to be greater than 50 mg·L⁻¹. Further studies are required to better understand the formation of OPAs under simulated environmental conditions on a large-scale (wave tank) and make better comparison to data generated from mixing flasks in small-scale lab studies. Also, to address inconsistent results regarding the influence of chemical

dispersant on the formation of OPAs, Page et al. (2000) reported that chemically enhanced dispersed oil droplets had less interaction with mineral fines than naturally dispersed oil, while subsequent studies by Khelifa et al. (2005, 2008) and Sun et al. (2013) have shown that chemically dispersed oil interacts favorably with suspended particles in the water column to produce OPAs.

8.3.3 A Model to predict the Sinking Rate of Oil-Particle-Aggregates

This study is linked to Chapter 5 that reports models for the time evolution of the density of various bitumen blends to determine under what condition bitumen products will sink. Chapter 5 takes into consideration that oil can interact with suspended sediments thus increasing its propensity to sink. An OPA model was developed and validated using empirical data generated from lab studies (Wu et al., 2016). The model is able to predict the sinking ratio of OPAs, with Access Western Blend (AWB) as the oil type, in a variety of conditions including energy dissipation rate, particle grain size and the application of dispersant (Wu et al., 2016). The model predictions were based on suspended sediments in Kitimat, BC coastal waters (a port area for a proposed terminal for the Northern Gateway Pipeline) that consists mainly of fine sediment of silt, sand, and clay with grain sizes ranging from 2 to 5 μ m. Based on previous studies, sediments with a smaller particle size (<5 μ m) are more favorable for the formation of OPAs (Gong et al., 2014). The influence of seawater density stratification (as experienced in the coastal area of Douglas Channel) on the sinking rate could be significant in summer, where approximately 20% of OPAs are expected to sink below the water surface, but not all the way to the sea bottom (Wu et al., 2016). However, further research is needed in this area, in particular

related to other oil sands products and how the oceanography and environment conditions specific to spill site location can influence oil sedimentation.

8.3.4 Coastal Microbial Community's Response to a Diluted Bitumen Spill

This study is linked to Chapter 5 that reports models for the time evolution of the physical properties of various bitumen blends weathered under simulated natural conditions. Biodegradation was considered to be one of the prevalent processes involved in the weathering of oil. A study was conducted to test the short term response of coastal microbes to diluted bitumen under varying nutrient conditions in cold (4°C) water (Ortmann et al., *inpress*). Hydrocarbon concentrations changed insignificantly over five days; however oil composition changed over time and the abundance of microbes increased. Addition of phosphate (in the presence and absence of nitrogen) increased the initial rate of change in the microbial community composition, but differences were minimal after three days. Nutrients were never exhausted in any treatment, which suggests that even at low inorganic nutrient concentrations, microbial communities can rapidly degrade hydrocarbons following a spill.

8.4 Limitations of the Research and Directions for Future Research

This dissertation has met success in achieving the objectives of the research. The study provided information on oil sands products weathered under seasonal conditions. However, as with all research there are limitations and new challenges and questions raised. This study was limited to only two seasons (spring and summer) and not the more extreme conditions of Canadian winters or aquatic areas that become influenced by the presence of ice. Under such conditions there are many challenges to consider and questions to answer including: 1) How will oil weather on, in or under ice; 2) How will

such conditions affect oil spill response capabilities? Also, a previous report (Fingas, 2004) indicated that temperature and time were greater factors in oil evaporation than surface wind speed or oil slick thickness for a wide range of crude oils. This study has shown that seasonal climatic factors and slick thickness can influence oil weathering; however, more research is needed on a variety of oil types and energetic seas conditions to further validate the density and viscosity hyperbolic functions developed in this study.

The dissolution model is limited to monocyclic aromatics released from oil into water, but through a mass balance provides an estimate of those same chemicals released to air. A limitation of the study that requires further investigation is to directly measure and model the evaporation of volatiles from the diluent released from bitumen blends directly into air in the vicinity of a spill. This will aid in better assessing impacts to those species living at the air/water boundary near the oil slick. Also, this dissertation only evaluated evaporation, dissolution, and dispersion of oil as it weathered on water and excluded other natural weathering processes such as photo-oxidation, biodegradation, sedimentation, and emulsification. However, during long periods (>48 hours) of weathering of oil, biodegradation is believed to have taken place. Most of these other natural processes that degrade oil are being considered by other federal departments such Environment and Climate Change Canada and the National Research Council of Canada, but further study is warranted.

The study generated an empirical expression to estimate changes in the density of oil after a spill, but it neglects interaction with suspended particles; a condition that is more prevalent in coastal areas. Oil interactions with suspended particles form oil-particle-aggregates that can increase the rate of sinking in those areas where suspended

particle concentrations are >10 ppm. Also, the study was not designed to determine if oil weathering affects its adhesion to suspended particles. However, this topic has been considered by other scientists working at the Department of Fisheries and Oceans Canada. Some of this has been addressed in the section on related studies.

For this study, alternative response options include chemical dispersant, oil, *in situ* burning and natural attenuation compared to oil containment and recovery, which is the only response option, considered in Canada, to treat surface spills of bitumen blends. Other potential options to consider are the application of mineral fines to disperse and promote oil-particle-aggregation and sedimentation, the use of bio-dispersants that are similar in function to chemical dispersant (and more acceptable for use by stakeholders), biostimulation to enhance biodegradation of oil, and the use of solidifiers (i.e. gelators) to change the oil from a liquid to a solid mass to allow containment and to mitigate the effects of oil discharges. There is insufficient literature on the effectiveness of these response options to treat bitumen blend spills, and therefore future research is warranted.

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10. Appendix

10.1 Chapter 4: Supporting Materials

Tables 4S.1 to 4S.2 contains physical properties and chemical of the oil tested, respectively.

Table 4S.1: Physical Properties of the test oils used in the Study.

Oil	Diluent (30 to 50%)	ρ g/cm ³	Kinematic viscosity, ν cSt	API°	Class
AWB	condensate	0.9189	244	22.3	Heavy
Synbit	synthetic crude	0.9304	205	20.4	Heavy
WCS	synthetic crude /condensate	0.9214	211	21.9	Heavy
Heidrun	none	0.9132	68.9	23.3	Medium

ρ -density; ν -viscosity at 15 °C

Table 4S.2: BTEX and Major Classes of Compounds in Crude Oils (Percentage by Weight in oil).

Crude Oil	B	T	EB	X	BTEX	S	Aro	Res	Asp
AWB	0.45	0.81	0.12	0.59	1.97	14	23	46	17
Synbit	0.08	0.18	0.10	0.21	0.57	20	10	57	13
WCS	0.18	0.33	0.06	0.31	0.88	20	10	52	18
Heidrun	0.14	0.61	0.09	0.38	1.22	38	40	20	2

B= Benzene; T=Toluene; EB=Ethylbenzene; X=o,m,p-Xylenes; S=Saturates; Aro=Aromatics; Res=Resins; Asp=Asphaltenes.

Tables 4S.3 to 4S.6 contain the spring and summer experimental data for the four oils.

Table 4S.3: Experimental Data Collected During Weathering Studies of AWB. *ST-Slick Thickness.

Weathering Study (AWB-Spring)					
Sampling Time (Hours)	AWB *ST (mm) (n=20)	Water Temp (°C)	Salinity ppt	Air Temp (°C)	Wind Speed (km/hr)
0		4.5	29.0	6.0	17.0
3		6.5	29.4	8.0	13.0
8		11	29.6	7.5	19.0
24		7.8	29.3	3.0	9.0
48		6.6	29.3	2.0	20.0
72		5.8	29.8	11.0	13.0
96		3.3	29.1	8.0	6.0
120		5.3	29.4	6.8	26.0
144		4.0	28.5	14.0	28.0
168		4.3	29.3	13.0	19.0
192		0.6	28.7	10.8	11.0
Average	4.01	5.5	29.2	8.4	16.4
Stdev.	0.07	2.8	0.4	3.9	7.2
Total Rain Fall (mm)		43			
Weathering Study (AWB-Summer)					
Sampling Time (Hours)	AWB *ST (mm) (n=20)	Water Temp (°C)	Salinity ppt	Air Temp (°C)	Wind Speed (km/hr)
0		14.0	29.8	20.0	13.1
3		14.1	29.8	22.0	15.2
8		13.5	29.5	26.0	11.1
24		14.9	29.6	16.0	13.0
48		14.1	29.4	15.0	7.2
72		14.9	29.4	14.0	9.0
96		14.0	29.6	17.0	6.1
120		14.8	29.8	16.0	4.0
144		14.6	29.6	19.0	7.3
168		14.3	29.6	19.0	4.4
192		13.8	29.6	21.0	11.1
Average	4.06	14.3	29.6	18.4	9.0
Stdev.	0.11	0.5	0.2	3.6	3.9
Total Rain Fall (mm)		0.3			

Table 4S.4: Experimental Data Collected During Weathering Studies of WCS.

Weathering Study (WCS-Spring)					
Sampling Time (Hours)	WCS *ST (mm) (n=20)	Water Temp (°C)	Salinity ppt	Air Temp (°C)	Wind Speed (km/hr)
0		5.4	29.8	8.1	17.2
3		5.9	29.8	9.7	17.0
8		5.7	29.9	11.4	17.2
24		6.3	29.8	6.9	30.2
48		5.1	29.0	6.9	26.1
72		6.5	29.8	8.8	35.2
96		6.0	30.0	10.5	20.3
120		6.7	29.8	10.7	33.1
144		6.7	30.7	11.3	28.1
168		6.4	29.1	9.1	22.1
192		7.2	29.8	4.3	17.4
Average	4.06	6.3	29.8	9.0	24.7
Stdev.	0.27	0.6	0.5	2.3	6.8
Total Rain Fall (mm)		43			
Weathering Study (WCS-Summer)					
Sampling Time (Hours)	WCS *ST (mm) (n=20)	Water Temp (°C)	Salinity ppt	Air Temp (°C)	Wind Speed (km/hr)
0		14.6	30.4	24.2	6.3
3		16.3	29.1	27.3	6.2
8		14.1	30.0	23.1	0
24		16.3	30.4	23.8	9.4
48		14.3	30.1	20.7	24.2
72		14.2	30.2	18.1	9.1
96		15.7	30.3	18.9	4.3
120		15.0	30.3	12.8	22.8
144		15.7	30.0	18.1	11.4
168		15.6	30.9	18.2	20.7
192		15.6	30.6	17.1	15.1
Average	4.03	15.2	30.2	20.5	11.4
Stdev.	0.06	0.8	0.5	4.2	8.3
Total Rain Fall (mm)		16			

Table 4S.5: Experimental Data Collected During Weathering Studies of Synbit.

Weathering Study (Synbit-Spring)					
Sampling Time (Hours)	Synbit *ST (mm) (n=20)	Water Temp (°C)	Salinity ppt	Air Temp (°C)	Wind Speed (km/hr)
0		6.3	28.9	9.6	6.1
3		6.0	28.9	10.7	12.9
8		6.8	29.0	8.3	14.8
24		5.7	28.7	6.2	19.2
48		7.0	29.0	6.4	21.9
72		6.2	28.9	9.0	17.5
96		6.3	29.0	8.5	25.9
120		6.5	28.9	8.3	18.7
144		6.3	28.2	7.8	23.6
168		6.3	28.4	8.9	33.1
192		6.2	28.0	10.6	16.9
Average	4.01	6.3	28.7	8.5	20.5
Stdev.	0.07	0.4	0.4	1.5	5.9
Total Rain Fall (mm)		55			
Weathering Study (Synbit-Summer)					
Sampling Time (Hours)	Synbit *ST (mm) (n=20)	Water Temp. (°C)	Salinity ppt	Air Temp. (°C)	Wind Spd. (km/hr)
0		12.8	30.1	17.9	4.3
3		14.5	31.2	22.1	8.7
8		14.8	31.0	19.8	6.2
24		14.5	31.2	20.2	27.8
48		15.3	31.2	23.7	15.3
72		14.8	31.0	23.3	10.7
96		14.5	31.2	23.6	11.4
120		15.7	31.3	20.6	16.6
144		14.2	30.7	21.6	7.1
168		14.2	31.1	24.4	23.9
192		15.9	30.9	19.9	19.1
Average	3.99	14.5	31.0	21.7	13.2
Stdev.	0.08	0.8	0.4	2.1	7.7
Total Rain Fall (mm)		0			

Table 4S.6: Experimental Data Collected During Weathering Studies of Heidrun.

Weathering Study (Heidrun-Spring)					
Sampling Time (Hours)	Heidrun *ST (mm) (n=20)	Water Temp (°C)	Salinity ppt	Air Temp (°C)	Wind Speed (km/hr)
0		6.0	30.0	9.9	8.9
3		6.6	30.2	12.0	11.1
8		7.7	31.2	15.4	10.8
24		7.5	30.5	10.0	4.2
48		7.0	29.9	9.6	37.1
72		5.7	29.8	8.7	18.9
96		7.0	30.1	8.9	12.5
120		5.6	29.5	8.0	11.5
144		7.2	29.6	9.1	4.2
168		5.9	29.7	9.2	16.8
192		6.5	29.7	11.6	9.1
Average	4.17	6.7	30.0	10.2	13.6
Stdev.	0.11	0.7	0.5	2.2	9.5
Total Rain Fall (mm)		38			
Weathering Study (Heidrun-Summer)					
Sampling Time (Hours)	AWB *ST (mm) (n=20)	Water Temp (°C)	Salinity ppt	Air Temp (°C)	Wind Speed (km/hr)
0		18.5	31.2	19.9	16.8
3		14.6	31.0	22.1	17.2
8		16.0	31.2	21.5	18.8
24		15.2	31.0	21.5	15.2
48		14.4	31.1	23.8	0
72		16.5	31.2	20.2	17.0
96		14.8	31.0	17.8	21.6
120		14.8	31.1	22.2	7.4
144		14.0	30.9	22.2	14.7
168		15.9	31.0	22.8	20.3
192		15.0	30.4	17.9	32.8
Average	4.11	15.5	31.1	21.1	14.9
Stdev.	0.08	1.3	0.1	1.7	6.5
Total Rain Fall (mm)		10			

Tables 4S.7 to 4S.10 contain individual chemical and summed BTEX concentrations.

Table 4S.7: Time-Series Averaged BTEX Concentrations ($\mu\text{g}\cdot\text{L}^{-1}$) in the Water Column for Access Western Blend (AWB) Weathering on Water During Spring (Spr) and Summer (Sum). Most averaged values are based on triplicate measurements.

Weathering Study (AWB)												
Time (hr)	B		T		E		m,p-X		o-X		Averaged ΣBTEX	
	$\mu\text{g}\cdot\text{L}^{-1}$ (average n=3 at each time point)											
	Spr	Sum	Spr	Sum	Spr	Sum	Spr	Sum	Spr	Sum	Spr	Sum
0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0 \pm 1	0 \pm 0
3	9.0	12.8	5.2	7.4	0.0	0.0	0.7	0.8	0.0	0.5	15 \pm 1	21.5
8	26.7	30.6	16.6	19.3	0.7	0.8	1.6	2.3	1.1	1.5	47 \pm 2	54.5
24	43.8	51.6	37.6	42.7	1.6	2.0	4.4	6.2	3.0	4.1	90 \pm 1	110 \pm 1
48	45.0	44.3	47.9	45.3	2.3	2.7	6.6	7.8	4.6	5.5	110 \pm 5	110 \pm 2
72	34.4	28.0	39.7	33.3	2.1	2.4	5.9	6.0	4.1	5.1	86 \pm 2	75 \pm 2
96	27.3	18.0	33.2	21.7	1.8	1.6	5.2	4.0	3.7	4.0	71 \pm 1	49 \pm 1
120	21.3	10.5	27.8	8.2	1.6	0.5	4.6	1.2	3.3	1.8	59 \pm 2	22 \pm 1
144	16.4	0.7	23.1	0.0	1.5	0.0	4.1	0.0	3.0	0.0	47 \pm 1	0.7 \pm 0
168	13.2	0.0	19.3	0.0	1.3	0.0	3.6	0.0	2.7	0.0	40 \pm 2	0 \pm 0
192	10.3	0.0	15.6	0.0	1.1	0.0	3.1	0.0	2.2	0.0	32 \pm 1	0 \pm 0

0.0 represents a detection limit of $<0.5 \mu\text{g}\cdot\text{L}^{-1}$.

Table 4S.8: Time-Series Averaged BTEX Concentrations ($\mu\text{g}\cdot\text{L}^{-1}$) in the Water Column for Western Canadian Select (WCS) Weathered on Water During Spring (Spr) and Summer (Sum). Most averaged values are based on triplicate measurements.

Weathering Study (WCS)												
Time (hr)	B		T		E		m,p-X		o-X		Averaged ΣBTEX	
	$\mu\text{g}\cdot\text{L}^{-1}$ (average n=3 at each time point)											
	Spr	Sum	Spr	Sum	Spr	Sum	Spr	Sum	Spr	Sum	Spr	Sum
0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0 \pm 0	0 \pm 0
3	8.9	8.8	6.3	5.2	0.0	0.0	0.8	0.7	0.0	0.0	16 \pm 1	15 \pm 1
8	21.1	15.8	20.0	10.3	1.1	0.6	3.1	1.4	1.9	1.0	47 \pm 1	29 \pm 1
24	26.1	7.7	25.1	2.8	1.3	1.9	3.9	1.2	2.5	1.0	59 \pm 2	15 \pm 1
48	25.8	0.9	28.7	0.6	1.7	0.0	5.0	0.0	3.3	0.0	64 \pm 1	1.5 \pm 0
72	17.4	0.0	22.2	0.0	1.4	0.0	4.2	0.0	2.8	0.0	48 \pm 2	0 \pm 0
96	12.9	0.0	18.2	0.0	1.2	0.0	3.8	0.0	2.5	0.0	39 \pm 1	0 \pm 0
120	8.7	0.0	14.1	0.0	1.0	0.0	3.2	0.0	2.2	0.0	29 \pm 2	0 \pm 0
144	5.2	0.0	9.3	0.0	0.9	0.0	2.4	0.0	1.6	0.0	19 \pm 2	0 \pm 0
168	3.9	0.0	5.6	0.0	0.6	0.0	2.3	0.0	1.7	0.0	14 \pm 2	0 \pm 0
192	2.0	0.0	4.9	0.0	0.0	0.0	1.9	0.0	1.3	0.0	10 \pm 2	0 \pm 0

Table 4.9: Time-Series Averaged BTEX Concentrations ($\mu\text{g}\cdot\text{L}^{-1}$) in the Water Column for Synthetic Bitumen (Synbit) Weathered on Water During Spring (Spr) and Summer (Sum). Most averaged values are based on triplicate measurements.

Weathering Study (Synbit)												
Time (hr)	B		T		E		m,p-X		o-X		Averaged ΣBTEX	
	$\mu\text{g}\cdot\text{L}^{-1}$ (average n=3 at each time point)											
	Spr	Sum	Spr	Sum	Spr	Sum	Spr	Sum	Spr	Sum	Spr	Sum
0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0±0	0±0
3	2.8	5.6	3.9	7.5	0.0	0.8	0.6	0.9	0.0	1.0	7.3±0	16±1
8	4.3	7.3	7.8	12.2	1.1	1.5	1.4	1.7	1.3	1.9	16±1	25±1
24	3.9	2.9	10.9	7.7	2.6	2.2	3.3	2.7	3.8	3.5	24±1	19±1
48	1.2	0.0	3.3	0.0	2.0	0.9	3.3	1.4	4.2	2.5	14±1	4.8±0
72	0.0	0.0	0.0	0.0	0.9	0.0	3.0	0.0	3.9	0.0	7.8±0.2	0±0
96	0.0	0.0	0.0	0.0	0.0	0.0	1.8	0.0	2.2	0.0	4.0±0.1	0±0
120	0.0	0.0	0.0	0.0	0.0	0.0	1.4	0.0	1.8	0.0	3.2±0.2	0±0
144	0.0	0.0	0.0	0.0	0.0	0.0	1.0	0.0	1.1	0.0	2.1±0	0±0
168	0.0	0.0	0.0	0.0	0.0	0.0	0.8	0.0	1.0	0.0	1.7±0.1	0±0
192	0.0	0.0	0.0	0.0	0.0	0.0	0.7	0.0	0.7	0.0	1.4±0.1	0±0

Table 4S.10: Time-Series Averaged BTEX Concentrations ($\mu\text{g}\cdot\text{L}^{-1}$) in the Water Column for Heidrun Crude Weathered on Water During Spring (Spr) and Summer (Sum). Most averaged values are based on triplicate measurements.

Weathering Study (Heidrun)												
Time (hr)	B		T		E		m,p-X		o-X		Averaged ΣBTEX	
	$\mu\text{g}\cdot\text{L}^{-1}$ (average n=3 at each time point)											
	Spr	Sum	Spr	Sum	Spr	Sum	Spr	Sum	Spr	Sum	Spr	Sum
0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0±0	0±0
3	1.1	2.2	2.1	2.6	0.0	0.0	0.0	0.0	0.0	0.0	3.2±0.1	4.8±0.1
8	2.2	2.6	3.3	3.2	0.0	0.0	0.6	0.0	0.0	0.0	6.1±0.2	5.9±0.2
24	0.9	1.9	4.5	0.9	0.6	0.0	1.3	0.0	0.9	0.0	8.3±0.4	2.6±0.2
48	0.0	0.0	3.2	0.0	0.6	0.0	1.2	0.0	1.0	0.0	6.0±0.3	0±0
72	0.0	0.0	2.2	0.0	0.0	0.0	1.0	0.0	0.9	0.0	4.1±0.1	0±0
96	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0±0	0±0
120	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0±0	0±0
144	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0±0	0±0
168	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0±0	0±0
192	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0±0	0±0

Tables 4S.11a to 4S11d contain results of the correlation analysis. Monocyclic concentration is the dependent variable and the independent variable is season. Within season there are a number of independents (air and water temperature, wind speed and sunlight intensity) that could bring about change in the concentration of the monocyclics. When 'r' is positive changes in the dependent variables (density and viscosity) increase with an increase in the values of the independent variables (air and water temperature, wind speed, and sunlight energy). A negative 'r' indicates increasing changes in the dependent variable with a decreasing change in the independent variables.

Table 4S.11a: Multiple Correlation Analysis of Climatic Factors and Monocyclic Aromatic Concentrations for AWB Weathered on Water in Spring and Summer. Values in the table are Pearson Coefficient of Determination (r). Regression Analysis is reported significant relationships in Table 4.2 for the values highlighted in grey. Temperature (Temp).

AWB Spring (Release of Monocyclics in Water)					
	Air Tem	Water Tem	Wind speed	Sunlight Intensity	Monocyclics
Air Temp	1				
Water Temp	0.38	1			
Wind speed	0.02	0.27	1		
Sunlight Intensity	0.99	0.43	0.00	1	
Monocyclics	-0.97	-0.16	0.12	-0.96	1
AWB Spring (Decay of Monocyclics in Water)					
	Air Tem	Water Tem	Wind speed	Sunlight Intensity	Monocyclics
Air Temp	1				
Water Temp	-0.14	1			
Wind speed	0.31	0.64	1		
Sunlight Intensity	-0.67	0.63	0.07	1	
Monocyclics	-0.65	0.49	-0.17	0.96	1
AWB Summer (Release of Monocyclics in Water)					
	Air Tem	Water Tem	Wind speed	Sunlight Intensity	Monocyclics
Air Temp	1				
Water Temp	-0.75	1			
Wind speed	0.39	0.24	1		
Sunlight Intensity	0.84	-0.51	0.70	1	
Monocyclics	-0.79	0.53	-0.64	-0.99	1
AWB Summer (Decay of Monocyclics in Water)					
	Air Tem	Water Tem	Wind speed	Sunlight Intensity	Monocyclics
Air Temp	1				
Water Temp	-0.26	1			
Wind speed	-0.48	0.18	1		
Sunlight Intensity	0.36	0.69	0.06	1	
Monocyclics	-0.85	-0.22	0.56	-0.70	1

Table 4S.11b: Multiple Correlation Analysis of Climatic Factors and Monocyclic Aromatic Concentrations for WCS Weathered on Water in Spring and Summer. Values in the table are Pearson Coefficient of Determination (r). Regression Analysis is reported for significant relationships in Table 4.2 for the values highlighted in grey. There were not enough data points for release of monocyclics in water during summer to provide a correlation. Temperature (Temp).

