State of Knowledge on Fate and Behaviour of Ship-Source Petroleum Product Spills: Volume 1, Introduction

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Rising Canadian oil production and increased tanker traffic elevates the risk of accidental oil spills in Canadian waters. In response, the Government of Canada announced the World Class Tanker Safety System and created the independent Tanker Safety Expert Panel to review Canada’s ship-source oil spill preparedness and response. Using the panel’s recommendations, the Government of Canada is establishing response plans for four pilot areas which have the highest tanker traffic in Canada: Saint John, NB, Port Hawkesbury and Canso Strait, NS, St. Lawrence Seaway, Qc, and the southern portion of British Columbia.

This is the first volume of a five volume report which contains introductory information on oil products and spills, relevant to any location, and meant to accompany subsequent volumes. Volumes 2-5 cover each of the four selected pilot ports identified above.

RÉSUMÉ

Ryan, S.A., Wohlgeschaffen, G., Jahan, N., Niu, H., Ortmann, A.C., Brown, T.N., King, T.L., and Clyburne, J. 2019. State of Knowledge on Fate and Behaviour of Ship-Source Petroleum Product Spills: Volume 1, Introduction. Can. Manuscr. Rep. Fish. Aquat. Sci. 3176: viii + 25 p.

L'augmentation de la production canadienne de pétrole et du trafic de navires-citernes augmente le risque de déversements accidentels d'hydrocarbures dans les eaux canadiennes. En réponse, le gouvernement du Canada a annoncé le Système de sécurité de classe mondiale pour les navires-citernes et créé le Comité d'experts indépendant sur la sécurité des navires-citernes pour examiner la préparation et l'intervention du Canada en cas de déversement d'hydrocarbures par les navires. À l'aide des recommandations du Comité, le gouvernement du Canada établit des plans d'intervention pour quatre zones pilotes où le trafic de navires-citernes est le plus élevé au Canada : Saint John (N.-B.), Port Hawkesbury et le détroit de Canso (N.-É.), la Voie maritime du Saint-Laurent (Qc) et la partie sud de la Colombie-Britannique.

Il s'agit du premier volume d'un rapport en cinq volumes qui contient des renseignements de base sur les produits pétroliers et les déversements, pertinent à tout endroit et destiné à accompagner les volumes suivants. Les volumes 2 à 5 couvrent chacun des quatre ports pilotes sélectionnés identifiés ci-dessus.

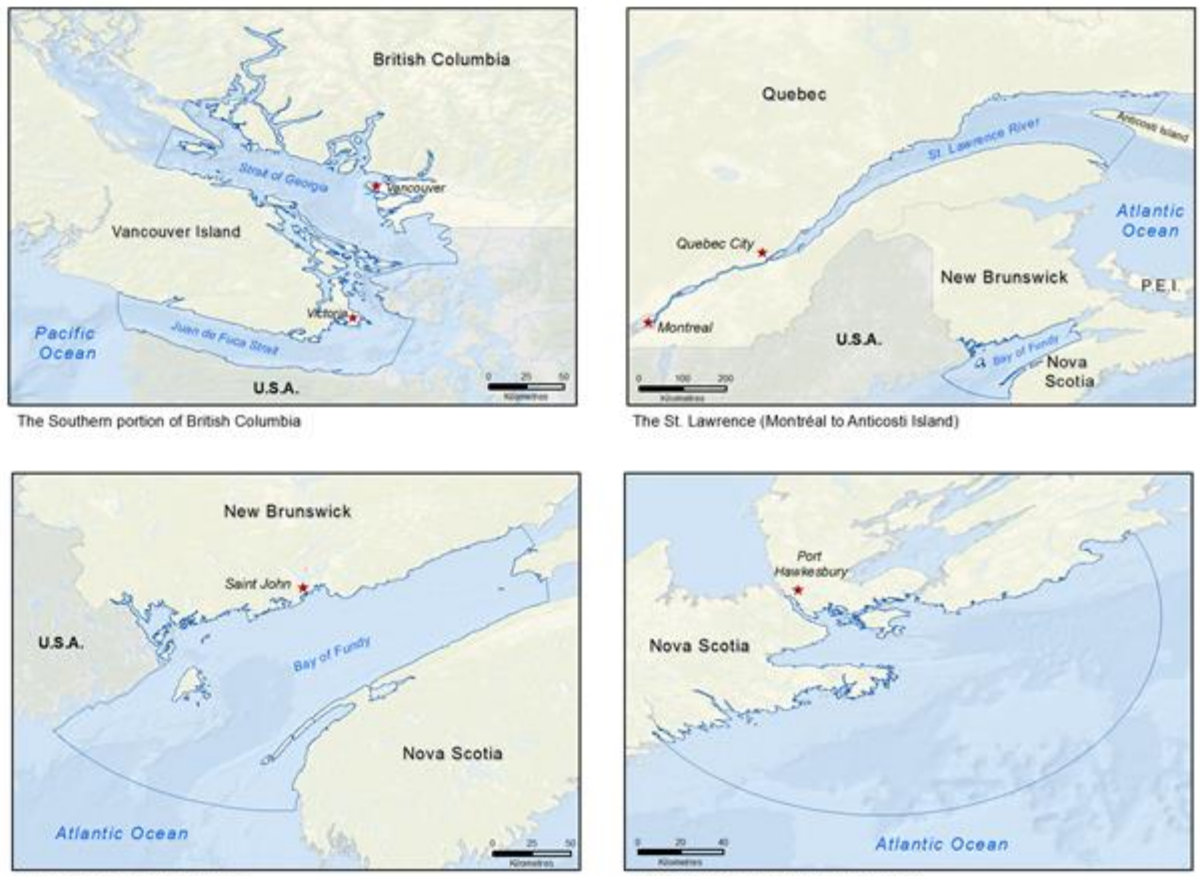
1 INTRODUCTION

As noted in the study by the Standing Senate Committee (2013), ocean “Tankers have made crude oil the most traded commodity in the world”. Each year in Canada, about 586 million barrels of petroleum products are shipped by tanker to and from global markets and suppliers, with approximately 90% of all overseas tanker traffic going through Québec and the Atlantic provinces (Standing Senate Committee 2013). As oil production in Canada continues to rise, tanker traffic will increase in Canadian waters, thus increasing the risk of accidental spills. Recognizing this increase, and in response to the lack of knowledge and public concern, the Government of Canada in 2013 announced the World Class Tanker Safety System (WCTSS) and the creation of an independent Tanker Safety Expert Panel to review Canada’s ship-source oil spill preparedness and response regime.

In November 2013, the Expert