WCS Spring (Release of Monocyclics in Water)					
	Water Tem	Air Tem	Wind Speed	Sunlight Intensity	Monocyclics
Water Tem	1				
Air Tem	0.05	1			
Wind Speed	0.13	-0.92	1		
Sunlight Intensity	0.25	0.56	-0.76	1	
Monocyclics	-0.29	-0.58	0.76	-0.99	1
WCS Spring (Decay of Monocyclics in Water)					
	Water Tem	Air Tem	Wind Speed	Sunlight Intensity	Monocyclics
Water Tem	1				
Air Tem	0.11	1			
Wind Speed	0.00	0.29	1		
Sunlight Intensity	-0.65	0.28	0.17	1	
Monocyclics	-0.73	0.24	0.30	0.98	1
WCS Summer (Decay of Monocyclics in Water)					
	Water Tem	Air Tem	Wind Speed	Sunlight Intensity	Monocyclics
Water Tem	1				
Air Tem	0.58	1			
Wind Speed	-0.01	-0.33	1		
Sunlight Intensity	-0.20	0.62	-0.70	1	
Monocyclics	0.10	0.78	-0.76	0.95	1

Table 4S.11c: Multiple Correlation Analysis of Climatic Factors and Monocyclic Aromatic Concentrations for Synbit Weathered on Water in Spring and Summer. Values in the table are Pearson Coefficient of Determination (r). Regression Analysis is reported for significant relationships in Table 4.2 for the values highlighted in grey. There were not enough data points for release of monocyclics in water during summer to provide a correlation. Temperature (Temp).

Synbit Spring (Release of Monocyclics in Water)					
	Water Tem	Air Tem	Wind Speed	Sunlight Intensity	Monocyclics
Water Tem	1				
Air Tem	0.25	1			
Wind Speed	-0.35	-0.71	1		
Sunlight Intensity	0.16	0.66	-0.98	1	
Monocyclics	-0.27	-0.86	0.97	-0.95	1
Synbit Spring (Decay of Monocyclics in Water)					
	Water Tem	Air Tem	Wind Speed	Sunlight Intensity	Monocyclics
Water Tem	1				
Air Tem	-0.82	1			
Wind Speed	-0.01	-0.20	1		
Sunlight Intensity	-0.37	0.29	0.27	1	
Monocyclics	0.78	-0.69	-0.22	-0.82	1
Synbit Summer (Decay of Monocyclics in Water)					
	Water Tem	Air Tem	Wind Speed	Sunlight Intensity	Monocyclics
Water Tem	1				
Air Tem	0.71	1			
Wind Speed	-0.40	-0.15	1		
Sunlight Intensity	-0.13	0.45	-0.36	1	
Monocyclics	-0.50	-0.96	0.09	-0.64	1

Table 4S.11d: Multiple Correlation Analysis of Climatic Factors and Monocyclic Aromatic Concentrations for Heidrun Weathered on Water in Spring and Summer. Values in the table are Pearson Coefficient of Determination. Regression Analysis is reported for significant relationships in Table 4.2 for the values highlighted in grey. There were not enough data points for release of monocyclics in water during Summer to provide a correlation. Temperature (Temp).

Heidrun Spring (Release of Monocyclics in Water)					
	Water Tem	Air Tem	Wind Speed	Sunlight Intensity	Monocyclics
Water Tem	1				
Air Tem	0.57	1			
Wind Speed	-0.25	0.64	1		
Sunlight Intensity	-0.66	0.23	0.82	1	
Monocyclics	0.94	0.26	-0.52	-0.88	1
Heidrun Spring (Decay of Monocyclics in Water)					
	Water Tem	Air Tem	Wind Speed	Sunlight Intensity	Monocyclics
Water Tem	1				
Air Tem	0.80	1			
Wind Speed	-0.25	-0.09	1		
Sunlight Intensity	0.59	0.95	-0.15	1	
Monocyclics	0.31	0.81	0.00	0.95	1
Heidrun Summer (Decay of Monocyclics in Water)					
	Water Tem	Air Tem	Wind Speed	Sunlight Intensity	Monocyclics
Water Tem	1				
Air Tem	-0.93	1			
Wind Speed	0.86	-0.90	1		
Sunlight Intensity	0.21	-0.06	0.48	1	
Monocyclics	0.24	-0.17	0.58	0.97	1

Table 4S.12: Summary of Definition of Terms Used in Table 4.2 Regression Analysis of Climatic Factors that had a Significant Effect on Monocyclic Aromatic Dissolution.

Term	Definition
Regression	Regression analysis is a set of statistical processes for estimating the relationships among variables.
ANOVA	ANOVA for Regression. Analysis of Variance (ANOVA) consists of calculations that provide information about levels of variability within a regression model and form a basis for tests of significance.
Variable	The independent variable is season. Within season the climatic factors are independent variables. The dependent variable is the concentration of monocyclics that change as a result of the independent variables.
n	The set of data points measured over time.
R²	Coefficient of determination
SE	Standard error is the approximate standard deviation of a statistical sample mean.
MSE	In statistics, the mean squared error (MSE) or mean squared deviation (MSD) of an estimator (of a procedure for estimating an unobserved quantity) measures the average of the squares of the errors—that is, the average squared difference between the estimated values and what is estimated.
p-value	A predictor that has a low <i>p</i> -value ($\alpha < 0.05$) is likely to be a meaningful addition to your model because changes in the predictor's value are related to changes in the response variable.

Table 4S.13: Summary of Definition of Terms Used in Table 4.3 ANOVA Comparing the Effects of Season on the Rate of Monocyclics Decayed in Water Released from Oils Weathered Under Simulated Natural Conditions.

Term	Definition
ANOVA	Analysis of Variance (ANOVA) Repeated measures investigate about the 1) changes in mean (concentration of monocyclics) scores over three or more time points and 2) differences in mean scores under different conditions (season).
Source of Variation	Season is the source of the variation or independent variable, which is represented by the difference in the climatic factors. The concentration of monocyclics in water will change with season and it is the dependent variable.
n	$n = n_1 + n_2$ Therefore, 'n' is the number of mean monocyclics concentrations in spring (n_1) added to the number of mean monocyclics concentrations in summer (n_2) over the same time points.
SRMSE	In statistics, the mean squared error (MSE) or mean squared deviation (MSD) measures the average of the squares of the errors—that is, the average squared difference between the sample means (monocyclics concentrations). The square root of the mean square error provides the average difference between sample means.
p-value	If <i>p</i> -value is less than α (0.05), you conclude that the mean difference between sample (i.e. monocyclics concentrations in spring versus) is statistically significant.

Example Calculations for AWB

Total oil amount: 240.4 grams

Mg BTEX/g of oil: 19.6 mg/g

Water Volume (Test tank): 1310 L

Water Temperature: 5.5 °C

Oil Slick Thickness: 4.01±0.07 mm

Max. BTEX released = 240.4 g X 19.6 mg/g= 4712 mg

Assumed 100% BTEX dissolution: 4712 mg/1310 L= 3.6 mg/L

Actual measured BTEX dissolution: 0.101 mg/L

Therefore, % BTEX dissolution = (0.101 mg/L)/(3.6 mg/L) * 100% = 2.8%

% BTEX Evaporation into air = (100 – 2.8) %= 97.2%

Table 4S.14: Percentage BTEX dissolution and evaporation and related data. Water volume is 1310 L.

Spring-Time									
Oil Type	Oil (g)	mg BTEX /g of oil	Max. BTEX released (mg)	If Assume 100% Dissolution BTEX (mg/L)	*BTEX (mg/L)/ time (hr)	% Dissolution (actual)	% EVAP into air	%EVAP /%Dissolved	Ave. Water Temp. (°C)
Spring-Time									
AWB	240	19.6	4712	3.6	0.101/48	2.8	97.2	35	5.5
WCS	245	8.7	2136	1.6	0.064/48	3.9	96.1	25	6.3
Synbit	244	5.6	1368	1.0	0.024/24	2.3	97.7	43	6.3
Heidrun	249	12.1	3014	2.3	0.008/24	0.3	99.7	330	6.7
Summer-Time									
AWB	243	19.6	4777	3.6	0.107/24	2.9	97.1	34	14.3
WCS	243	8.7	2120	1.6	0.029/24	1.8	98.2	55	15.2
Synbit	242	5.6	1360	1.0	0.024/8	2.3	97.7	43	14.5
Heidrun	245	12.1	2972	2.3	0.007/8	0.3	99.7	330	15.5

*based on maximum concentration measured in water over time. See supplementary material for raw experimental data

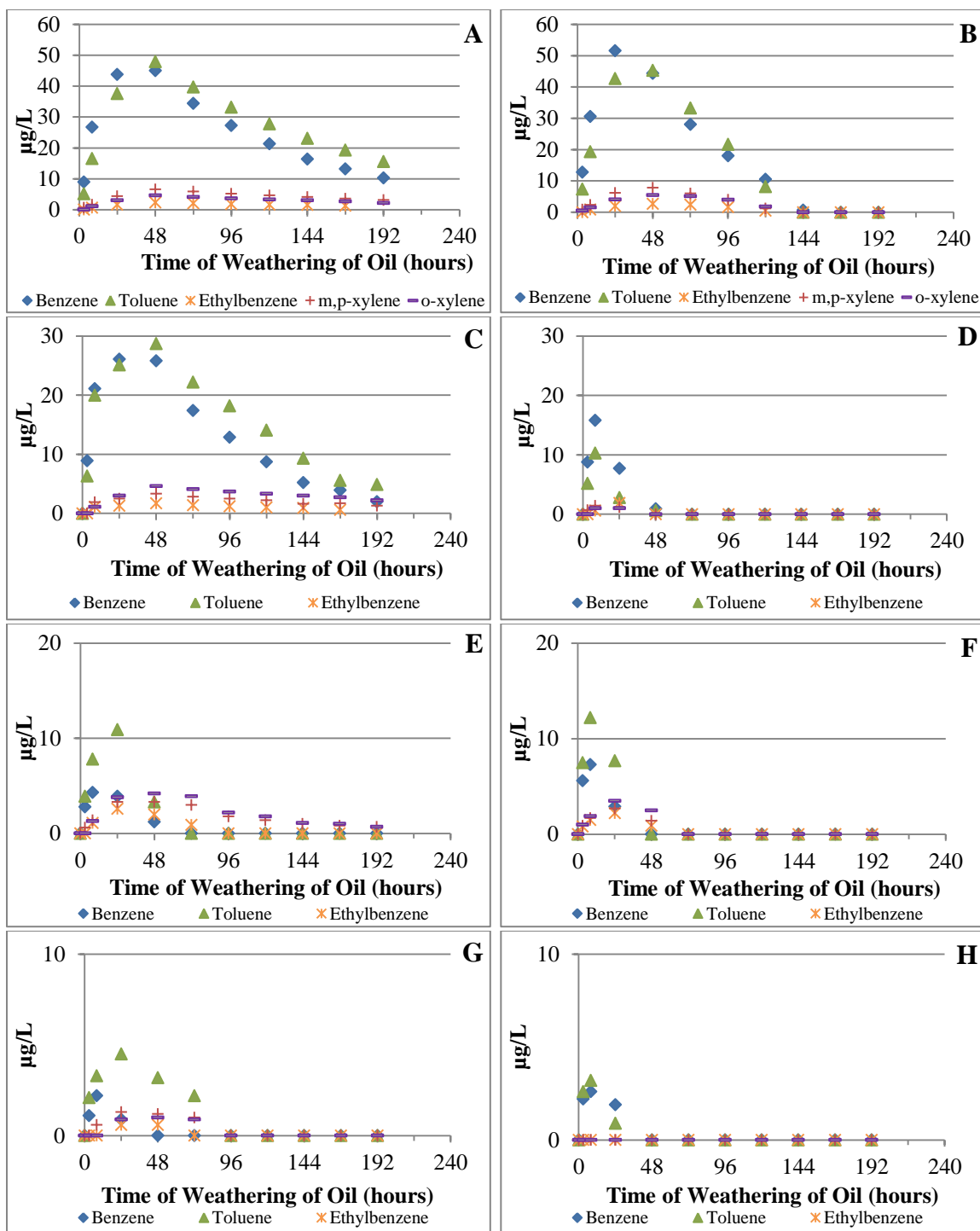


Figure 4S.1: Monocyclic aromatic (Benzene, Toluene, Ethylbenzene, and xylenes) concentrations in the water column as a function of time of weathering of oils: A) AWB-spring, B) AWB-summer, C) WCS-spring, D) WCS-summer, E) Synbit-spring, F) Synbit-summer, G) Heidrun-spring, and H) Heidrun-summer.

Figures 4S2 to 4S9 provide air and water temperature and wind speed profiles for all oils weathered in spring and summer of 2017. Figures 4S-10 to 4S-17 profiles light intensity over the 8 day experiments conducted in spring and summer of 2017.

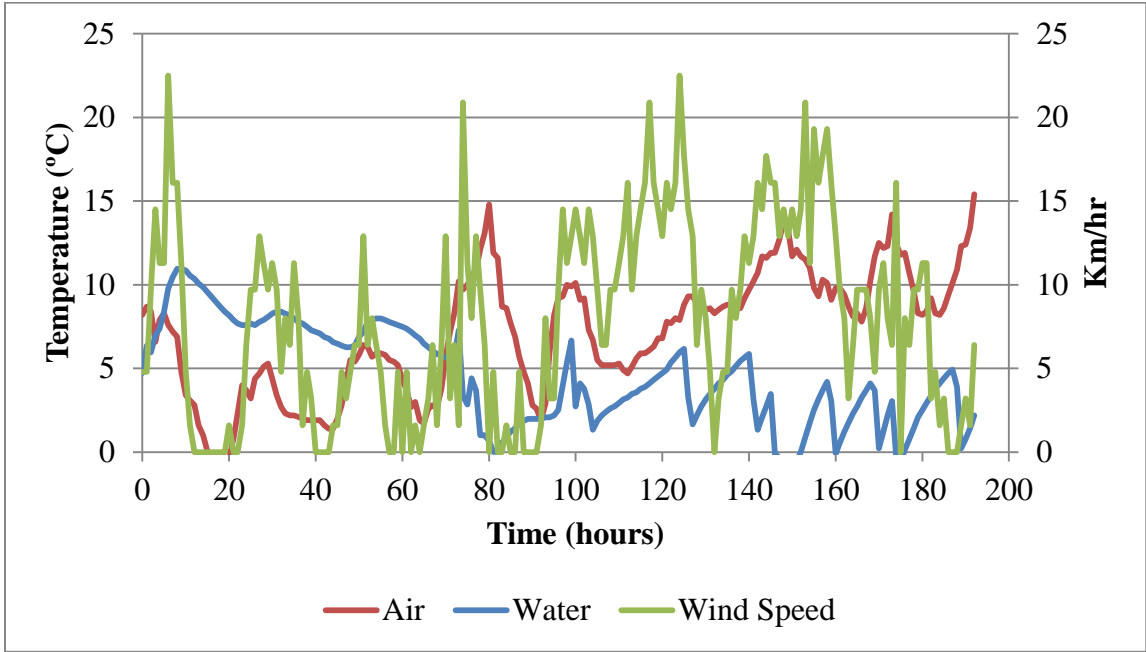


Figure 4S.2: Water and air temperature and wind speed profiles for the time of weathering of Access Western Blend (AWB) on water during spring-time of 2017.

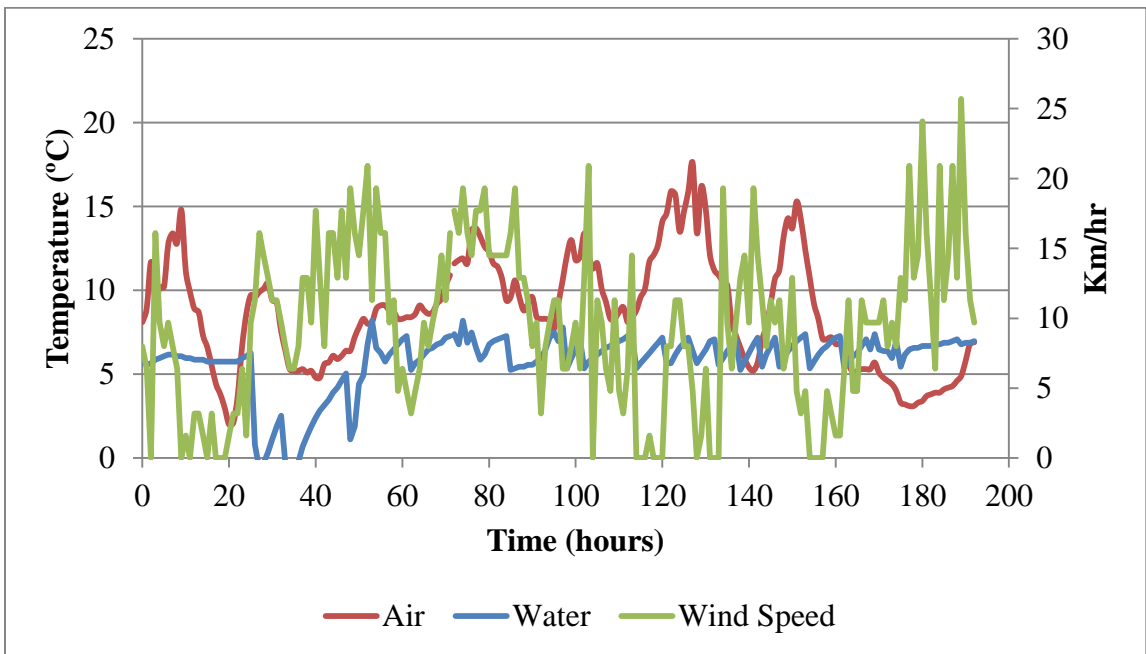


Figure 4S.3: Water and air temperature and wind speed profiles for the time of weathering of Western Canadian Select (WCS) on water during spring-time of 2017.

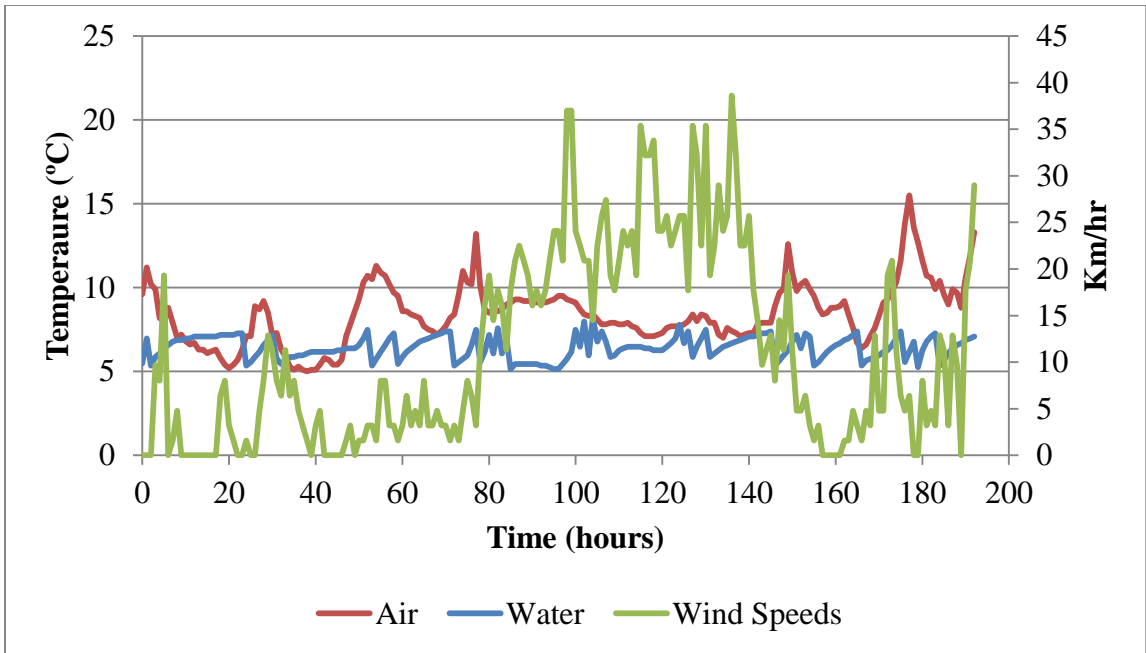


Figure 4S.4: Water and air temperature and wind speed profiles for the time of weathering of Synthetic Bitumen (Synbit) on water during spring-time of 2017.

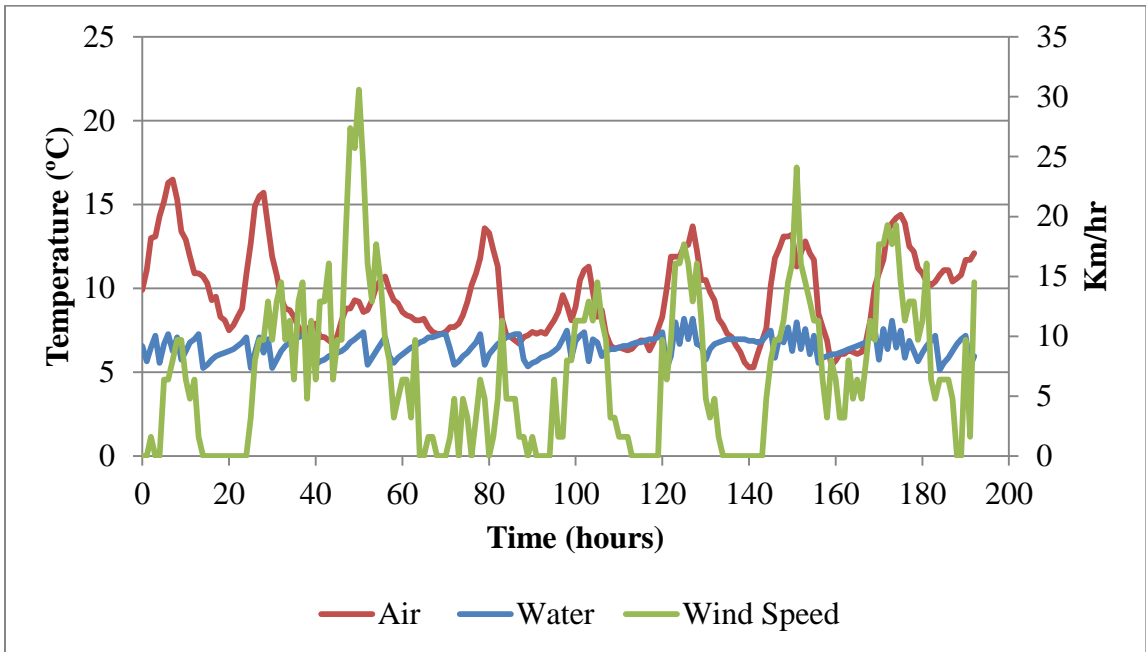


Figure 4S.5: Water and air temperature and wind speed profiles for the time of weathering of Heidrun on water during spring-time of 2017.

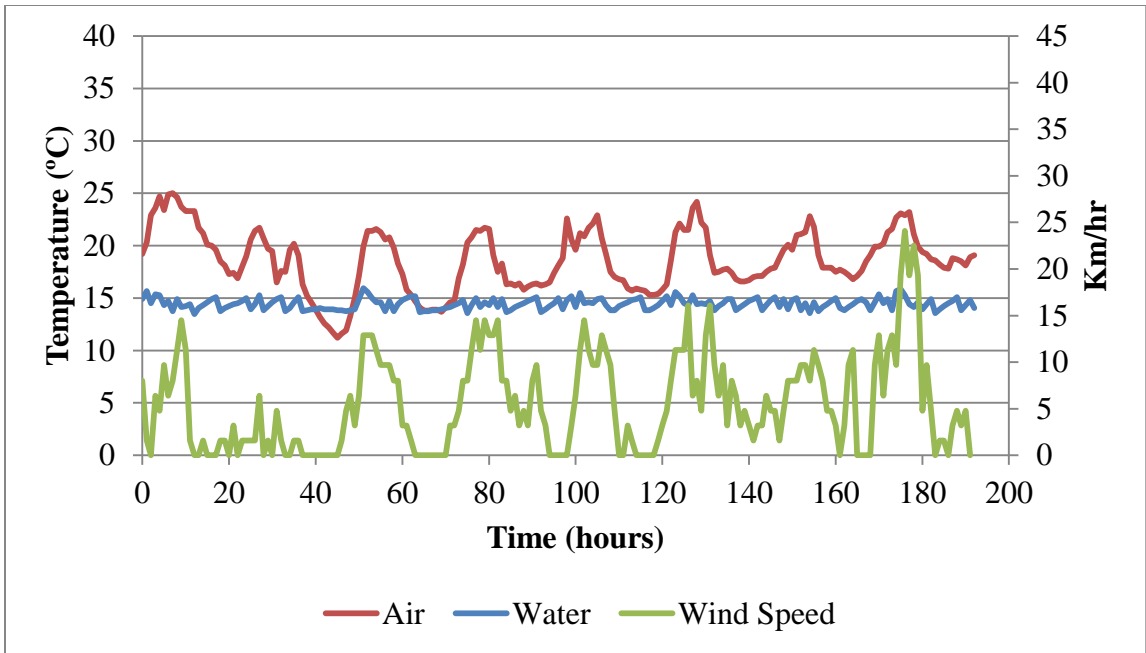


Figure 4S.6: Water and air temperature and wind speed profiles for the time of weathering of Access Western Blend (AWB) on water during summer-time of 2017.

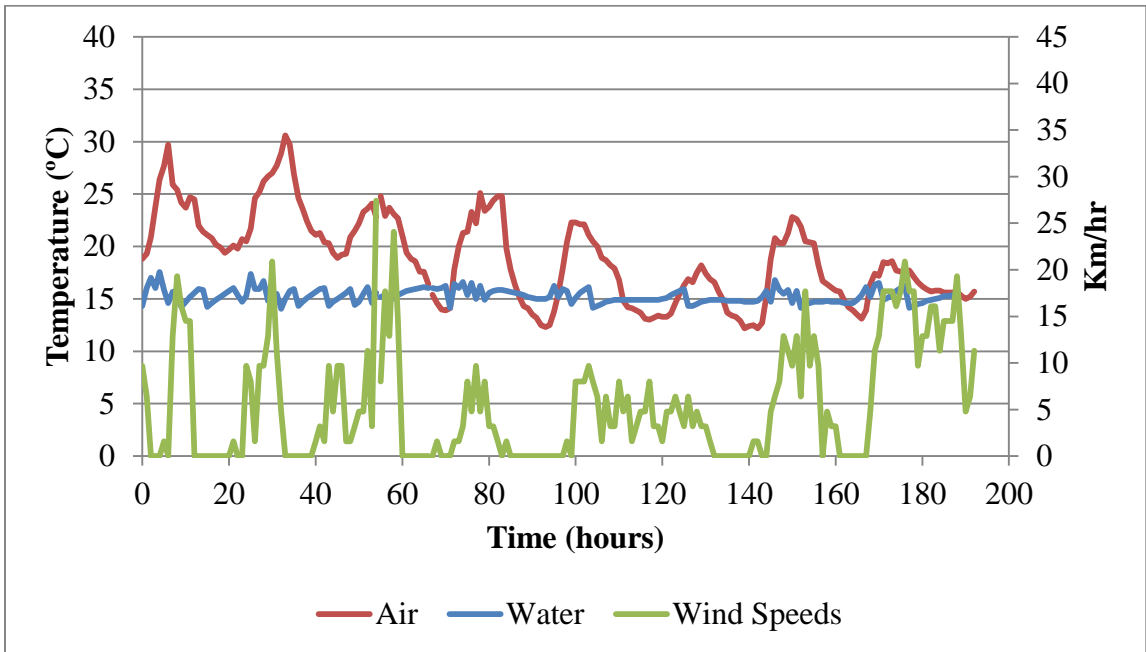


Figure 4S.7: Water and air temperature and wind speed profiles for the time of weathering of Western Canadian Select (WCS) on water during summer-time of 2017.

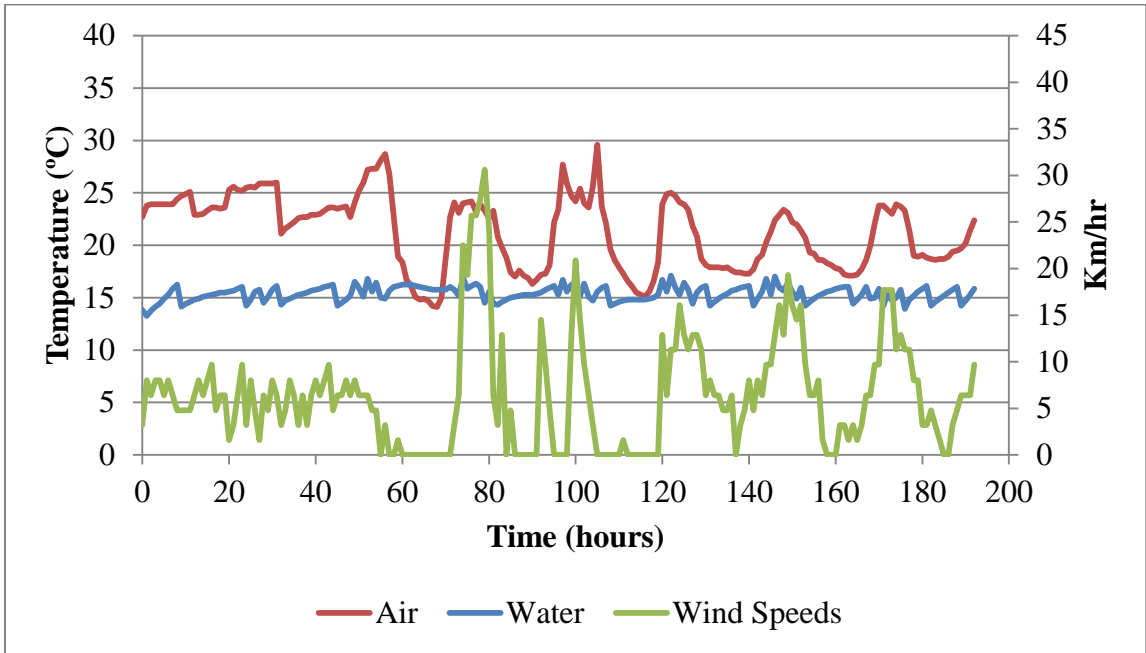


Figure 4S.8: Water and air temperature and wind speed profiles for the time of weathering of Synthetic Bitumen (Synbit) on water during summer-time of 2017.

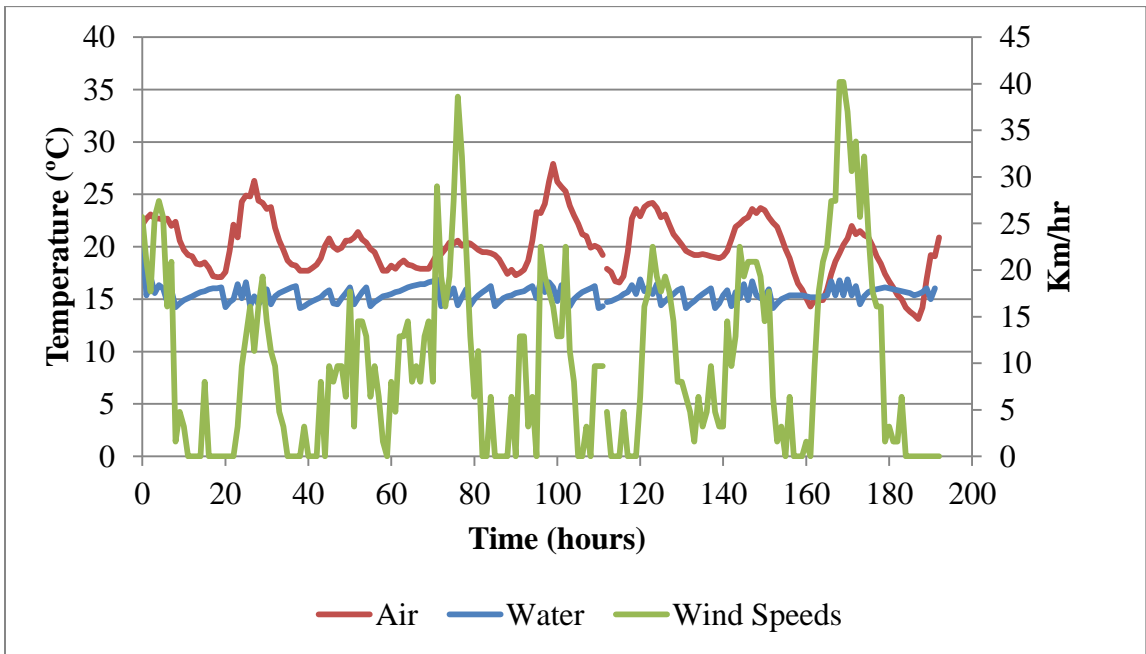


Figure 4S.9: Water and air temperature and wind speed profiles for the time of weathering of Heidrun on water during summer-time of 2017.

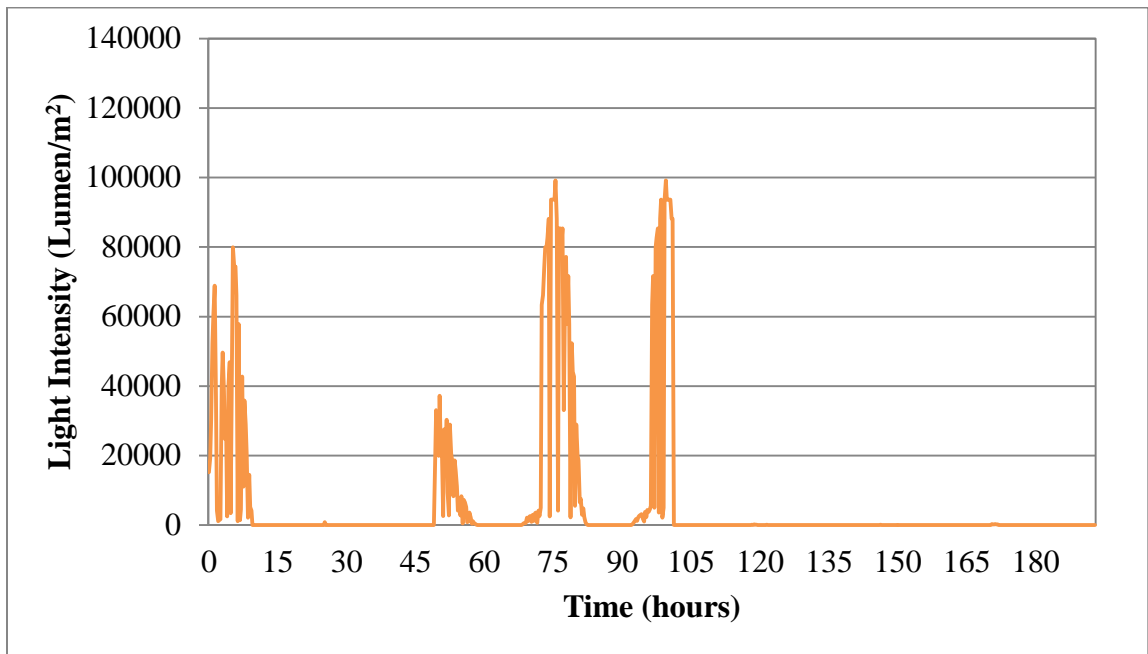


Figure 4S.10: Light Intensity profiles for the time of weathering of Access Western Blend (AWB) on water during spring-time of 2017.

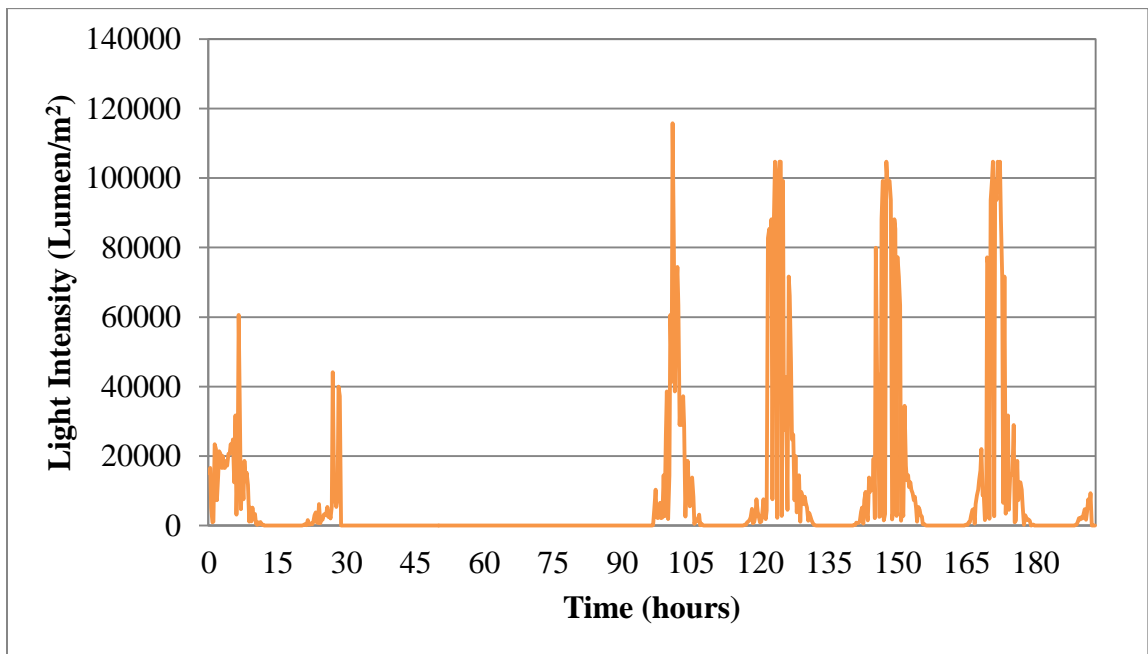


Figure 4S.11: Light Intensity profiles for the time of weathering of Western Canadian Select (WCS) on water during spring-time of 2017.

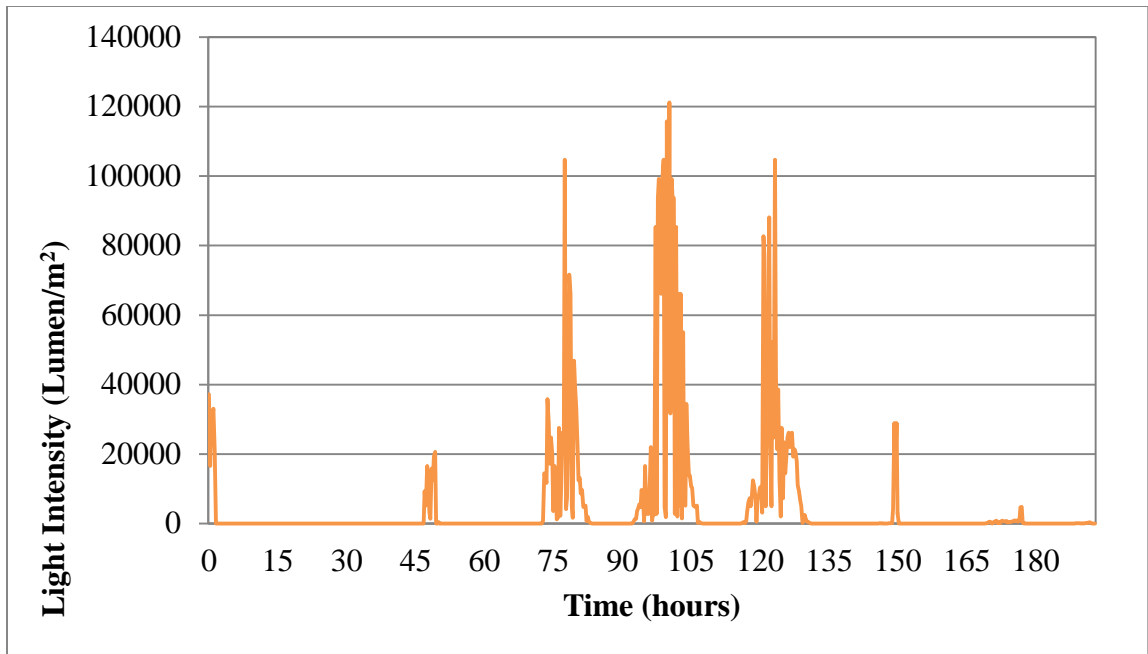


Figure 4S.12: Light Intensity profiles for the time of weathering of Synthetic Bitumen (synbit) on water during spring-time of 2017.

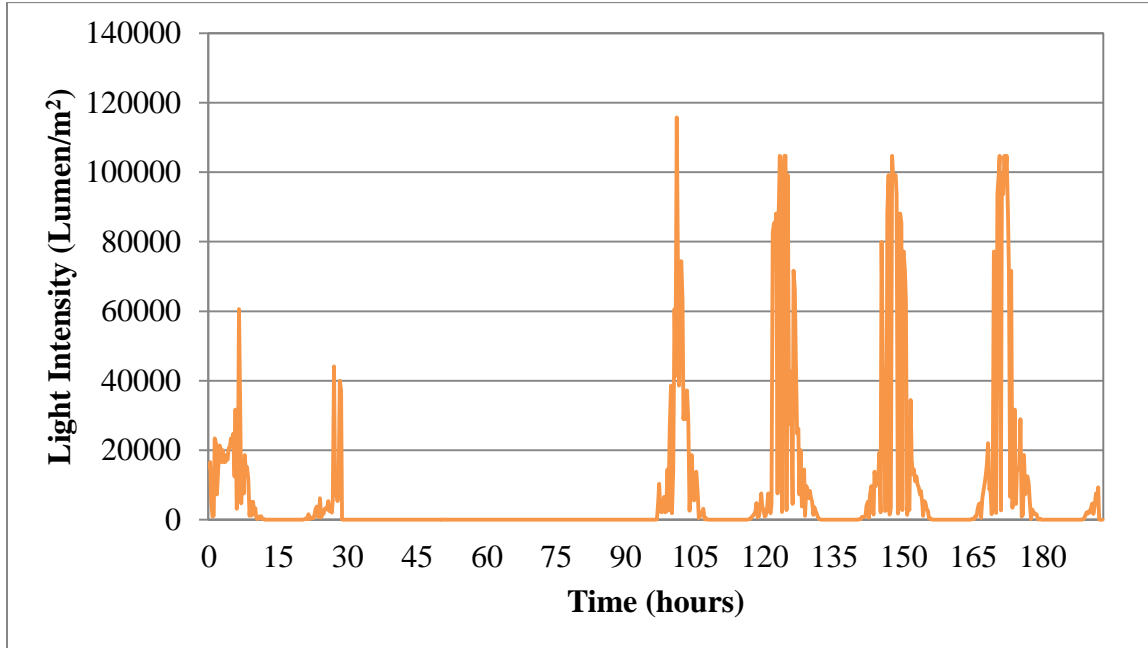


Figure 4S.13: Light Intensity profiles for the time of weathering of Heidrun on water during spring-time of 2017.

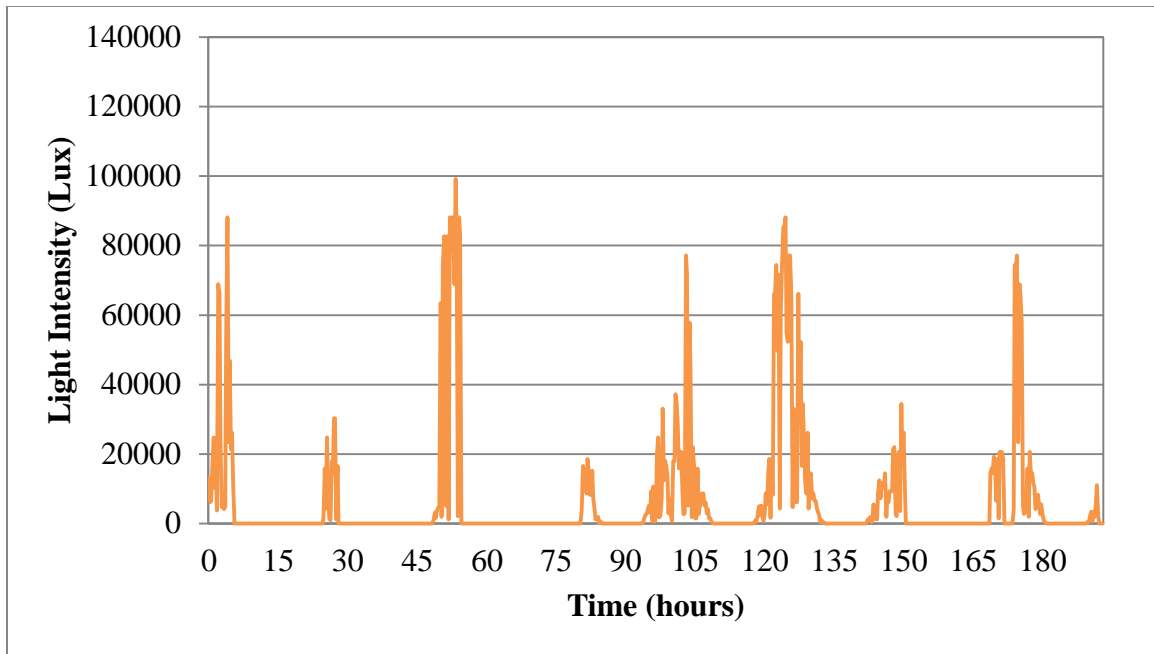


Figure 4S.14: Light Intensity profiles for the time of weathering of Access Western Blend (AWB) on water during summer-time of 2017.

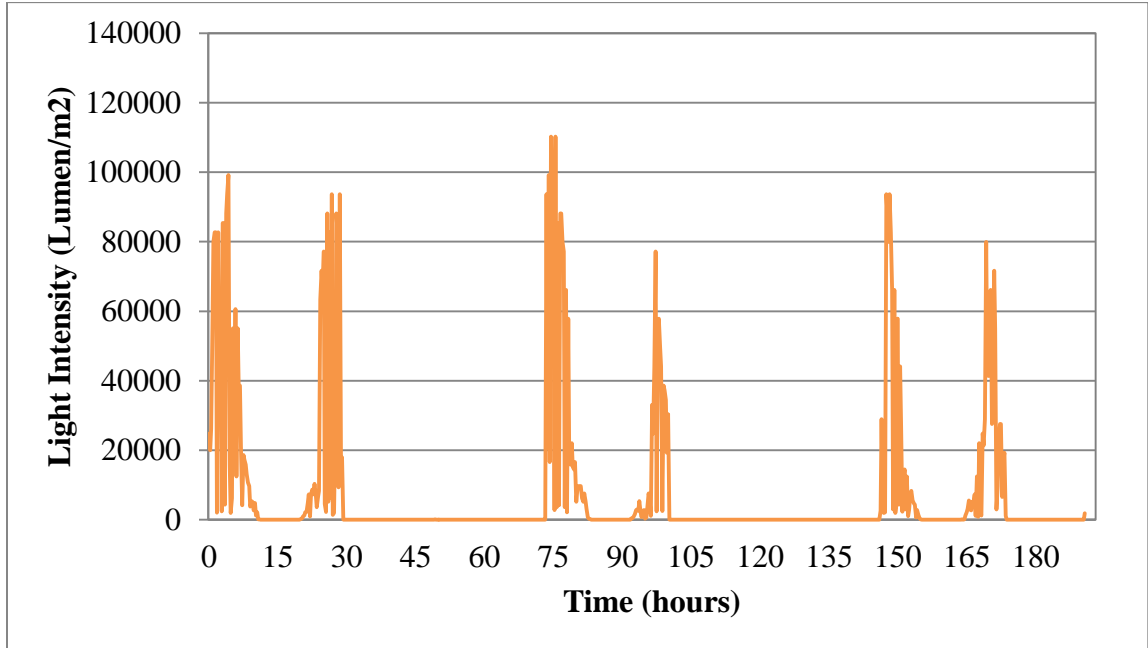


Figure 4S.15: Light Intensity profiles for the time of weathering of Western Canadian Select (WCS) on water during summer-time of 2017.

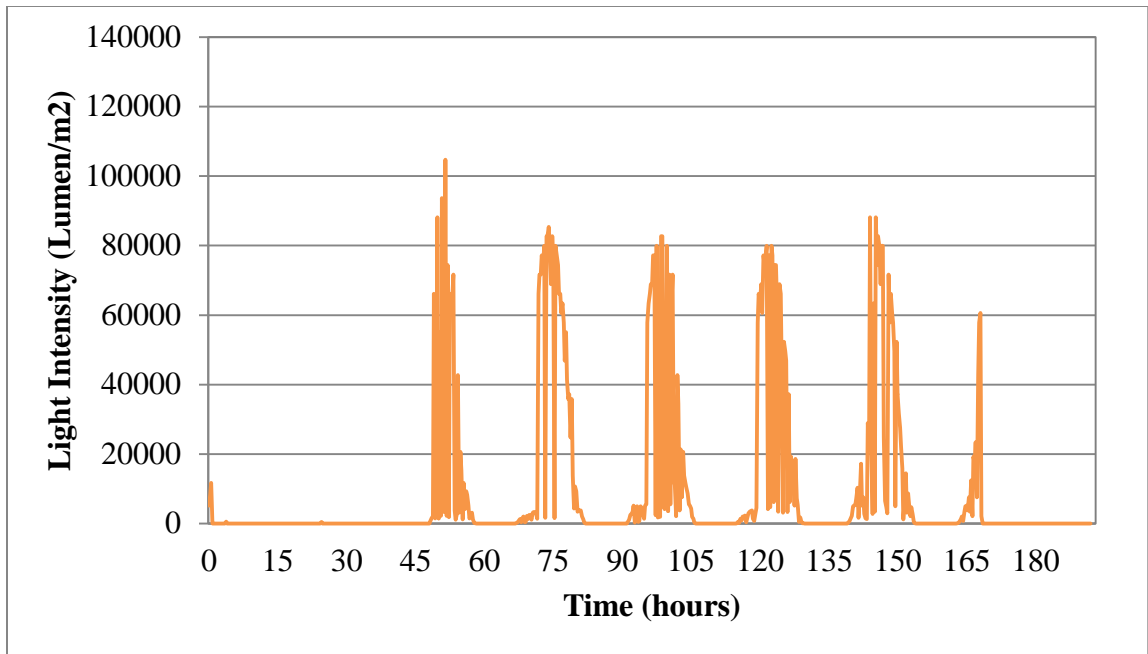


Figure 4S.16: Light Intensity profiles for the time of weathering of Synthetic Bitumen (synbit) on water during summer-time of 2017.

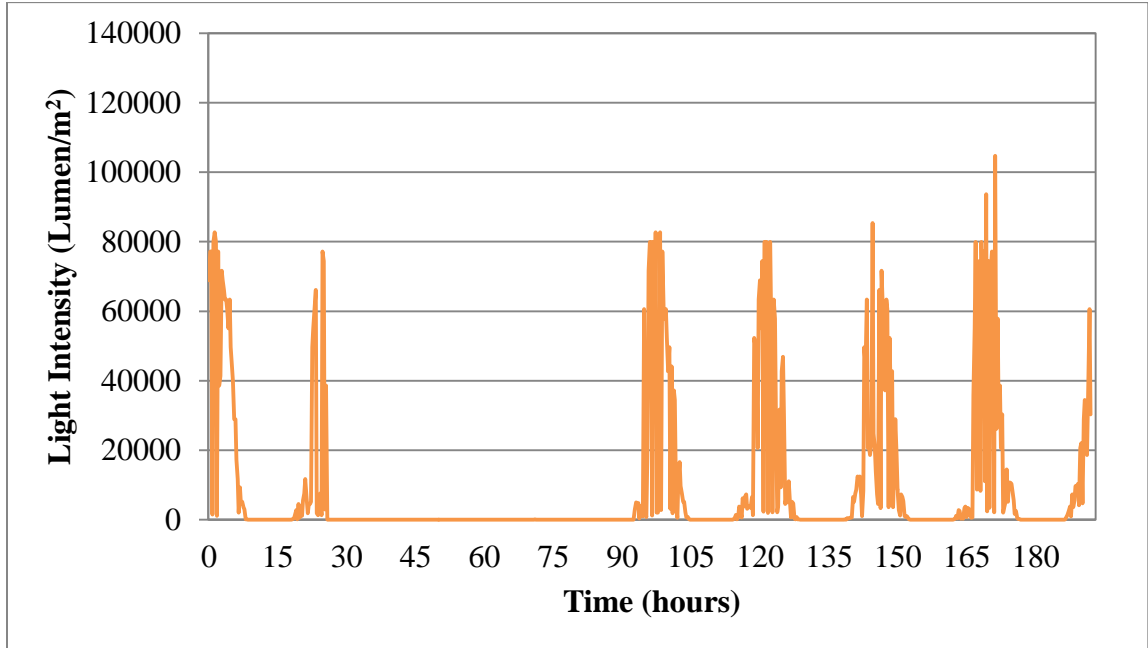


Figure 4S.17: Light Intensity profiles for the time of weathering of Heidrun on water during summer-time of 2017.

10.2 Chapter 5: Supporting Materials

Tables 5S.1 to 5S.8 contain triplicate measurements, averages and standard deviations of the physical properties (e.g. density and viscosity) of oils as a function of weathering time taking into consideration the slick thickness of the oils, water temperature and wind speeds.

Table 5S.1: Density and Viscosity Data for AWB-W (6.6 mm, 21.9 °C, 12.9 km/hr).

Time (hr)	Density					Viscosity				
	1	2	3	Ave	SD	1	2	3	Ave	SD
	g/cm ³					cSt.				
0	0.9194	0.9193	0.9187	0.9189		241	246	246	244	3
3	0.9763	0.9747	0.9746	0.9752	0.0010	14357	14578	14425	14453	113
8	0.9809	0.9802	0.9826	0.9812	0.0012	28684	29026	30144	29285	764
24	0.9889	0.9888	0.9889	0.9889	0.0001	38208	38307	38253	38256	50
72	0.9968	0.9967	0.9968	0.9968	0.0001	77109	81008	78927	79015	1951
96	0.9971	0.9970	0.9969	0.9970	0.0001	95807	90976	87874	91552	3998
120	0.9968	0.9963	0.9965	0.9965	0.0003	136598	136194	142044	138278	3267
240	0.9994	0.9982		0.9988	0.0008	185808	175314		180561	7421
264	0.9997	0.9993	0.9993	0.9994	0.0002	198544	194544	192576	195221	3041

Table 5S.2: Density and Viscosity Data for AWB-W (3.7 mm, 22.0 °C, 13.3 km/hr).

Time (hr)	Density					Viscosity				
	1	2	3	Ave	SD	1	2	3	Ave	SD
	g/cm ³					cSt.				
0	0.9194	0.9193	0.9187	0.9189	0.0004	241	246	246	244	3
3	0.9857	0.9813	0.9792	0.9821	0.0033	25888	25964	25870	25907	50
8	0.9838			0.9838		62007			62007	
24	0.9946	0.9944	0.9941	0.9944	0.0003	189431	190125	189031	189529	554
48	0.9957	0.9970	0.9971	0.9966	0.0008	280232	286242	253207	273227	17597
72	0.9991	0.9991	0.9990	0.9991	0.0001	301075	363197	341470	335248	31525
144	1.0010	1.0006	1.0002	1.0006	0.0004	500257	465115	529168	498180	32077
192	1.0014	1.0018	1.0020	1.0017	0.0003	470878	476071	474970	473973	2736
240	1.0025	1.0028	1.0026	1.0026	0.0002	816403	787408	819068	807626	17561
284	1.0044	1.0030	1.0033	1.0036	0.0007	895099	791979	903742	863606	62182

Table 5S.3: Density and Viscosity Data for IFO 180 (6.9 mm, 21.9 °C, 12.9 km/hr).

Time (hr)	Density					Viscosity				
	1	2	3	Ave	SD	1	2	3	Ave	SD
	g/cm ³					cSt.				
0	0.9627	0.9631	0.9659	0.9639	0.0017	2344	2340	2342	2342	2
3	0.9670	0.9670	0.9671	0.9670	0.0001	3344	3417	3399	3387	38
8	0.9637	0.9647	0.9590	0.9625	0.0030	3186	3226	3223	3212	23
24	0.9682	0.9682	0.9682	0.9682	0.0000	4194	4174	4140	4169	27
72	0.9697	0.9697	0.9698	0.9697	0.0001	5500	5564	5943	5669	239
96	0.9707	0.9707	0.9707	0.9707	0.0000	6433	6501	6598	6510	83
120	0.9710	0.9708	0.9709	0.9709	0.0001	5725	5992	5841	5853	134
192	0.9729	0.9732	0.9730	0.9730	0.0002	9869	10075	10553	10166	351
240	0.9739	0.9739	0.9740	0.9739	0.0001	16663	13989	16070	15574	1405
264	0.9796	0.9797		0.9797	0.0001	20460	19508		19984	673

Table 5S.4: Density and Viscosity Data for IFO 180 (4.0 mm, 22.0 °C, 13.3 km/hr).

Time (hr)	Density					Viscosity				
	1	2	3	Ave	SD	1	2	3	Ave	SD
	g/cm ³					cSt.				
0	0.9627	0.9631	0.9659	0.9639	0.0017	2344	2340	2342	2342	2
3	0.9643	0.9644	0.9644	0.9644	0.0001	3798	3666	3762	3742	68
8	0.9636			0.9636		3876			3876	
24	0.9643	0.9643	0.9646	0.9644	0.0002	4044	4071	4173	4096	68
48	0.9704	0.9703	0.9703	0.9703	0.0001	5033	5880	6076	5663	554
72	0.9701	0.9704	0.9760	0.9722	0.0033	6993	6739	6780	6837	136
144	0.9720	0.9721	0.9710	0.9717	0.0006	8404	8543	8563	8504	87
192	0.9723	0.9725	0.9724	0.9724	0.0001	10773	11970	11970	11571	691
240	0.9739	0.9739	0.9883	0.9787	0.0083	14994	15227	15560	15260	285

Table 5S.5: Density and Viscosity Data for CLB-S (7.1 mm, 13.2 °C, 17.6 km/hr).

Time (hr)	Density					Viscosity				
	1	2	3	Ave	SD	1	2	3	Ave	SD
	g/cm ³					cSt.				
0	0.9393	0.9393	0.9401	0.9396	0.0005	720	720	749	730	17
3	0.9605	0.9605	0.9605	0.9605	0.0000	3478	3484	3487	3483	5
8	0.9659	0.9659	0.9659	0.9659	0.0000	5504	5486	5490	5493	9
24	0.9745	0.9745	0.9745	0.9745	0.0000	11680	12250	12062	11997	290
72	0.9849	0.9843	0.9844	0.9845	0.0003	36907	37966	37398	37424	530
96	0.9869	0.9869	0.9869	0.9869	0.0000	35521	35402	35356	35426	85
144	0.9885	0.9880	0.9883	0.9883	0.0003	38304	38175	37966	38148	171
192	0.9914	0.9870	0.9879	0.9888	0.0023	52570	50794	50989	51451	974
240	0.9915	0.9895	0.9891	0.9900	0.0013	68100	56526	73620	66082	8724
288	0.9901	0.9903	0.9902	0.9902	0.0001	82551	82469	80489	81836	1168
360	0.9938	0.9928	0.9922	0.9929	0.0008	153560	134991	115654	134735	18954

Table 5S.6: Density and Viscosity Data for CLB-S (3.6 mm, 19.3 °C, 14.9 km/hr).

Time (hr)	Density					Viscosity				
	1	2	3	Ave	SD	1	2	3	Ave	SD
	g/cm ³					cSt.				
0	0.9393	0.9393	0.9401	0.9396	0.0005	749	749	749	730	0
3	0.9881	0.9881	0.9882	0.9881	0.0001	56180	52006	52038	53408	2401
24	0.9869	0.9870	0.9870	0.9870	0.0001	51300	51209	50972	51160	169
96	0.9945	0.9944	0.9944	0.9944	0.0003	147228	146053	144787	146023	1221
120	0.9970	0.9969	0.9970	0.9970	0.0001	225061	223851	223871	224261	693
168	0.9958	0.9952	0.9952	0.9954	0.0004	195089	202202	199566	198952	3596
192	0.9966	0.9967	0.9965	0.9966	0.0003	222532	223539	220606	222226	1491
264	0.9975	0.9981	0.9982	0.9979	0.0004	251313	249255	247794	249454	1768
312	0.9947	0.9951		0.9949	0.0003	305836	313142		309489	5166

Table 5S.7: Density and Viscosity Data for Heidrun (3.6 mm, 19.3 °C, 14.9 km/hr).

Time (hr)	Density					Viscosity				
	1	2	3	Ave	SD	1	2	3	Ave	SD
	g/cm ³					cSt.				
0	0.9131	0.9131	0.9154	0.9139	0.0013	71	71	77	73	3
3	0.9239	0.9239	0.9239	0.9239	0.0000	142	143	143	143	0
8	0.9265	0.9264	0.9264	0.9264	0.0001	175	173	173	174	1
24	0.9319	0.9318	0.9318	0.9318	0.0001	272	271	272	272	0
96	0.9412	0.9393	0.9397	0.9401	0.0010	516	546	536	532	15
120	0.9447	0.9437	0.9388	0.9424	0.0032	610	662	679	650	36
168	0.9433	0.9432	0.9422	0.9429	0.0006	616	619	618	618	1
192	0.9446	0.9429	0.9496	0.9457	0.0035	717	764	751	744	24
264	0.9434	0.9434	0.9434	0.9434	0.0000	830	827	820	826	5
312	0.9444	0.9449	0.9491	0.9461	0.0026	843	843	873	853	17

Table 5S.8: Density and Viscosity Data for Synbit (3.8 mm, 13.2 °C, 17.6 km/hr).

Time (hr)	Density					Viscosity				
	1	2	3	Ave	SD	1	2	3	Ave	SD
	g/cm ³					cSt.				
0	0.9390	0.9321	0.9322	0.9344	0.0040	232	235	235	234	2
3	0.9572	0.9572	0.9572	0.9572	0.0000	1475	1471	1469	1471	3
8	0.9600	0.9601	0.9601	0.9601	0.0001	1968	1961	1954	1961	7
24	0.9654	0.9643	0.9642	0.9646	0.0007	3059	3071	3041	3057	15
72	0.9710	0.9703	0.9708	0.9707	0.0004	6514	6393	6389	6432	71
96	0.9721	0.9716	0.9715	0.9717	0.0003	7956	7826	7577	7786	193
144	0.9771	0.9738	0.9735	0.9748	0.0020	10144	10246	9828	10073	218
192	0.9751	0.9753	0.9752	0.9752	0.0001	14017	13351	12797	13388	611
240	0.9782	0.9783	0.9779	0.9781	0.0002	17366	16823	16766	16985	331
288	0.9800	0.9802	0.9796	0.9799	0.0003	29429	28628	24642	27566	2564
360	0.9823	0.9824	0.9823	0.9823	0.0001	36499	36991	36370	36620	328

Tables 5S.9 to 5S.12 contain raw data collected during the flume tank studies.

Table 5S.9: Experimental Data Collected During Oil Weathering Study #1.

Time (Hours)	AWB-W *ST (mm)	IFO 180 ST (mm)	Water Temp. (°C)	Salinity p.s.u.	Air Temp. (°C)	Wind Speed (km/hr)
0			20.3	25.1	22.9	16.5
3	7.2	7.1	22.3	25.2	22.9	16.5
8	6.7	7.7	24.4	25.1	22.9	16.5
24	6.4	6.2	21.9	25.3	20.1	11.5
72	6.8	6.4	20.8	25.2	16.0	13.3
96	6.4	6.1	18.6	24.8	17.9	19.5
120	6.3	6.7	19.8	24.5	16.6	14.3
192	6.7	7.3	22.0	24.8	18.8	7.8
240	6.9	6.8	23.1	24.8	20.8	7.1
264	6.2	6.7	24.5	24.9	21.7	6.0
288	6.8	7.7	24.8	25.4	21.9	7.5
Average	6.6	6.9	21.9	25.0	20.2	12.9
SD	0.3	0.6	2.1	0.3	2.7	4.6

*ST- slick thickness; SD-Standard Deviation

Table 5S.10: Experimental Data Collected During Oil Weathering Study #2.

Time (Hours)	AWB-W ST (mm)	IFO 180 ST(mm)	Water Temp. (°C)	Salinity p.s.u.	Air Temp. (°C)	Wind Speed (km/hr)
0			21.7	26.6	22.5	21.0
3	4.4	4.4	23.8	26.7	24.9	7.0
8	3.7	4.1	25.6	26.5	20.6	15.0
24	3.4	4.1	23.7	26.3	17.8	23.0
48	3.4	3.5	21.3	26.7	19.3	20.0
72	3.8	4.2	21.3	26.5	21.9	7.0
144	3.7	3.8	20.5	26.7	23.1	7.0
192	3.7	4.0	22.4	26.8	20.8	10.0
240	3.5	3.8	18.4	27.3	17.2	18.0
288	3.6	3.7	21.3	28.0	15.7	5.0
Average	3.7	4.0	22.0	26.8	20.4	13.3
SD	0.3	0.3	2.0	0.5	2.9	6.8

Table 5S.11: Experimental Data Collected During Oil Weathering Study #3.

Time (Hours)	CLB-S ST (mm)	Heidrun ST (mm)	Water Temp. (°C)	Salinity p.s.u.	Air Temp. (°C)	Wind Speed (km/hr)
0			16.0	28.0	21.6	18
3	4.7	3.6	18.5	28.2	24.2	18.0
8	3.7	3.7	20.2	28.2	23.3	10.0
24	3.5	4.0	21.0	27.4	20.1	4.0
96	3.5	3.7	19.5	27.9	14.8	24.0
120	3.3	3.5	19.9	29.7	15.2	12.0
168	4.2	3.5	19.9	27.4	18.3	21.0
192	3.6	3.6	17.6	27.3	14.1	11.0
264	3.2	3.5	17.8	27.4	19.0	17.0
312	3.8	3.4	21.8	28.0	22.3	14.0
Average	3.7	3.6	19.3	28.0	19.3	14.9
SD	0.5	0.2	1.8	0.7	3.7	5.9

Table 5S.12: Experimental Data Collected During Oil Weathering Study #4.

Time (Hours)	CLB-S ST (mm)	Synbit ST(mm)	Water Temp. (°C)	Salinity p.s.u.	Air Temp. (°C)	Wind Speed (km/hr)
0			14.9	26.3	10.9	17.0
3	7.1	3.7	14.9	26.3	11.9	22.0
8	7.1	3.9	14.2	26.6	11.2	15.0
24	7.0	3.6	14.9	26.5	13.8	10.0
72	6.9	3.9	12.0	26.1	6.1	15.0
96	7.0	3.7	10.2	25.8	4.6	20.0
144	7.0	3.9	12.9	26.3	8.1	20.0
192	7.1	4.2	13.0	26.1	10.3	22.0
240	6.9	3.4	12.7	25.6	13.1	13.0
280	7.2	3.7	13.3	26.5	2.3	15.0
360	7.3	3.6	13.4	25.5	11.9	25.0
Average	7.1	3.8	13.2	26.1	9.5	17.6
SD	0.1	0.2	1.4	0.4	3.7	4.5

Tables 4S.13 to 4S.15 contain empirical model physical property predictions for AWB-W, IFO 180, and CLB-S as a function of weathering time at 7 mm and 4 mm slick thickness.

Table 5S.13: AWB-W Density and Viscosity Predictions as a Function of Time of Weathering of Oil at a Slick Thickness of 7 mm and 4 mm.

(7mm, 21.9 °C, 12.9 km/hr)			(4 mm, 22.0 °C, 13.3 km/hr)	
t (hrs)	ρ (g/cm ³)	ν (cSt)	ρ (g/cm ³)	ν (cSt)
0	0.9189	244	0.9189	244
3	0.9656	6533	0.9683	22194
8	0.9822	16160	0.9857	56398
10	0.9850	19742	0.9886	69313
24	0.9927	41292	0.9966	149314
48	0.9959	68062	1.0000	254485
72	0.9971	86900	1.0011	332661
96	0.9976	100877	1.0017	393053
120	0.9980	111659	1.0021	441110
144	0.9982	120230	1.0023	480260
192	0.9985	132994	1.0026	540197
240	0.9987	142045	1.0028	583925
264	0.9988	145651	1.0029	601636
288	0.9988	148798	1.0029	617237
360	0.9989	156226	1.0031	654581

Table 5S.14: IFO 180 Density and Viscosity Predictions as a Function of Time of Weathering of Oil at a Slick Thickness of 7 mm and 4 mm.

IFO 180 (7mm, 21.9 °C, 12.9 km/hr)			IFO 180 (4mm, 22.0 °C, 13.3 km/hr)	
t (hrs)	ρ (g/cm ³)	ν (cSt)	ρ (g/cm ³)	ν (cSt)
0	0.9652	2342	0.9639	2342
3	0.9696	2342	0.9641	3042
8	0.9699	2632	0.9643	3222
10	0.9700	2748	0.9644	3294
24	0.9708	3560	0.9651	3798
48	0.9723	4952	0.9663	4662
72	0.9737	6344	0.9675	5526
96	0.9752	7736	0.9687	6390
120	0.9766	9128	0.9699	7254
144	0.9780	10520	0.9711	8118
192	0.9809	13304	0.9735	9846
240	0.9838	16088	0.9759	11574
264	0.9852	17480	0.9771	12438
360	0.9910	23048	0.9819	15894

Table 5S.15: CLB-S Density and Viscosity Predictions as a Function of Time of Weathering of Oil at a Slick Thickness of 7 mm and 4 mm.

CLB-S (7mm, 13.2 °C, 17.6 km/hr)			CLB-S (4mm, 19.3 °C, 14.9 km/hr)	
t (hrs)	ρ (g/cm ³)	ν (cSt)	ρ (g/cm ³)	ν (cSt)
0	0.9396	730	0.9396	749
3	0.9541	2351	0.9746	15378
8	0.9663	4968	0.9863	36278
10	0.9692	5986	0.9882	43628
24	0.9796	12688	0.9934	83649
72	0.9876	31171	0.9964	149969
96	0.9888	38462	0.9967	166549
144	0.9901	50344	0.9971	187274
192	0.9908	59616	0.9973	199709
244	0.9912	67606	0.9975	208567
264	0.9914	70245	0.9975	211187
288	0.9915	73150	0.9975	213920
360	0.9918	80482	0.9976	220190

Table 5S.16: Summary of Definition of Terms in Table 5.2 Statistic t-Test Comparing the Effects of Oil Slick Thickness on the Density and Viscosity of Oil Weathered under Natural Conditions.

Term	Definition
t-Test	A t-test is a type of statistical test used to determine if there is a significant difference between the means of the dependent variables (density and viscosity) as the result of change in the independent variable (4 versus 7 mm oil slick thickness).
n	$n = n_1 + n_2$ Therefore 'n' is the number of mean density or viscosity measurements (n_1) at 4 mm oil slick thickness added to the number of mean density or viscosity measurements at 7mm oil slick thickness (n_2) over the same points in time.
T-Statistic	The T-statistic is computed from the data and represents how much the variability among the means (i.e. density or viscosity) exceeds that expected due to oil slick thickness.
T-Critical	It is the value that a test statistic must exceed in order for the the null hypothesis to be rejected. A T-statistic greater than the T-critical value is equivalent to a <i>p</i> -value less than alpha (0.05) and both means (rate of change in density and viscosity at 4 versus 7 mm oil slick thickness) are different.
variables	Oil slick thickness is the independent variable, since it is the one that is changed through control. The dependent variables are density and viscosity, since they are increasing at different rates as a result of the change.
<i>p</i>-value	If <i>p</i> -value is less than alpha (0.05), you conclude that the mean difference between sample (i.e. mean density values at 4 versus 7 mm) is statistically significant. In other words, both means are different.

Plots of empirical models predicting the effects of oil slick thickness on the changes in density and viscosity as a function of oil weathering time on seawater are illustrated in Figure S-1 and 2.

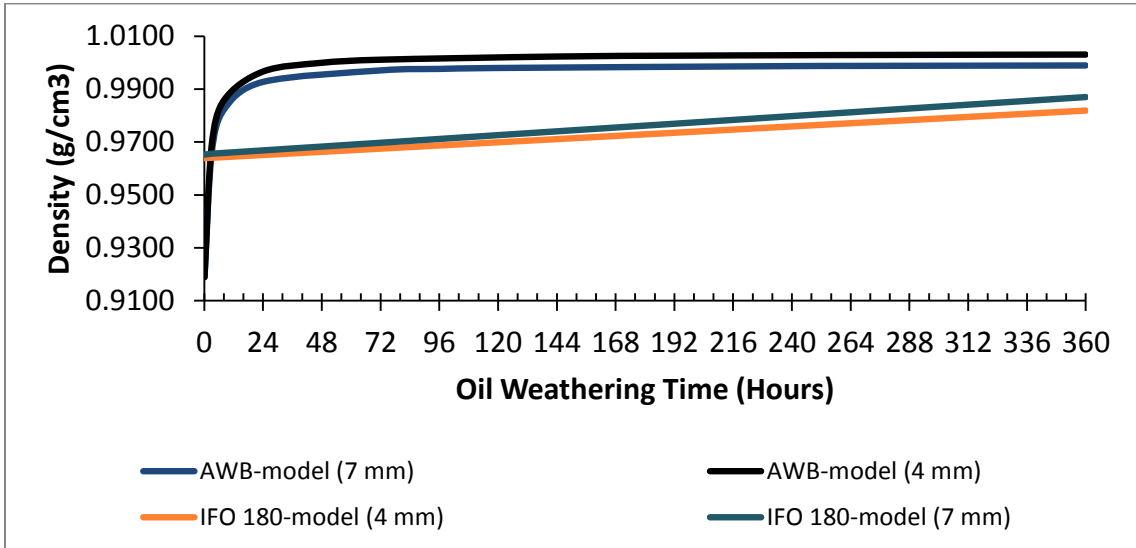


Figure 5S.1: A Plot Showing Empirical Models Predicting of the Effects of Oil Slick Thickness on the Changes in Density as a Function of weathering time of oil (AWB and IFO 180) on Seawater in a Flume Tank.

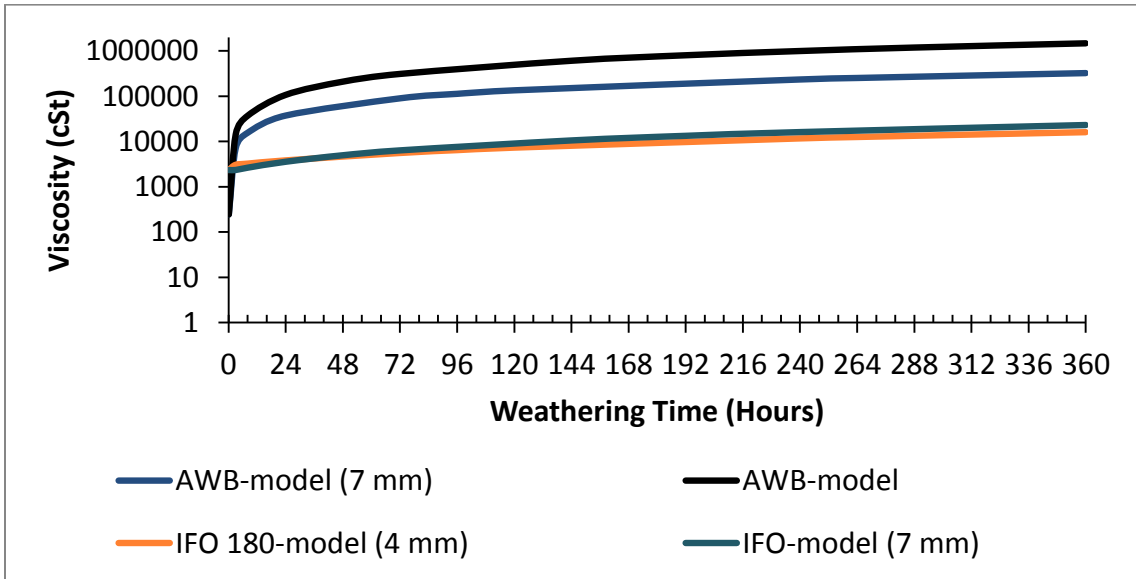


Figure 5S.2: Plot of Empirical Models Predicting the Effects of Oil Slick Thickness on the Changes in Viscosity as a Function of Time of Weathering of Oil (AWB and IFO 180) on Seawater in a Flume Tank.

10.3 Chapter 6: Supporting Materials

Tables 6S.1 to 6S.4 contain the spring and summer experimental data for the four oils.

The raw data for the density and viscosity measurements are found in Tables 6S-1 to 6S-2.

%Difference = $\frac{(\rho_f - \rho_i)}{\frac{(\rho_f + \rho_i)}{2}}$ where ρ_f and ρ_i are the final and initial density values respectively.

Table 6S.1: Density (average \pm standard deviation) data for all oils weathered on seawater in spring and summer conditions. Density values have been adjusted to 15 °C for spring and summer.

Weathering Study (Spring)				
Sampling Time (Hours)	AWB (g/cm³)	WCS (g/cm³)	Synbit (g/cm³)	Heidrun (g/cm³)
0	0.9181±0.0003	0.9252±0.0001	0.9326±0.0003	0.9149±0.0002
3	0.9596±0.0017	0.9491±0.0013	0.9484±0.0016	0.9212±0.0023
8	0.9684±0.040	0.9538±0.0038	0.9526±0.0001	0.9255±0.0005
24	0.9719±0.0001	0.9652±0.0002	0.9572±0.0017	0.9277±0.0005
48	0.9781±0.0017	0.9680±0.0002	0.9609±0.0005	0.9291±0.0064
72	0.9807±0.0004	0.9708±0.0012	0.9631±0.0012	0.9305±0.0003
96	0.9816±0.0022	0.9724±0.0019	0.9650±0.0002	0.9313±0.0002
120	0.9816±0.0014	0.9719±0.0001	0.9666±0.0003	0.9320±0.0005
144	0.9820±0.0006	0.9731±0.0003	0.9673±0.0004	0.9332±0.0002
168	0.9830±0.0006	0.9735±0.0028	0.9687±0.0001	0.9341±0.0005
192	0.9834±0.0003	0.9748±0.0010	0.9692±0.0004	0.9356±0.0024
% Difference	6.9	5.2	3.8	2.2
Weathering Study (Summer)				
Sampling Time (Hours)	AWB (g/cm³)	WCS (g/cm³)	Synbit (g/cm³)	Heidrun (g/cm³)
0	0.9210±0.0011	0.9274±0.0010	0.9373±0.0004	0.9151±0.0002
3	0.9512±0.0027	0.9562±0.0013	0.9499±0.0002	0.9280±0.0002
8	0.9652±0.0012	0.9657±0.0020	0.9543±0.0002	0.9312±0.0019
24	0.9699±0.0005	0.9661±0.0082	0.9603±0.0045	0.9323±0.0020
48	0.9770±0.0008	0.9714±0.0015	0.9625±0.0009	0.9318±0.0022
72	0.9800±0.0006	0.9734±0.0002	0.9679±0.0002	0.9347±0.0002
96	0.9829±0.0004	0.9754±0.0012	0.9695±0.0003	0.9370±0.0012
120	0.9841±0.0003	0.9771±0.0015	0.9702±0.0003	0.9388±0.0010
144	0.9872±0.0010	0.9782±0.0032	0.9711±0.0002	0.9444±0.0042
168	0.9877±0.0003	0.9840±0.0034	0.9736±0.002	0.9431±0.0005
192	0.9871±0.0004	0.9839±0.0047	0.9728±0.0002	0.9432±0.0017
%Difference	6.9	5.9	3.8	3.0

%Difference = $\frac{(v_f - v_i)}{2(v_f + v_i)}$ where v_f and v_i are the final and initial viscosity values respectively.

Table 6S.2: Viscosity (average \pm standard deviation) data for all oils weathered on seawater in spring and summer conditions. Viscosity values have been adjusted to 15 °C for spring and summer.

Weathering Study (Spring)				
Sampling Time (Hours)	AWB (cSt)	WCS (cSt)	Synbit (cSt)	Heidrun (cSt)
0	265 \pm 1	260 \pm 1	242 \pm 1	75 \pm 1
3	3711 \pm 10	1143 \pm 40	632 \pm 10	111 \pm 1
8	6110 \pm 10	1570 \pm 20	911 \pm 10	139 \pm 2
24	13510 \pm 140	4057 \pm 50	1478 \pm 30	165 \pm 2
48	21625 \pm 330	5267 \pm 60	2393 \pm 20	203 \pm 3
72	27083 \pm 330	7498 \pm 60	2598 \pm 60	224 \pm 1
96	26563 \pm 890	7280 \pm 80	3059 \pm 60	236 \pm 1
120	33085 \pm 220	8085 \pm 200	3795 \pm 110	257 \pm 3
144	32447 \pm 1800	9388 \pm 30	4168 \pm 80	285 \pm 2
168	36268 \pm 720	11838 \pm 220	4386 \pm 40	313 \pm 2
192	36439 \pm 1600	11444 \pm 40	4568 \pm 50	345 \pm 10
%Difference	197	191	180	129
Weathering Study (Summer)				
Sampling Time (Hours)	AWB (cSt)	WCS (cSt)	Synbit (cSt)	Heidrun (cSt)
0	299 \pm 1	308 \pm 5	242 \pm 3	75 \pm 1
3	2071 \pm 20	2330 \pm 70	776 \pm 5	182 \pm 1
8	6074 \pm 40	3867 \pm 90	1113 \pm 4	221 \pm 2
24	11970 \pm 60	4980 \pm 50	1939 \pm 20	253 \pm 5
48	20102 \pm 340	8090 \pm 150	3202 \pm 40	274 \pm 4
72	25054 \pm 650	10600 \pm 80	4472 \pm 110	295 \pm 3
96	36610 \pm 2100	12956 \pm 450	5694 \pm 80	323 \pm 2
120	45679 \pm 940	15712 \pm 1200	6525 \pm 90	387 \pm 5
144	56079 \pm 2100	20201 \pm 1500	7603 \pm 40	476 \pm 20
168	66246 \pm 1700	24201 \pm 2100	10195 \pm 240	514 \pm 10
192	69309 \pm 1700	25073 \pm 1200	10924 \pm 60	557 \pm 6
%Difference	198	195	191	152

Raw data collected during the oil weathering experiments is found in Tables 6S.3 to 6S.6. Light intensity (lux or lumen/m²) is the average amount received over the 8 day experiment.

Table 6S.3: Experimental Data Collected for Access Western Blend (AWB, dilbit) during the Oil Weathering Studies. *ST-slick thickness. Temp-Temperature.

Weathering Study (AWB-Spring)						
Sampling Time (Hours)	AWB *ST (mm) in duplicate		Water Temp (Celsius)	Salinity (ppt)	Air Temp. (Celsius)	Wind Speed (km/hr)
0			4.5	29.0	6.0	17.0
3	4.0	4.0	6.5	29.4	8.0	13.0
8	4.0	3.9	10.8	29.6	7.5	19.0
24	4.1	4.0	7.8	29.3	3.0	9.0
48	3.9	4.0	6.6	29.3	2.0	20.0
72	4.1	4.0	5.8	29.8	11.0	13.0
96	4.0	4.0	3.3	29.1	8.0	6.0
120	4.1	4.0	5.3	29.4	6.8	26.0
144	4.0	4.0	4.0	28.5	14.0	28.0
168	4.1	4.1	4.3	29.3	13.0	19.0
192	4.0	3.9	0.6	28.7	10.8	11.0
Average	4.0	4.0	5.5	29.2	8.4	16.4
Standard Deviation	0.1	0.1	2.8	0.4	3.9	7.2
Total Rain Fall (mm)			42.8			
Weathering Study (AWB-Summer)						
Sampling Time (Hours)	AWB *ST (mm) in duplicate		Water Temp (Celsius)	Salinity (ppt)	Air Temp. (Celsius)	Wind Speed (km/hr)
0			14.0	29.8	20.0	13.1
3	4.0	4.0	14.1	29.8	22.0	15.2
8	4.2	4.0	13.5	29.5	26.0	11.1
24	4.1	4.0	14.9	29.6	16.0	13.0
48	4.0	3.9	14.1	29.4	15.0	7.2
72	4.0	4.0	14.9	29.4	14.0	9.0
96	4.0	4.0	14.0	29.6	17.0	6.1
120	4.1	4.0	14.8	29.8	16.0	4.0
144	4.1	4.1	14.6	29.6	19.0	7.3
168	4.0	4.2	14.3	29.6	19.0	4.4
192	4.1	4.4	13.8	29.6	21.0	11.1
Average	4.1	4.1	14.3	29.6	18.4	9.0
Standard Deviation	0.1	0.1	0.5	0.2	3.6	3.9
Total Rain Fall (mm)			0.25			

Table 6S.4: Experimental Data Collected for Western Canadian Select (WCS, dilsynbit) during the Oil Weathering Studies. *ST-slick thickness. Temp-Temperature

Weathering Study (WCS-Spring)						
Sampling Time (Hours)	WCS *ST (mm) in duplicate		Water Temp (Celsius)	Salinity (ppt)	Air Temp (Celsius)	Wind Speed (km/hr)
0			5.4	29.8	8.1	17.2
3	4.0	3.8	5.9	29.8	9.7	17.0
8	3.9	3.9	5.7	29.9	11.4	17.2
24	4.2	4.0	6.3	29.8	6.9	30.2
48	4.1	4.0	5.1	29.0	6.9	26.1
72	4.0	5.1	6.5	29.8	8.8	35.2
96	4.1	4.1	6.0	30.0	10.5	20.3
120	3.9	4.1	6.7	29.8	10.7	33.1
144	4.1	4.1	6.7	30.7	11.3	28.1
168	4.0	3.9	6.4	29.1	9.1	22.1
192	4.1	3.9	7.2	29.8	4.3	17.4
Average	4.0	4.1	6.3	29.8	9.0	24.7
Standard Deviation	0.1	0.4	0.6	0.5	2.3	6.8
Total Rain Fall (mm)			43.3			
Weathering Study (WCS-Summer)						
Sampling Time (Hours)	WCS *ST (mm) in duplicate		Water Temp (Celsius)	Salinity (ppt)	Air Temp (Celsius)	Wind Spd. (km/hr)
0			14.6	30.4	24.2	6.3
3	4.1	4.0	16.3	29.1	27.3	6.2
8	4.0	4.1	14.1	30.0	23.1	0
24	4.1	4.1	16.3	30.4	23.8	9.4
48	4.0	4.0	14.3	30.1	20.7	24.2
72	4.0	4.0	14.2	30.2	18.1	9.1
96	4.1	4.1	15.7	30.3	18.9	4.3
120	4.0	4.0	15.0	30.3	12.8	22.8
144	4.0	4.0	15.7	30.0	18.1	11.4
168	4.0	4.0	15.6	30.9	18.2	20.7
192	4.1	4.0	15.6	30.6	17.1	15.1
Average	4.0	4.0	15.2	30.2	20.5	11.8
Standard Deviation	0.1	0.1	0.8	0.5	4.2	7.6
Total Rain Fall (mm)			15.8 mm			

Table 6S.5: Experimental Data Collected for Synthetic Bitumen (Synbit) during the Oil Weathering Studies. *ST-slick thickness. Temp-Temperature.

Weathering Study (Synbit-Spring)						
Sampling Time (Hours)	Synbit *ST (mm) in duplicate		Water Temp (Celsius)	Salinity (ppt)	Air Temp (Celsius)	Wind Spd. (km/hr)
0			6.3	28.9	9.6	6.1
3	4.1	4.0	6.0	28.9	10.7	12.9
8	4.0	4.0	6.8	29.0	8.3	14.8
24	3.9	4.1	5.7	28.7	6.2	19.2
48	4.1	4.0	7.0	29.0	6.4	21.9
72	4.0	4.1	6.2	28.9	9.0	17.5
96	4.0	4.0	6.3	29.0	8.5	25.9
120	3.9	4.0	6.5	28.9	8.3	18.7
144	4.0	4.0	6.3	28.2	7.8	23.6
168	3.9	4.1	6.3	28.4	8.9	33.1
192	4.0	4.0	6.2	28.0	10.6	16.9
Average	4.0	4.0	6.3	28.7	8.5	20.5
Standard Deviation	0.1	0.1	0.4	0.4	1.5	5.9
Total Rain Fall (mm)			54.5			
Weathering Study (Synbit-Summer)						
Sampling Time (Hours)	Synbit *ST (mm) in duplicate		Water Temp (Celsius)	Salinity (ppt)	Air Temp (Celsius)	Wind Spd. (km/hr)
0			12.8	30.1	17.9	4.3
3	4.1	3.9	14.5	31.2	22.1	8.7
8	4.1	3.9	14.8	31.0	19.8	6.2
24	3.9	4.2	14.5	31.2	20.2	27.8
48	3.9	3.9	15.3	31.2	23.7	15.3
72	4.1	3.9	14.8	31.0	23.3	10.7
96	4.1	4.0	14.5	31.2	23.6	11.4
120	4.0	4.0	15.7	31.3	20.6	16.6
144	4.0	4.0	14.2	30.7	21.6	7.1
168	3.9	4.0	14.2	31.1	24.4	23.9
192	4.0	3.9	15.9	30.9	19.9	19.1
Average	4.0	4.0	14.5	31.0	21.7	13.2
Standard Deviation	0.1	0.1	0.8	0.4	2.1	7.7
Total Rain Fall (mm)			0.0 mm			

Table 6S.6: Experimental Data Collected for Heidrun during the Oil Weathering Studies. *ST-slick thickness. Temp-Temperature.

Weathering Study (Heidrun-Spring)						
Sampling Time (Hours)	Heidrun *ST (mm) in duplicate		Water Temp (Celsius)	Salinity (ppt)	Air Temp (Celsius)	Wind Speed (km/hr)
0			6.0	30.0	9.9	8.9
3	4.3	4.3	6.6	30.2	12.0	11.1
8	4.3	4.1	7.7	31.2	15.4	10.8
24	4.2	4.3	7.5	30.5	10.0	4.2
48	4.1	4.1	7.0	29.9	9.6	37.1
72	4.1	4.1	5.7	29.8	8.7	18.9
96	4.4	4.2	7.0	30.1	8.9	12.5
120	4.2	4.2	5.6	29.5	8.0	11.5
144	4.1	4.0	7.2	29.6	9.1	4.2
168	4.2	4.1	5.9	29.7	9.2	16.8
192	4.1	4.2	6.5	29.7	11.6	9.1
Average	4.2	4.2	6.7	30.0	10.2	13.6
Standard Deviation	0.1	0.1	0.7	0.5	2.2	9.5
Total Rain Fall (mm)			38.4			
Weathering Study (Heidrun-Summer)						
Sampling Time (Hours)	AWB *ST (mm) in duplicate		Water Temp (Celsius)	Salinity (ppt)	Air Temp (Celsius)	Wind Speed (km/hr)
0			18.5	31.2	19.9	16.8
3	4.3	4.1	14.6	31.0	22.1	17.2
8	4.2	4.1	16.0	31.2	21.5	18.8
24	4.2	4.0	15.2	31.0	21.5	15.2
48	4.2	4.1	14.4	31.1	23.8	0
72	4.1	4.2	16.5	31.2	20.2	17.0
96	4.2	4.0	14.8	31.0	17.8	21.6
120	4.2	4.2	14.8	31.1	22.2	7.4
144	4.0	4.1	14.0	30.9	22.2	14.7
168	4.0	4.1	15.9	31.0	22.8	20.3
192	4.0	4.2	15.0	30.4	17.9	32.8
Average	4.1	4.1	15.5	31.1	21.1	14.9
Standard Deviation	0.1	0.1	1.3	0.1	1.7	6.5
Total Rain Fall (mm)			9.8			

Table 6S.7a: Multiple Correlation Analysis of Climatic Factors and Density and Viscosity of AWB Weathered on Water in Spring and Summer. Values in the table are Pearson Coefficient of Determination (r). When 'r' is positive changes in the dependent variables (density and viscosity) increase with an increase in the values of the independent variables (air and water temperature, wind speed, and sunlight energy). A negative 'r' indicates increasing changes in the dependent variable with a decreasing change in the independent variables. Regression Analysis is reported for significant relationships in Table 4.2 for values highlighted in grey. Temperature (Temp).

AWB Spring					
	Air Temp	Water Temp	Wind speed	Sunlight Intensity	density
Air Temp	1				
Water Temp	-0.50	1			
Wind speed	0.24	0.13	1		
Light Intensity	-0.17	0.63	-0.07	1	
density	0.40	-0.74	0.15	-0.92	1
AWB Summer					
	Air Temp	Water Temp	Wind speed	Sunlight Intensity	density
Air Temp	1				
Water Temp	-0.75	1			
Wind speed	0.43	-0.21	1		
Light Intensity	0.73	-0.42	0.68	1	
density	-0.40	0.21	-0.77	-0.86	1
AWB Spring					
	Air Tem	Water Tem	Wind Speed	Sunlight Intensity	Viscosity
Air Tem	1				
Water Tem	-0.48	1			
Wind Speed	0.31	-0.03	1		
Sunlight Intensity	-0.16	0.81	0.00	1	
Viscosity	0.63	-0.88	0.33	-0.78	1
AWB Summer					
	Air Tem	Water Tem	Wind Speed	Sunlight Intensity	Viscosity
Air Tem	1				
Water Tem	-0.56	1			
Wind Speed	0.03	0.08	1		
Sunlight Intensity	0.31	0.51	0.31	1	
Viscosity	0.86	-0.44	-0.36	0.31	1

Table 6S.7b: Multiple Correlation Analysis of Climatic Factors and Density and Viscosity of WCS Weathered on Water in Spring and Summer. Values in the table are Pearson Coefficient of Determination (r). Regression Analysis is reported for significant relationships in Table 4.2 for values highlighted in grey. Temperature (Temp).

WCS Spring					
	Air Tem	Water Tem	Wind speed	Sunlight Intensity	density
Air Temp	1				
Water Temp	-0.12	1			
Wind speed	0.30	0.10	1		
Sunlight Intensity	0.21	0.17	-0.10	1	
density	0.61	-0.05	0.50	-0.20	1
WCS Summer					
	Air Temp	Water Temp	Wind speed	Sunlight Intensity	density
Air Temp	1				
Water Temp	0.27	1			
Wind speed	-0.10	-0.56	1		
Sunlight Intensity	0.14	0.80	-0.54	1	
density	-0.08	-0.84	0.53	-0.85	1
WCS Spring					
	Air Temp	Water Temp	Wind speed	Sunlight Intensity	Viscosity
Air Temp	1				
Water Temp	-0.19	1			
Wind speed	0.20	0.06	1		
Sunlight Intensity	0.59	0.29	0.11	1	
Viscosity	0.67	-0.26	0.19	0.64	1
WCS Summer					
	Air Temp	Water Temp	Wind speed	Sunlight Intensity	Viscosity
Air Temp	1				
Water Temp	0.35	1			
Wind speed	-0.19	-0.53	1		
Sunlight Intensity	0.21	0.78	-0.49	1	
Viscosity	-0.02	-0.83	0.37	-0.74	1

Table 6S.7c: Multiple Correlation Analysis of Climatic Factors and Density and Viscosity of Synbit Weathered on Water in Spring and Summer. Values in the table are Pearson Coefficient of Determination (r). Regression Analysis is reported for significant relationships in Table 4.2 for values highlighted in grey. Temperature (Temp).

Synbit Spring					
	Air Temp	Water Temp	Wind speed	Sunlight Intensity	density
Air Temp	1				
Water Temp	-0.21	1			
Wind speed	0.06	-0.34	1		
Sunlight Intensity	-0.13	0.57	-0.71	1	
density	0.10	-0.39	0.87	-0.88	1
Synbit Summer					
	Air Temp	Water Temp	Wind speed	Sunlight Intensity	density
Air Temp	1				
Water Temp	-0.49	1			
Wind speed	0.05	-0.25	1		
Sunlight Intensity	-0.04	0.00	-0.28	1	
density	0.04	0.08	-0.27	0.96	1
Synbit Spring					
	Air Temp	Water Temp	Wind speed	Sunlight Intensity	viscosity
Air Temp	1				
Water Temp	-0.21	1			
Wind speed	0.05	-0.20	1		
Sunlight Intensity	-0.21	0.71	-0.42	1	
density	0.12	-0.11	0.79	-0.82	1
Synbit Summer					
	Air Temp	Water Temp	Wind speed	Sunlight Intensity	viscosity
Air Temp	1				
Water Temp	0.52	1			
Wind speed	0.44	0.12	1		
Sunlight Intensity	-0.03	0.07	-0.24	1	
density	0.42	0.44	0.09	0.81	1

Table 6S.7d: Multiple Correlation Analysis of Climatic Factors and Density and Viscosity of Heidrun Weathered on Water in Spring and Summer. Values in the table are Pearson Coefficient of Determination (r). Regression Analysis is reported for significant relationships in Table 4.2 for values highlighted in grey. Temperature (Temp).

Heidrun Spring					
	Air Temp	Water Temp	Wind speed	Sunlight Intensity	Density
Air Temp	1				
Water Temp	0.64	1			
Wind speed	-0.05	-0.20	1		
Sunlight Intensity	0.11	0.66	-0.37	1	
density	0.02	-0.39	0.30	-0.92	1
Heidrun Summer					
	Air Temp	Water Temp	Wind speed	Sunlight Intensity	Density
Air Temp	1				
Water Temp	-0.15	1			
Wind speed	0.30	-0.76	1		
Sunlight Intensity	-0.01	0.22	0.04	1	
density	-0.13	-0.23	0.37	-0.69	1
Heidrun Spring					
	Air Temp	Water Temp	Wind speed	Sunlight Intensity	Viscosity
Air Temp	1				
Water Temp	0.64	1			
Wind speed	-0.05	-0.20	1		
Sunlight Intensity	0.11	0.66	-0.37	1	
Viscosity	-0.22	-0.58	0.33	-0.94	1
Heidrun Summer					
	Air Temp	Water Temp	Wind speed	Sunlight Intensity	Viscosity
Air Temp	1				
Water Temp	-0.39	1			
Wind speed	0.37	-0.79	1		
Sunlight Intensity	0.43	0.06	0.34	1	
Viscosity	-0.67	0.05	-0.30	-0.87	1

Table 6S.8: Summary of Definition of Terms in Table 6.4 ANOVA Comparing the Effects of Season on the Changes in Density and Viscosity of Oils Weathered Under Simulated Natural Conditions.

Term	Definition
ANOVA	Analysis of Variance (ANOVA) Repeated measures investigate about the 1) changes in mean scores over three or more time points and 2) differences in mean scores under different conditions. The <i>p</i> -value is the level of marginal significance within a statistical hypothesis test representing the probability of the occurrence of a given event.
Source of Variation	Season is the source of variation, which is represented by the difference in temperature.
n	$n=n_1+n_2$ Therefore 'n' is the number of mean physical property values (density and viscosity) in spring (n_1) added to the number of mean physical property values (density and viscosity) in summer (n_2) over the same time points.
SRMSE	In statistics, the mean squared error (MSE) or mean squared deviation (MSD) measures the average of the squares of the errors—that is, the average squared difference between the sample means (monocyclics concentrations). The square root of the mean square error provides the average difference between sample means.
variables	Season is the source of the variation or independent variable, which is represented by the difference in the climatic factors. The dependent variables are density and viscosity, since they are increasing at different rates as a result of the change in season.
<i>p</i>-value	If <i>p</i> -value is less than alpha (0.05), you conclude that the mean difference between sample (i.e. monocyclics concentrations in spring versus) is statistically significant.

Figures 6S.1 to 6S.8 provide air and water temperature and wind speed profiles for all oils weathered in spring and summer of 2017. Figures 6S.9 to 6S.16 profiles light intensity over the 8 day experiments conducted in spring and summer of 2017.

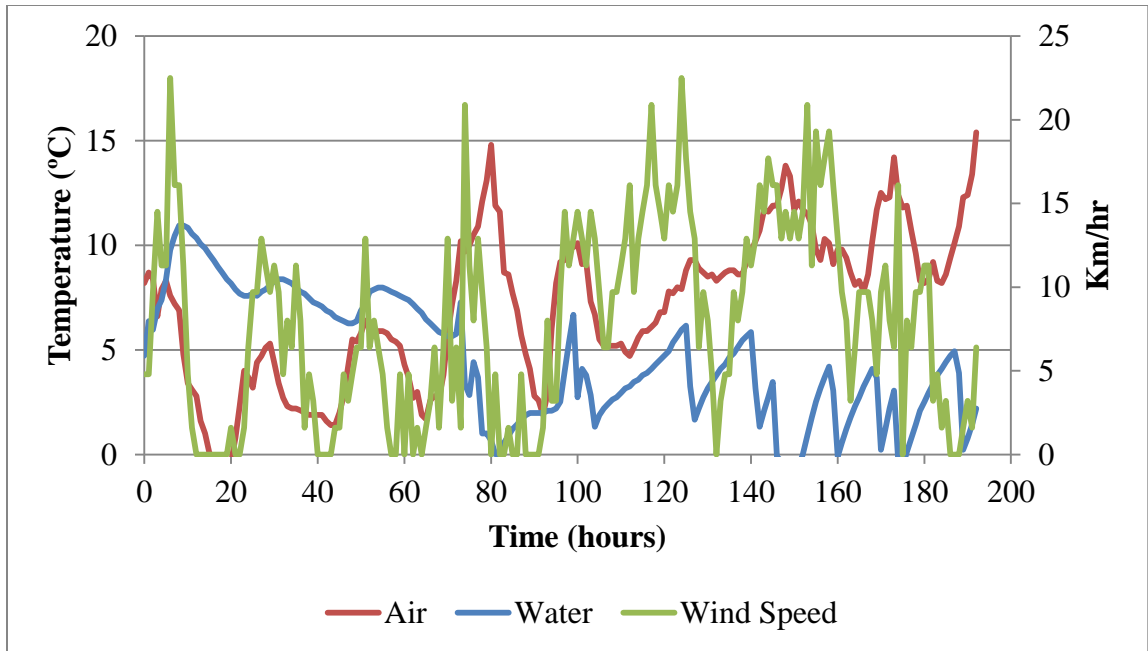


Figure 6S.1: Water and air temperature and wind speed profiles for the time of weathering of Access Western Blend (AWB) on water during spring-time of 2017.

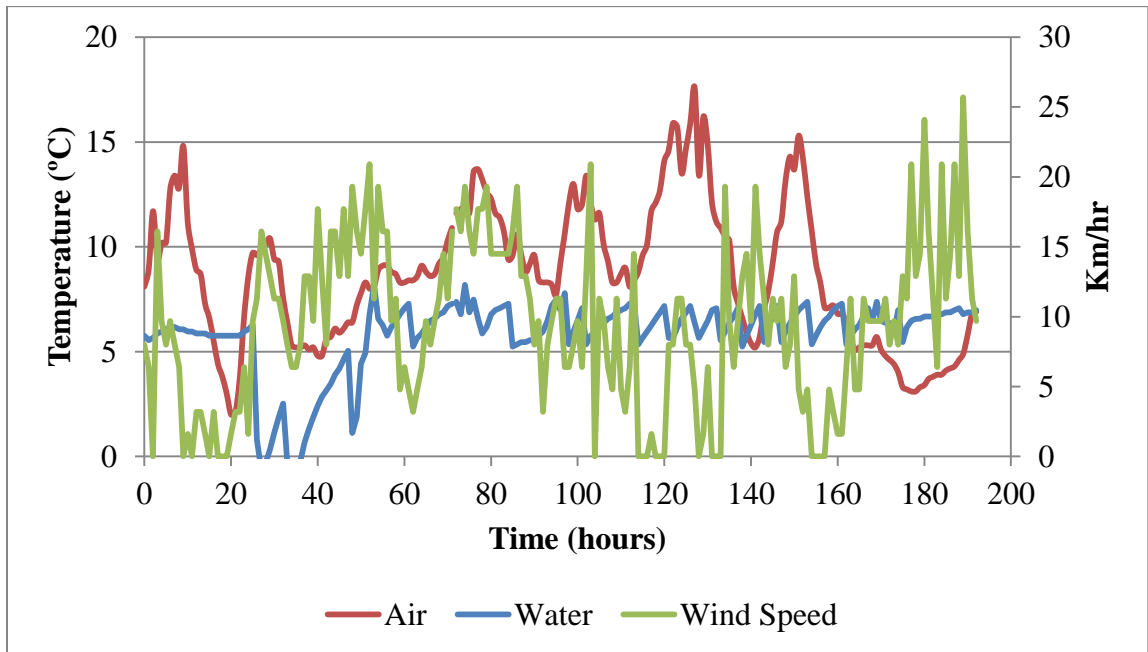


Figure 6S.2: Water and air temperature and wind speed profiles for the time of weathering of Western Canadian Select (WCS) on water during spring-time of 2017.

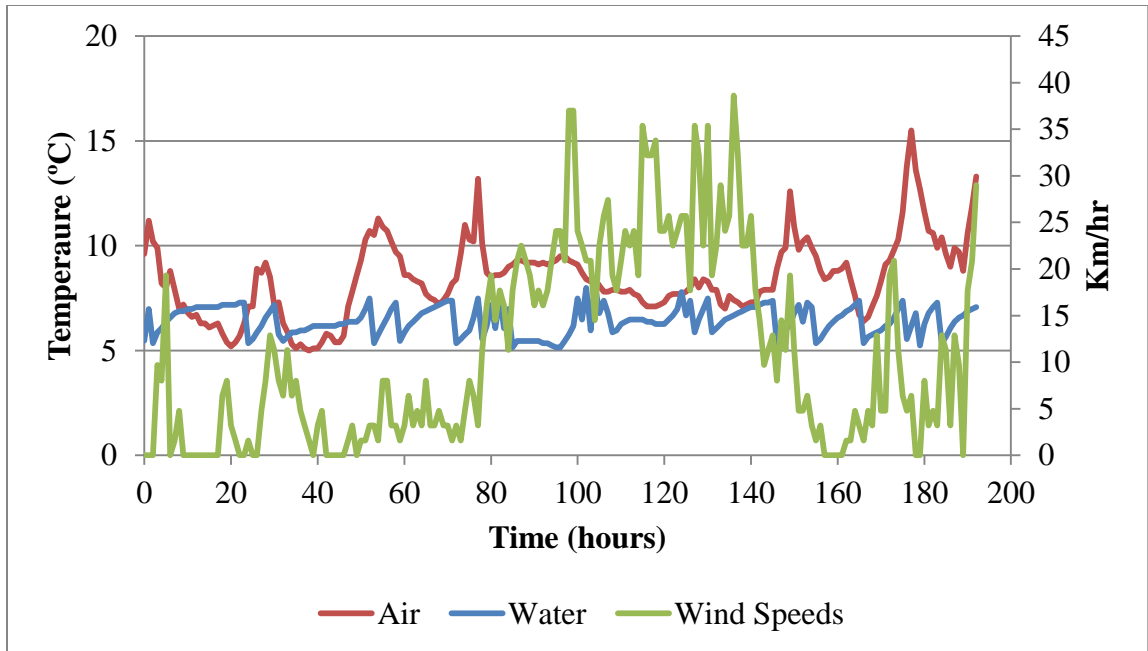


Figure 6S.3: Water and air temperature and wind speed profiles for the time of weathering of Synthetic Bitumen (Synbit) on water during spring-time of 2017.

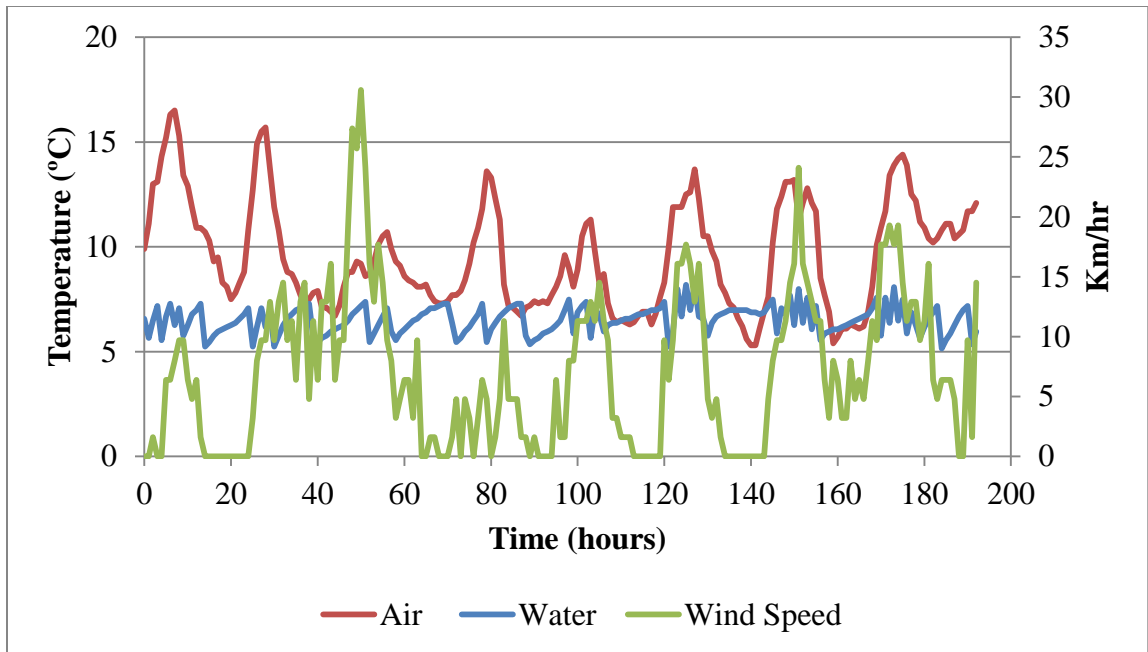


Figure 6S.4: Water and air temperature and wind speed profiles for the time of weathering of Heidrun on water during spring-time of 2017.

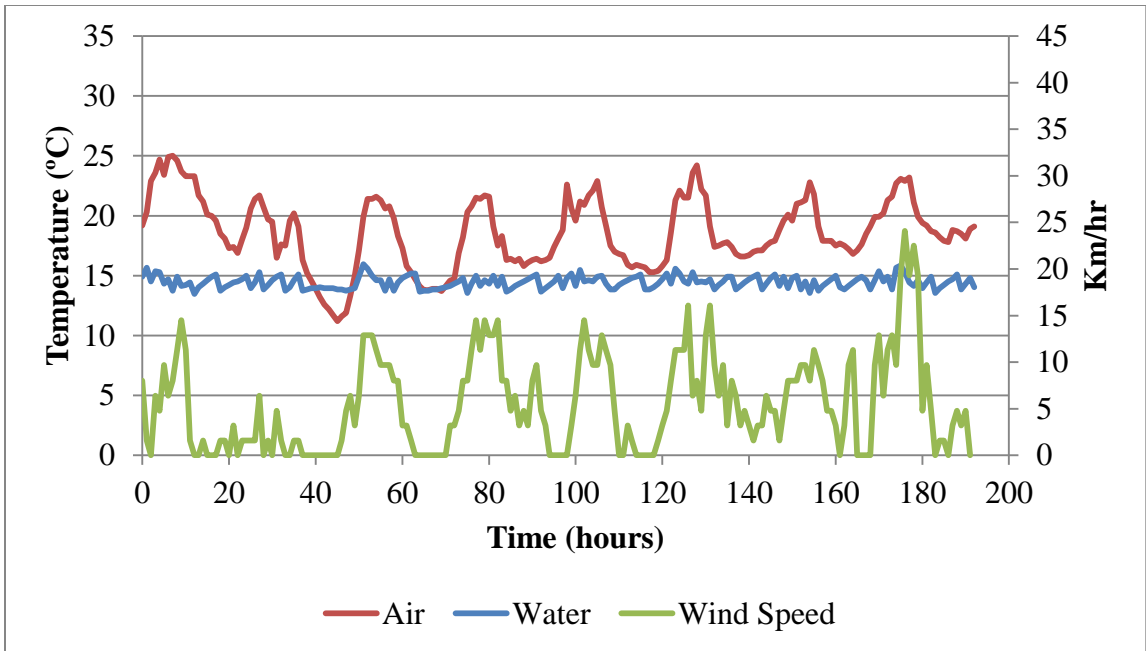


Figure 6S.5: Water and air temperature and wind speed profiles for the time of weathering of Access Western Blend (AWB) on water during summer-time of 2017.

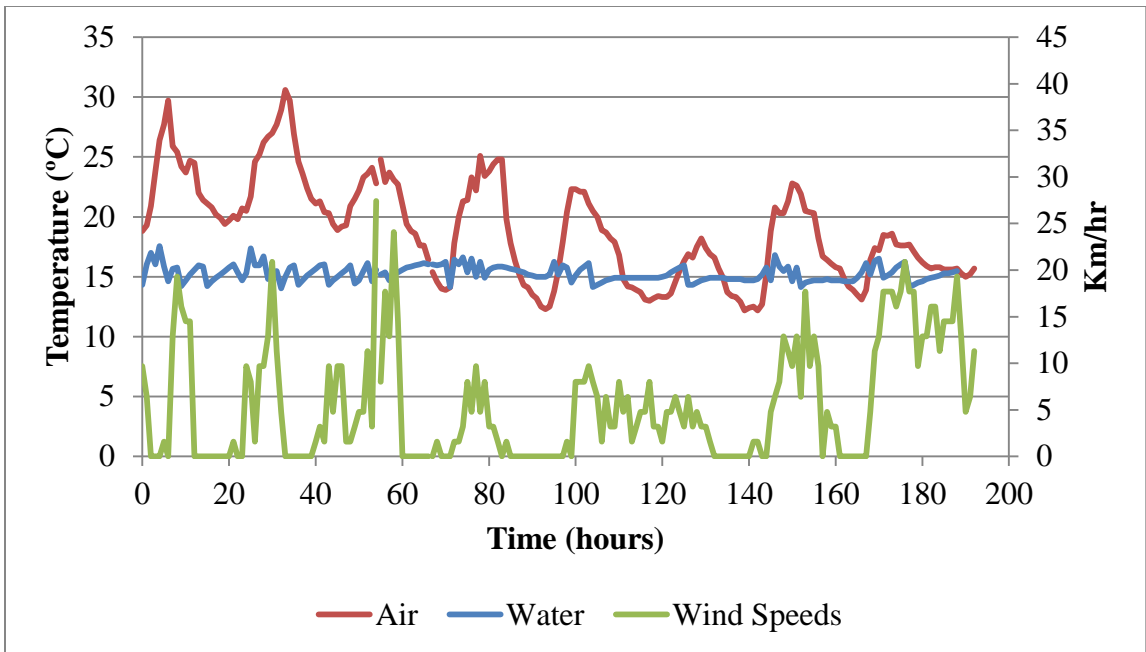


Figure 6S.6: Water and air temperature and wind speed profiles for the time of weathering of Western Canadian Select (WCS) on water during summer-time of 2017.

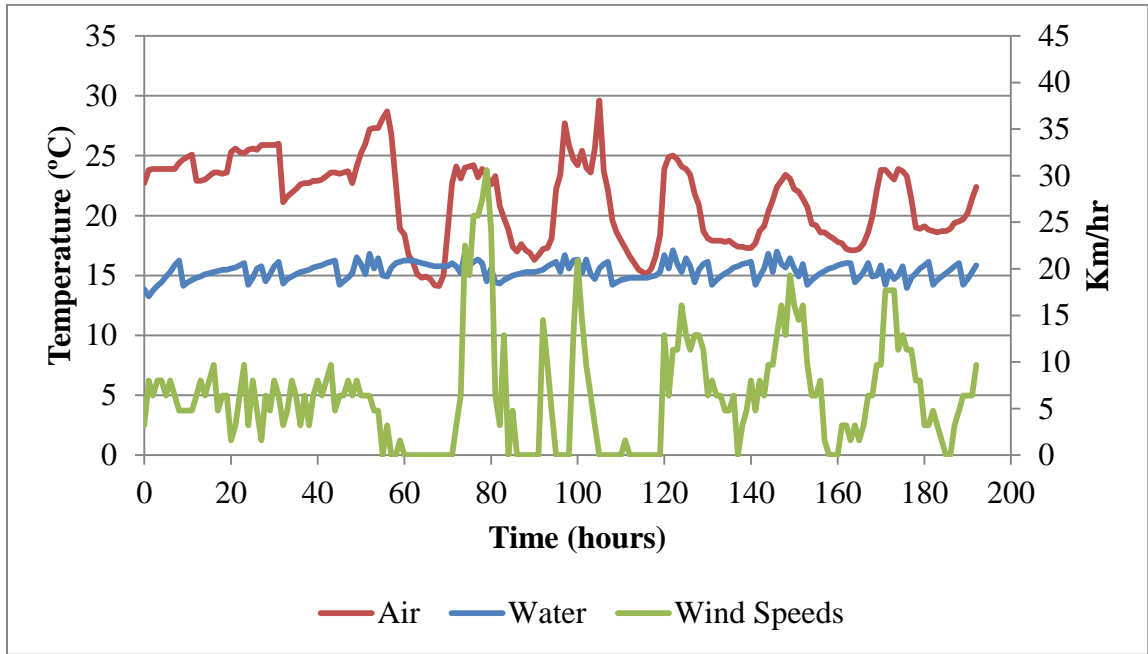


Figure 6S.7: Water and air temperature and wind speed profiles for the time of weathering of Synthetic Bitumen (Synbit) on water during summer-time of 2017.

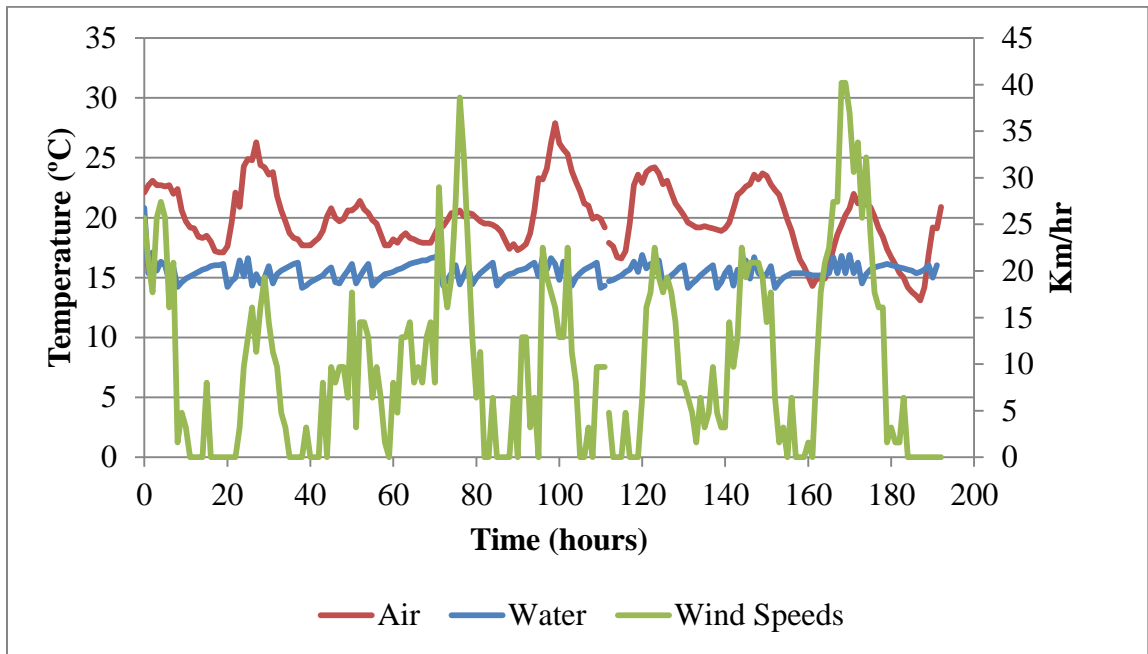


Figure 6S.8: Water and air temperature and wind speed profiles for the time of weathering of Heidrun on water during summer-time of 2017.

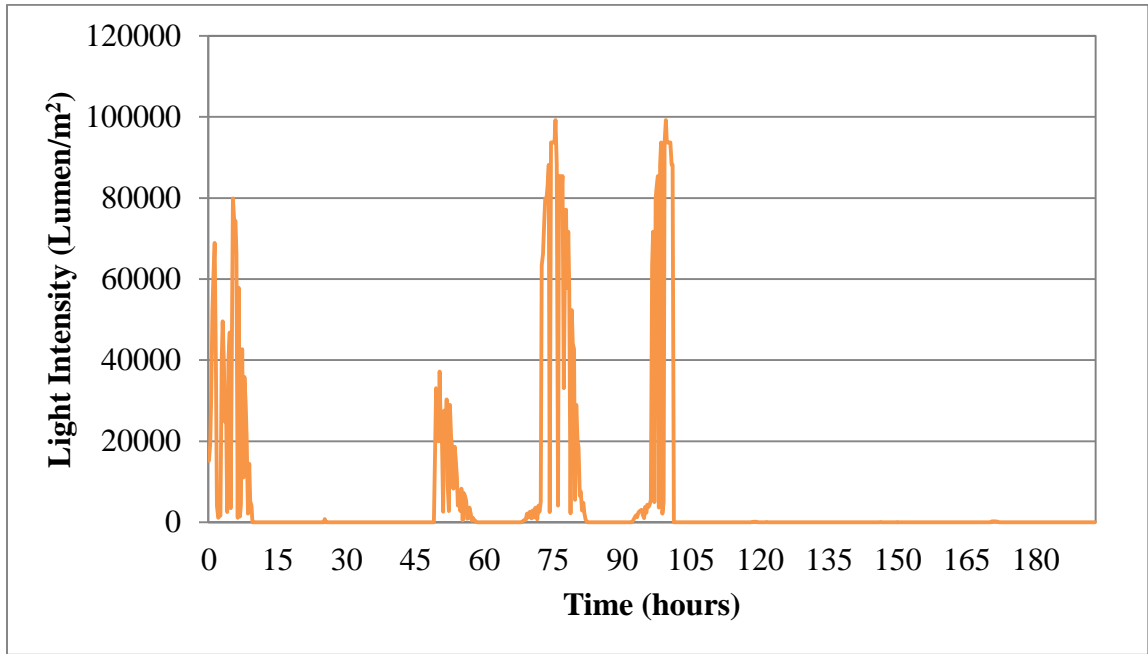


Figure 6S.9: Light Intensity profiles for the time of weathering of Access Western Blend (AWB) on water during spring-time of 2017.

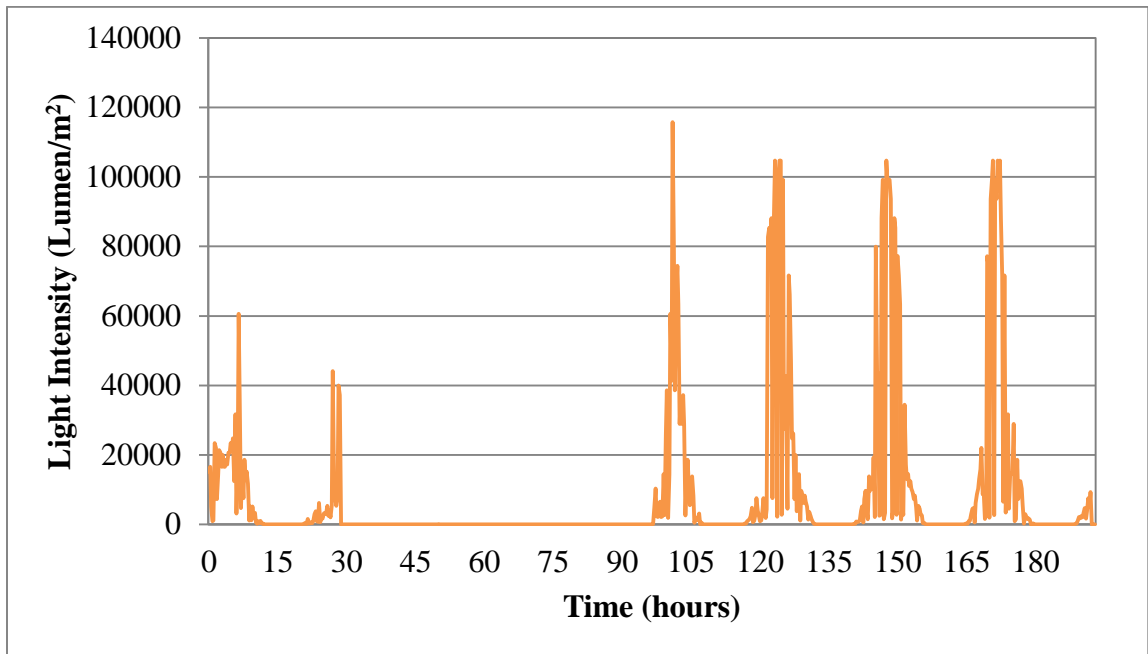


Figure 6S.10: Light Intensity profiles for the time of weathering of Western Canadian Select (WCS) on water during spring-time of 2017.

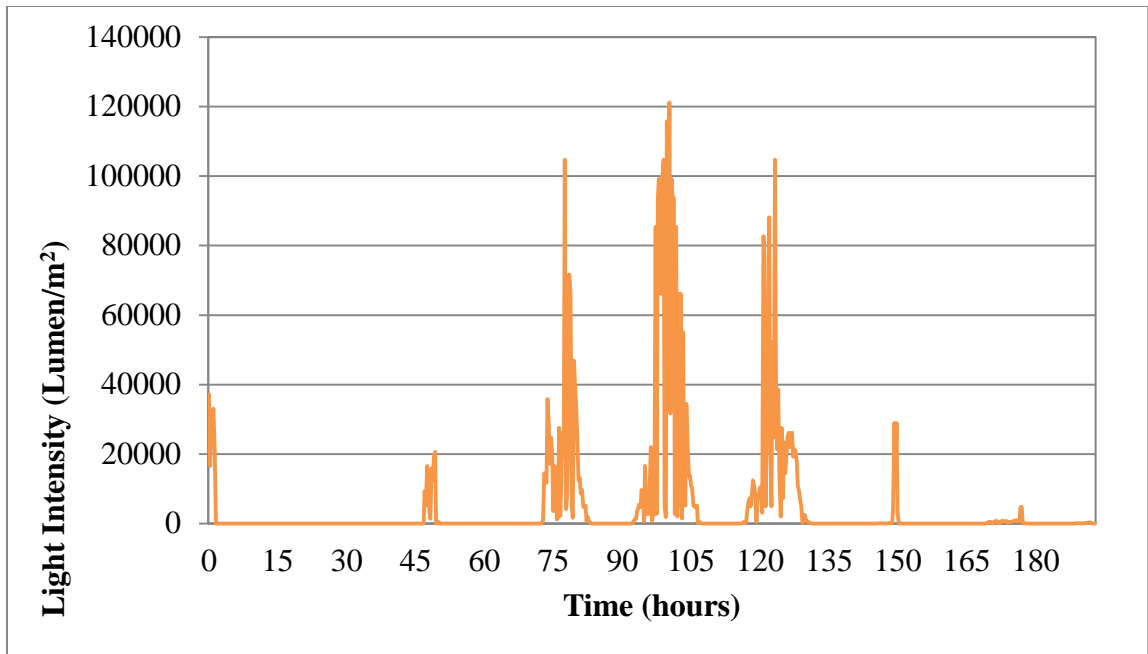


Figure 6S.11: Light Intensity profiles for the time of weathering of Synthetic Bitumen (synbit) on water during spring-time of 2017.

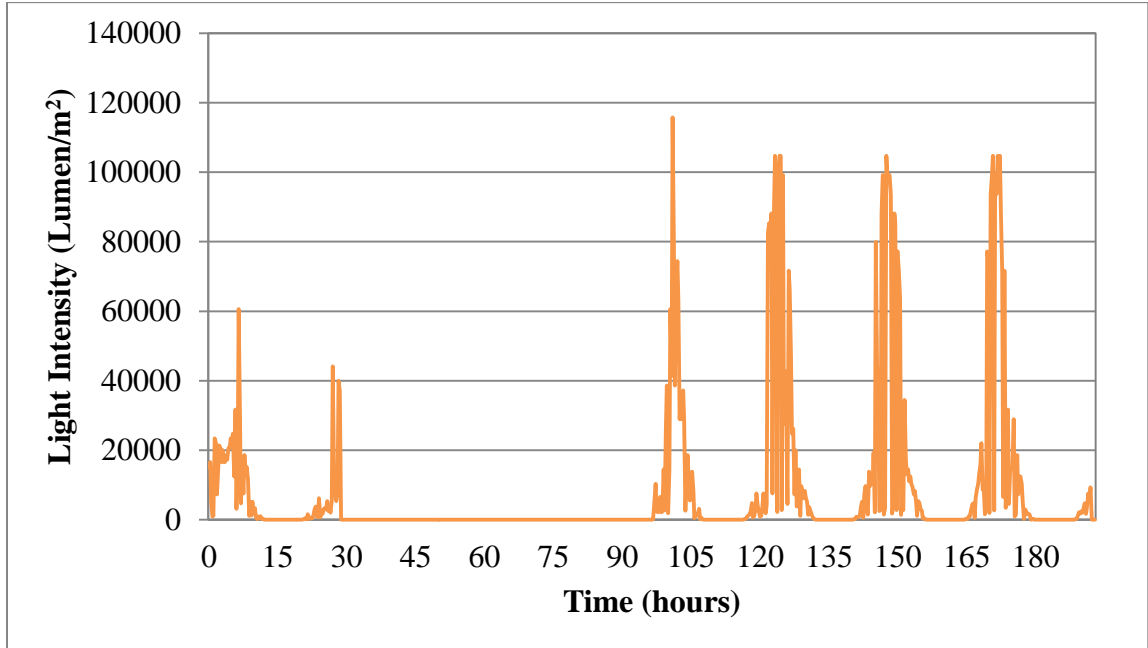


Figure 6S.12: Light Intensity profiles for the time of weathering of Heidrun on water during spring-time of 2017.

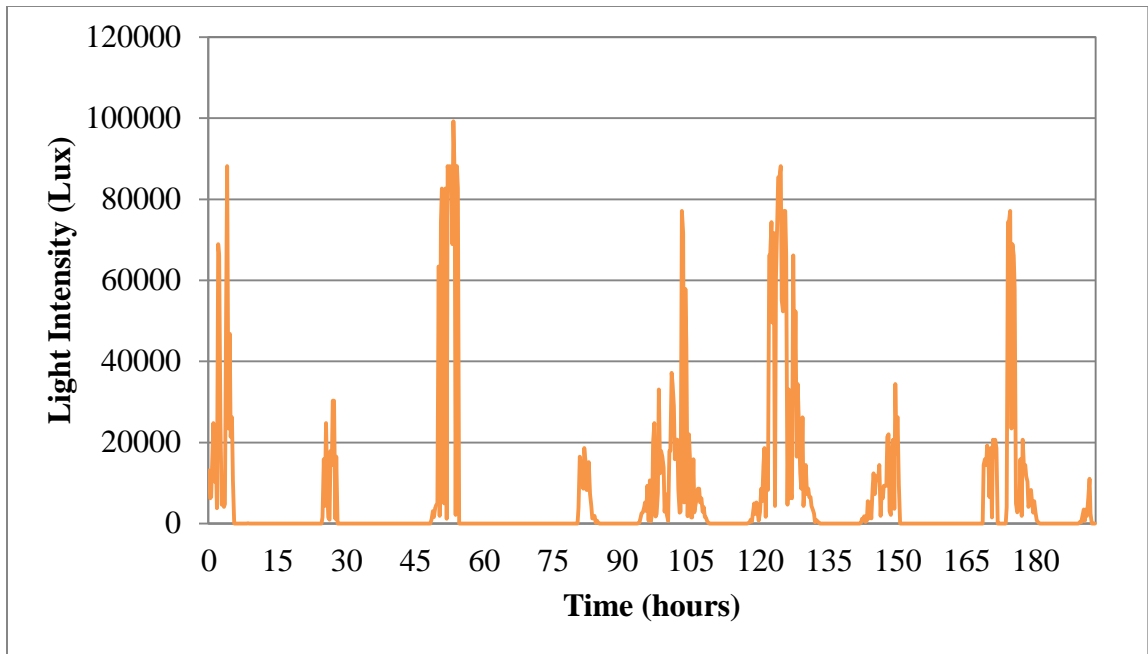


Figure 6S.13: Light Intensity profiles for the time of weathering of Access Western Blend (AWB) on water during summer-time of 2017.

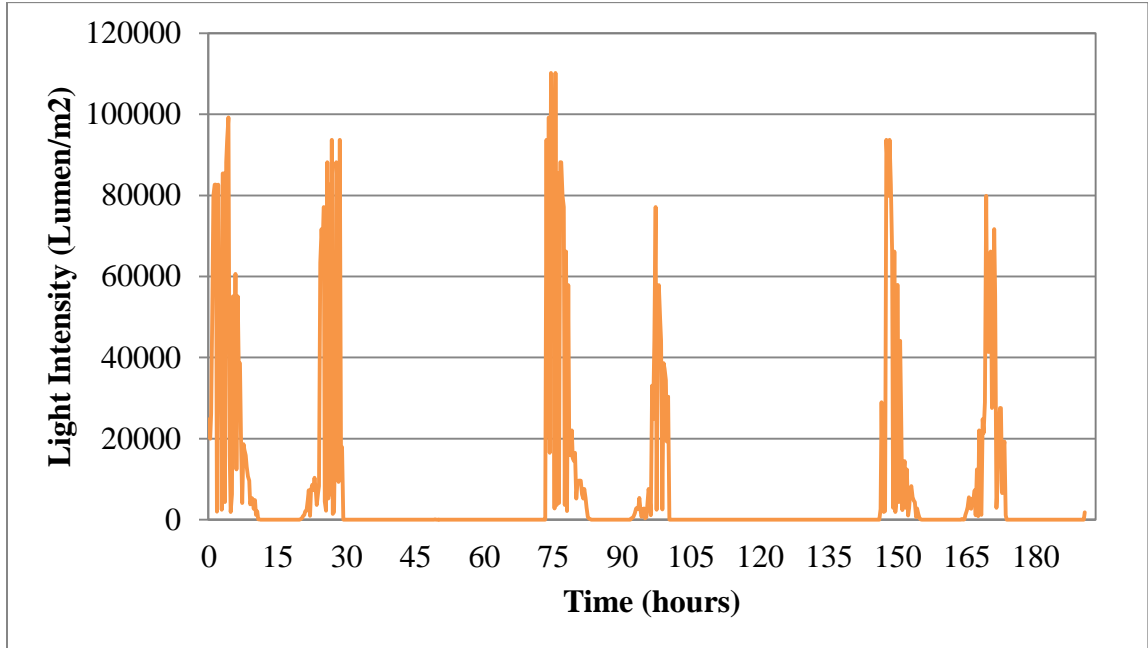


Figure 6S.14: Light Intensity profiles for the time of weathering of Western Canadian Select (WCS) on water during summer-time of 2017.

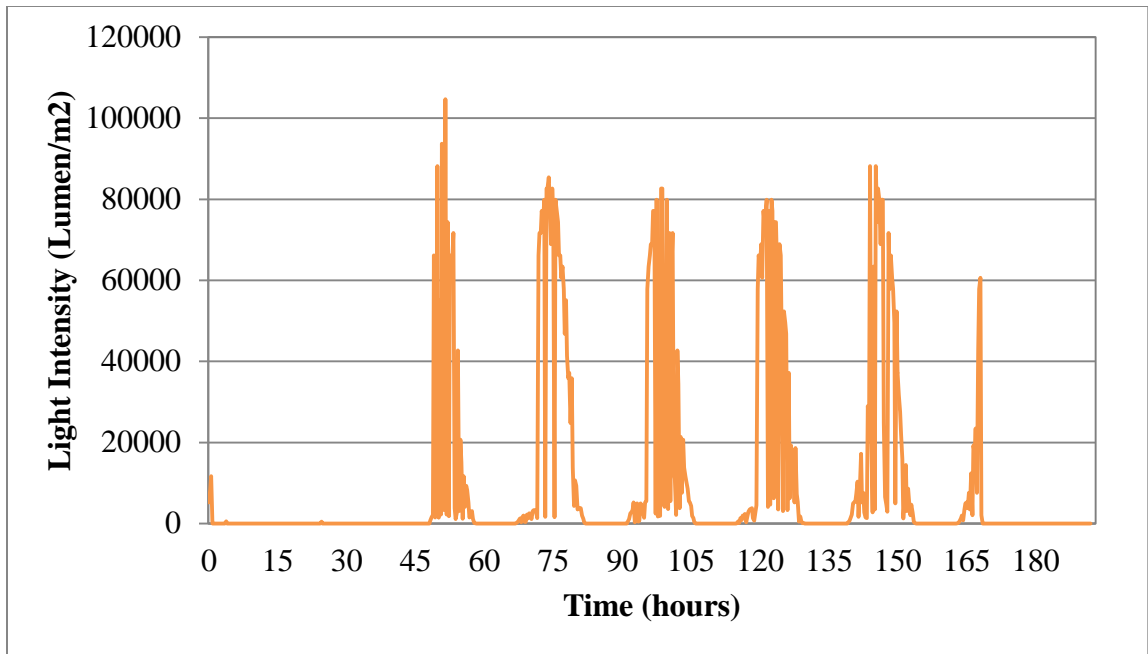


Figure 6S.15: Light Intensity profiles for the time of weathering of Synthetic Bitumen (synbit) on water during summer-time of 2017.

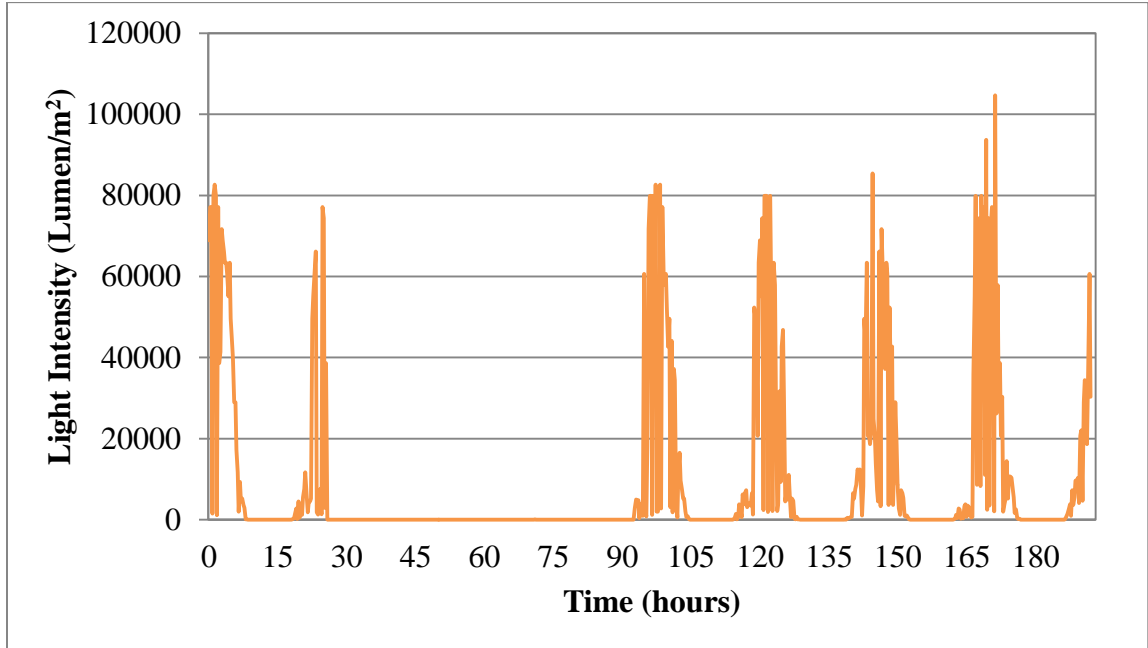


Figure 6S.16: Light Intensity profiles for the time of weathering of Heidrun on water during summer-time of 2017.

10.4 Chapter 7: Supporting Materials

Table 7S.1: Summary of Test Conditions, Physical Properties of Test Oils, and Dispersion Effectiveness Measurements. ν -viscosity, ρ -density, DOR-Dispersant-to-oil ratio, DE-dispersant effectiveness, cSt- centistokes, ppth- parts-per-thousand.

Oil*	ν cSt	ρ g/cm ³	Water Temp. °C	Salinity ppth	Oil Mass g	Oil thickness mm	Dispersant	DOR	DE %
Heidrun	107	0.9177	8.0	26.5	244	2.12	none		3.9
Heidrun	110	0.9182	7.3	27.2	243	2.11	none		1.6
Heidrun	109	0.9181	7.5	27.6	243	2.11	none		2.5
Heidrun	67	0.9124	15.6	29.3	238	1.99	none		3.1
Heidrun	64	0.9120	16.1	29.2	240	2.00	none		4.2
Heidrun	63	0.9117	16.6	28.9	241	2.10	none		5.7
Heidrun	107	0.9177	8.0	29.4	242	2.10	COREXIT	1:20	72.2
Heidrun	118	0.9187	6.6	29.0	243	2.11	COREXIT	1:20	70.6
Heidrun	118	0.9187	6.6	29.8	240	1.99	COREXIT	1:20	68.9
Heidrun	64	0.9120	16.2	29.0	245	2.14	COREXIT	1:20	73.6
Heidrun	67	0.9124	15.6	29.1	246	2.15	COREXIT	1:20	70.1
Heidrun	56	0.9103	18.6	28.7	249	2.18	COREXIT	1:20	84.3
Synbit	4505	0.9205	4.0	29.9	241	2.01	none		1.1
Synbit	4228	0.9202	4.5	29.9	240	1.99	none		7.0
Synbit	4682	0.9207	3.7	30.3	242	2.01	none		4.5
Synbit	932	0.9521	18.0	29.1	242	2.02	none		2.4
Synbit	900	0.9518	18.4	29.0	243	2.03	none		5.6
Synbit	932	0.9521	18.0	28.7	246	2.06	none		3.9
Synbit	4281	0.9202	4.4	30.4	243	2.03	COREXIT	1:20	43.6
Synbit	4175	0.9201	4.6	30.2	242	2.02	COREXIT	1:20	48.4
Synbit	3872	0.9197	5.2	30.3	240	1.99	COREXIT	1:20	53.2
Synbit	893	0.9518	18.5	28.7	238	1.99	COREXIT	1:20	58.6
Synbit	1264	0.9546	14.5	28.7	243	2.03	COREXIT	1:20	62.4
Synbit	1097	0.9534	16.1	29.0	244	2.04	COREXIT	1:20	56.6
WCS	4094	0.9604	6.2	28.0	241	2.00	none		2.9
WCS	3969	0.9602	6.5	27.8	240	1.99	none		1.0
WCS	3769	0.9598	7.0	27.3	242	2.01	none		4.1
WCS	1154	0.9508	19.7	29.3	244	2.04	none		2.4
WCS	1214	0.9512	19.1	29.1	241	2.02	none		4.3
WCS	1398	0.9524	17.5	29.3	242	2.02	none		3.8
WCS	4137	0.9603	6.1	27.5	248	2.06	COREXIT	1:20	36.4
WCS	4010	0.9601	6.4	27.5	238	1.97	COREXIT	1:20	43.7

<i>Table 6S.1 continued</i>									
WCS	3655	0.9595	7.3	25.5	241	2.00	COREXIT	1:20	43.8
WCS	1633	0.9536	15.7	28.8	240	2.00	COREXIT	1:20	49.2
WCS	1633	0.9536	15.7	28.7	237	1.98	COREXIT	1:20	54.0
WCS	1535	0.9531	16.4	29.1	240	2.00	COREXIT	1:20	57.2
AWB	8212	0.9646	8.0	29.5	247.8	2.05	none		0.0
AWB	6806	0.9635	9.7	27.9	264.8	2.19	none		3.1
AWB	6956	0.9636	9.5	27.5	293.8	2.43	none		1.9
AWB	4553	0.9611	13.5	28.8	230.7	1.91	none		1.2
AWB	4370	0.9308	13.9	29.1	236.3	1.96	none		1.2
AWB	2482	0.9571	19.7	28.1	238.4	1.98	none		3.1
AWB	9846	0.9656	6.4	29.2	253.6	2.09	COREXIT	1:20	28.1
AWB	7349	0.9670	9.0	29.4	252.3	2.08	COREXIT	1:20	33.7
AWB	8687	0.9649	7.5	29.4	276.1	2.28	COREXIT	1:20	30.1
AWB	3178	0.9578	17.1	23.7	239.2	1.99	COREXIT	1:20	56.9
AWB	4370	0.9608	13.9	28.7	233.2	1.93	COREXIT	1:20	50.4
AWB	3403	0.9592	16.4	28.7	238.5	1.98	COREXIT	1:20	52.3

*AWB, WCS and Synbit weathered (7% w/w) and Heidrun was unweathered prior to dispersion effectiveness testing. ν -viscosity and ρ -density.

Table 7S.2: Summary of Definition of Terms in Table 7.1 ANOVA Analysis Show the Dispersion Effectiveness (DE) of Dispersant to the Natural Dispersion of Four Oils Under Breaking Waves.

Term	Definition
ANOVA	Analysis of Variance (ANOVA) Repeated measures investigate about the 1) changes in mean scores over three or more time points and 2) differences in mean scores under different conditions.
Source of Variation	Treatment (with and without dispersant) is the source of variation, which is represented by the difference in temperature.
n	$n=n_1+n_2$ Therefore, 'n' is the number of mean dispersant effectiveness values (%) without dispersant (n_1) added to the number of mean dispersant effectiveness values (%) with dispersant (n_2).
Difference (Diff) %	Difference (Diff) % is difference in the Value % (i.e. DE (%) without dispersant subtracted from DE (%) with dispersant).
variables	The independent variable is treatment, since it is changed. The DE (%) changes as a result of the treatment; therefore, DE (%) is the dependent variable.
p-value	If p -value is less than alpha (0.05), you conclude that the mean difference between sample (i.e. treatments) is statistically significant.

Table 7S.3: Summary of Definition of Terms in Table 7.2 ANOVA Analysis Show the Dispersant Effectiveness (DE) of Oils Affected by Seasonal Water Temperatures Under Breaking Waves.

Term	Definition
ANOVA	Analysis of Variance (ANOVA) Repeated measures investigate about the 1) changes in mean scores over three or more time points and 2) differences in mean scores under different conditions. The <i>p</i> -value is the level of marginal significance within a statistical hypothesis test representing the probability of the occurrence of a given event.
Source of Variation	Season is the source of variation, which is represented by the difference in temperature for the dispersant to treat a surface spill of oil.
n	$n=n_1+n_2$ Therefore 'n' is the number of mean dispersant effectiveness values (%) in spring (n_1) added to the number of mean dispersant effectiveness values (%) in summer (n_2) for dispersant application.
Difference (Diff) %	Difference (Diff) % is the difference in the Value % (DE% calculated in spring subtracted from DE% in summer for chemical dispersant application).
variable	The independent variable is season (temperature) since it is changed. The DE (%) changes as a result of the season; therefore, DE (%) is the dependent variable.
<i>p</i>-value	If <i>p</i> -value is less than alpha (0.05), you conclude that the mean difference between sample (i.e. treatments) is statistically significant.

Table 7S.4: Predicted Data for Viscosity (Chapter 5) and Dispersion Effectiveness (Eq. 6.3) for Time of Weathering of Four Oils in Spring and Summer.

Summer			Spring		
Heidrun (4.1 mm, 15.5 °C, 14.9 km/hr)			Heidrun (4.2 mm, 6.7 °C, 13.6 km/hr)		
Viscosity	DE (%)	Time (hr)	Viscosity	DE (%)	Time (hr)
75	76.6	0	131	72.2	0
174	69.9	3	244	67.3	3
215	68.3	8	296	65.7	8
279	66.2	24	382	63.7	24
329	64.9	48	451	62.4	48
361	64.2	72	496	61.7	72
384	63.7	96	529	61.2	96
402	63.3	120	554	60.8	120
416	63.1	144	575	60.5	144
428	62.8	168	592	60.3	168
438	62.7	192	607	60.1	192
447	62.5	216	619	59.9	216
454	62.4	240	630	59.8	240
461	62.3	264	640	59.7	264
466	62.2	288	648	59.6	288
471	62.1	312	656	59.5	312
476	62.0	336	663	59.4	336

Table 7S.4 continued

480	61.9	360	669	59.3	360
AWB (4.0 mm, 14.3 °C, 9.0 km/hr)			AWB (4.0 mm, 5.5 °C, 16.4 km/hr)		
318	65.2	0	507	61.5	0
1114	55.3	3	3264	46.8	3
4107	45.0	8	13734	35.4	8
15237	34.6	24	48716	25.4	24
27280	30.0	48	81245	21.4	48
34879	28.1	72	99750	19.8	72
39988	27.0	96	111485	18.9	96
43633	26.3	120	119554	18.3	120
46359	25.8	144	125432	18.0	144
48471	25.5	168	129901	17.7	168
50155	25.2	192	133412	17.5	192
51528	25.0	216	136243	17.3	216
52669	24.8	240	138573	17.2	240
53632	24.7	264	140525	17.1	264
54456	24.5	288	142183	17.0	288
55168	24.4	312	143609	16.9	312
55790	24.4	336	144848	16.8	336
56338	24.3	360	145935	16.8	360
AWB (4.0 mm, 22.0 °C, 13.3 km/hr)					
244	69.1	0			
22194	26.2	3			
56398	19.8	8			
149314	14.4	24			
254485	11.8	48			
332661	10.5	72			
393053	9.7	96			
441110	9.1	120			
480260	8.7	144			
512770	8.3	168			
540197	8.0	192			
563646	7.7	216			
583925	7.5	240			
601636	7.3	264			
617237	7.1	288			
631085	6.9	312			
643458	6.8	336			
654581	6.7	360			

Table 7S.4 continued

Synbit (4.0 mm, 14.5 °C, 13.2 km/hr)			Synbit (4.0 mm, 6.3 °C, 20.5 km/hr)		
Viscosity	DE (%)	Time (hr)	Viscosity	DE (%)	Time (hr)
318	65.2	0	462	62.2	0
454	62.4	3	920	56.8	3
951	56.5	8	1795	51.5	8
2494	48.9	24	4182	44.8	24
4173	44.8	48	6563	41.3	48
5299	43.0	72	8093	39.6	72
6093	41.9	96	9150	38.6	96
6682	41.1	120	9922	38.0	120
7134	40.6	144	10510	37.5	144
7492	40.2	168	10972	37.2	168
7783	39.9	192	11346	36.9	192
8023	39.7	216	11653	36.7	216
8225	39.5	240	11911	36.6	240
8397	39.3	264	12130	36.4	264
8545	39.2	288	12319	36.3	288
8675	39.1	312	12483	36.2	312
8788	39.0	336	12627	36.1	336
8889	38.9	360	12754	36.0	360
WCS (4.0 mm, 15.2 °C, 11.4 km/hr)			WCS (4.0 mm, 6.3 °C, 24.7 km/hr)		
318	65.2	0	499	61.6	0
1254	54.3	3	1406	53.4	3
2642	48.5	8	4457	44.3	8
6281	41.6	24	12931	35.9	24
10274	37.7	48	19594	32.6	48
13180	35.8	72	23047	31.3	72
15395	34.5	96	25137	30.7	96
17141	33.7	120	26533	30.2	120
18552	33.1	144	27531	29.9	144
19717	32.6	168	28279	29.7	168
20696	32.2	192	28861	29.6	192
21529	31.9	216	29326	29.4	216
22247	31.6	240	29706	29.3	240
22872	31.4	264	30023	29.3	264
23422	31.2	288	30291	29.2	288
23909	31.1	312	30521	29.1	312
24343	30.9	336	30720	29.1	336
24732	30.8	360	30894	29.0	360

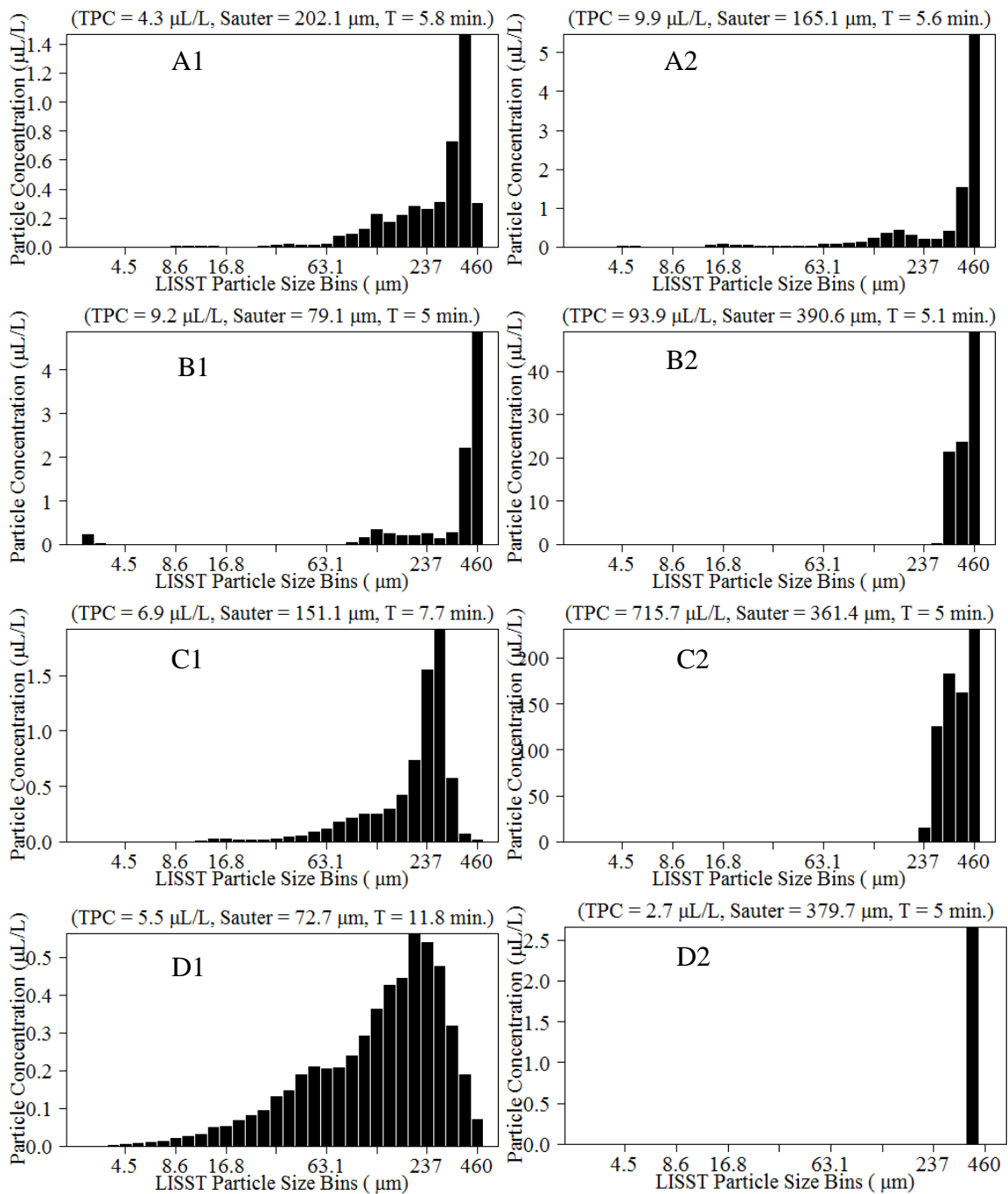


Figure 7S.1: The Plots Represent the Seasonal Effects on Particle Size Distribution Data (LISST 100X-#1; 1.2 m from oil release) Obtained at the Time Point of Maximum Total Particle Concentration During the Natural Dispersion of Four Oils: A1) Heidrun-Spring, A2) Heidrun-Summer, B1) AWB-Spring, B2) AWB-Summer, C1) Synbit-Spring, C2) Synbit-Summer, D1) WCS-Spring, and D2) WCS-Summer. X-Axis Values Represent the 32 Logarithmically-Spaced Particle Size Bins Generated by the LISST 100X Instrument.

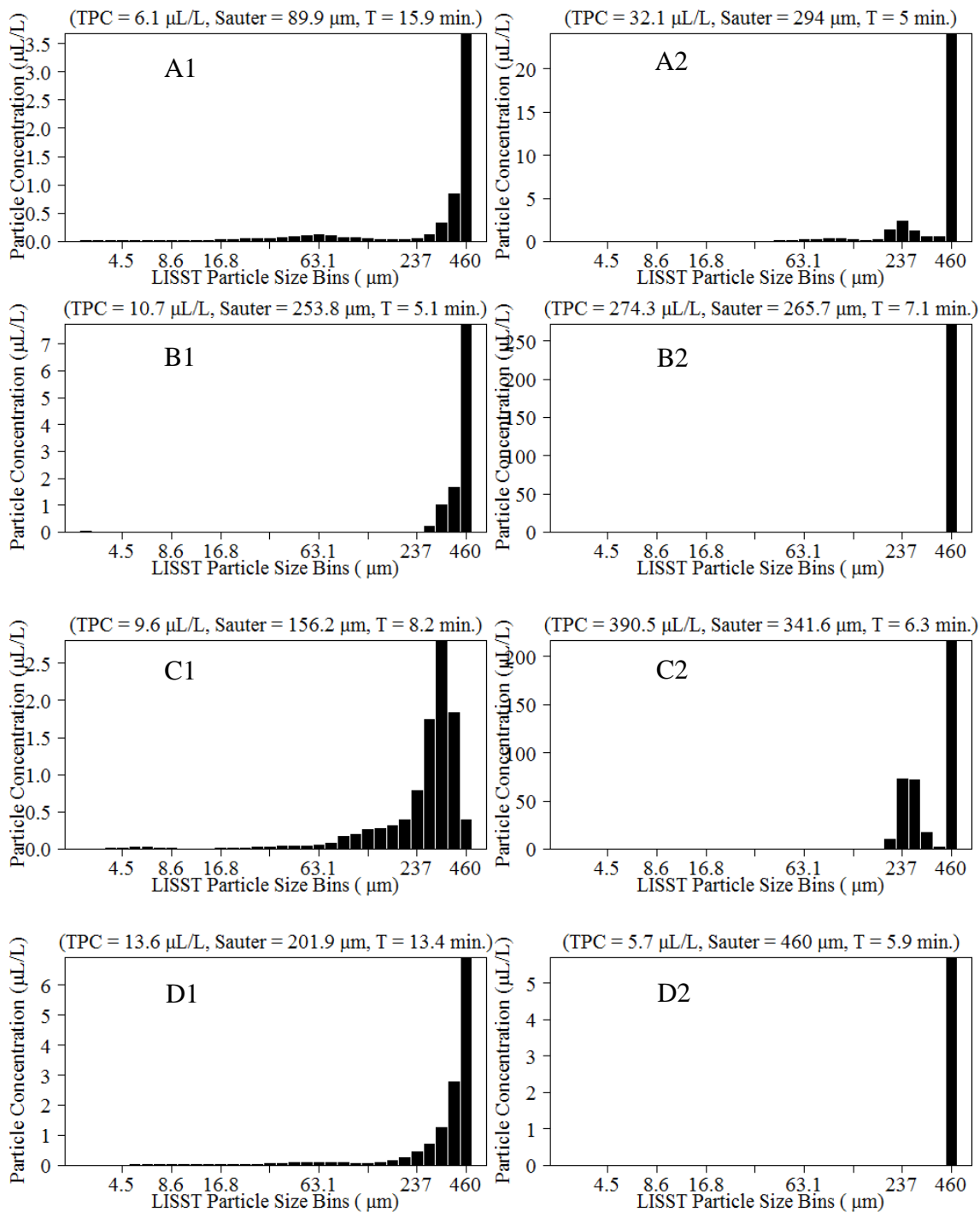


Figure 7S.2: The Plots Represent the Seasonal Effects on Particle Size Distribution Data (LISST 100X-#2; 12 m from oil release) Obtained at the Time Point of Maximum Total Particle Concentration During the Natural Dispersion of Four Oils: A1) Heidrun-Spring, A2) Heidrun-Summer, B1) AWB-Spring, B2) AWB-Summer, C1) Synbit-Spring, C2) Synbit-Summer, D1) WCS-Spring, and D2) WCS-Summer. X-Axis Values Represent the 32 Logarithmically-Spaced Particle Size Bins Generated by the LISST 100X Instrument.

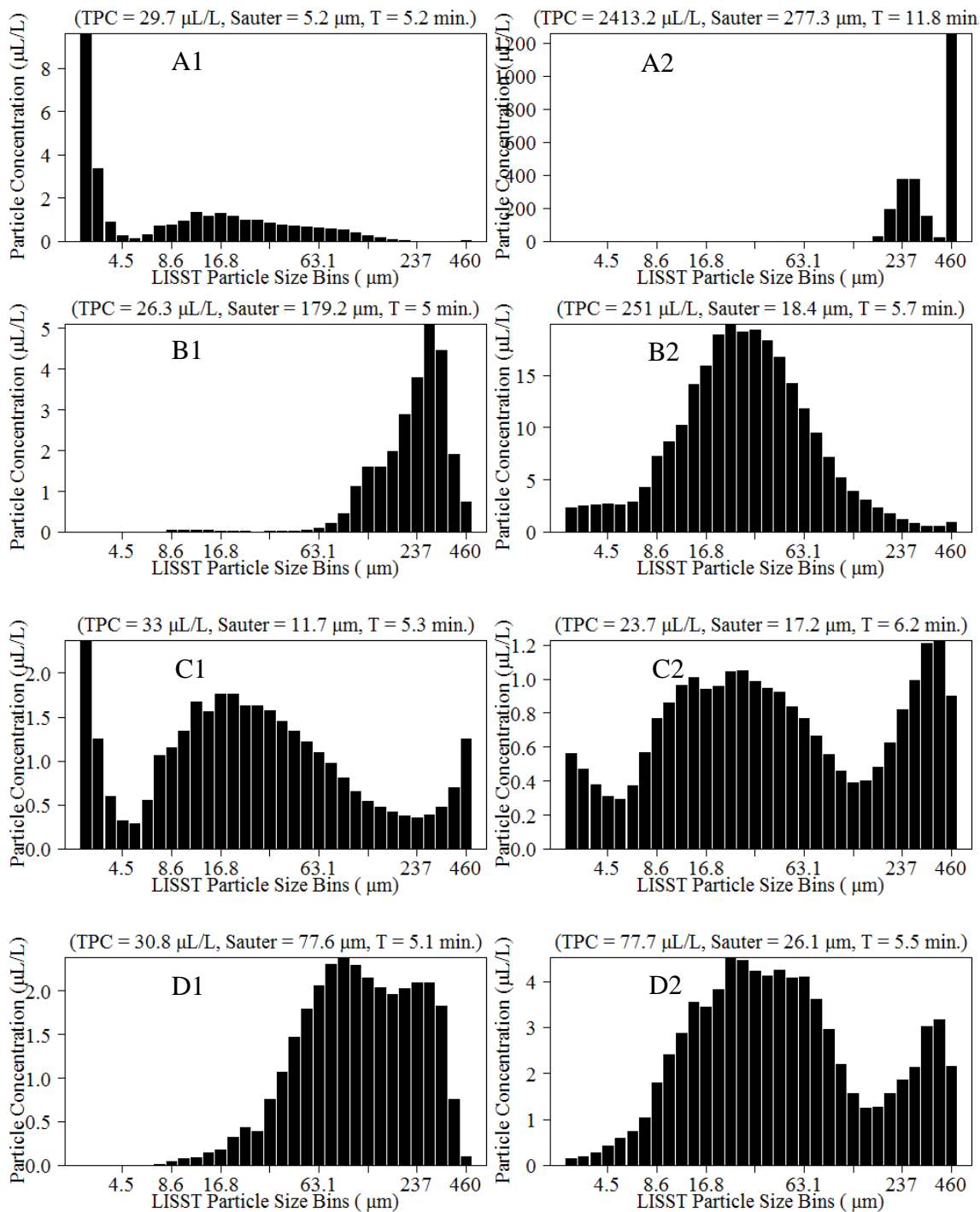


Figure 7S.3: The Plots Represent the Seasonal Effect on Particle Size Distribution Data (LISST 100X-#1; 1.2 m from oil release) Obtained at the Time Point of Maximum Total Particle Concentration During the Chemically Enhanced Dispersion of Four Oils: A1) Heidrun-Spring, A2) Heidrun-Summer, B1) AWB-Spring, B2) AWB-Summer, C1) Synbit-Spring, C2) Synbit-Summer, D1) WCS-Spring, and D2) WCS-Summer. X-Axis Values Represent the 32 Logarithmically-Spaced Particle Size Bins Generated by the LISST 100X Instrument.

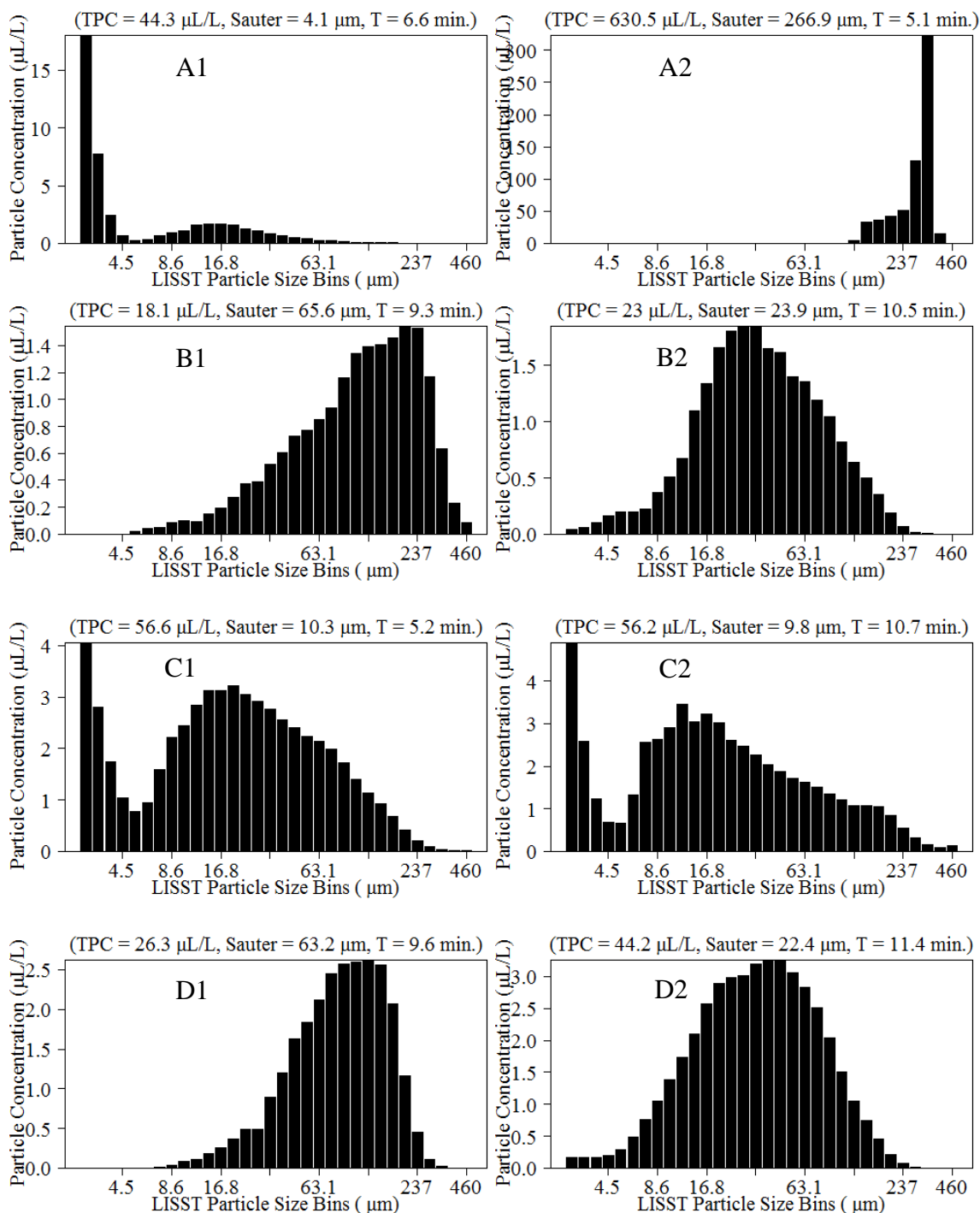


Figure 7S.4: The Plots Represent the Seasonal Effects on Particle Size Distribution Data (LISST 100X-#2; 12 m from Oil Release) Obtained at the Time Point of Maximum Total Particle Concentration During the Chemically Enhanced Dispersion of Four Oils: A1) Heidrun-Spring, A2) Heidrun-Summer, B1) AWB-Spring, B2) AWB-Summer, C1) Synbit-Spring, C2) Synbit-Summer, D1) WCS-Spring, and D2) WCS-Summer. X-Axis Values Represent the 32 Logarithmically-Spaced Particle Size Bins Generated by the LISST 100X Instrument.

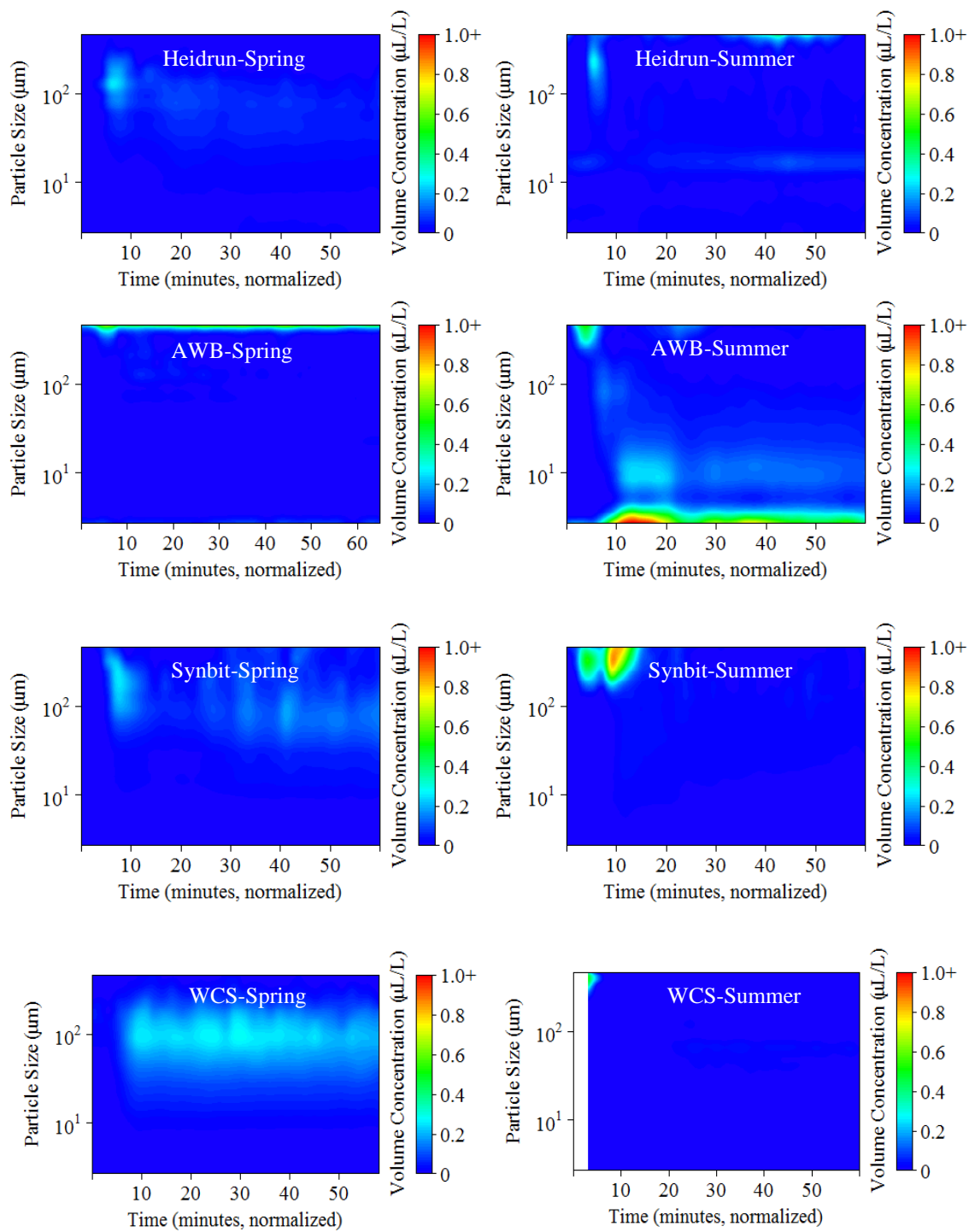


Figure 7S.5: Contour Plots (LISST 100X-#1 data, 1.2 m from Oil Release) Illustrating Seasonal Effects on the Concentration of Oil Particle Sizes Simulated in the Wave Tank for Natural Dispersion of Four Oil Types.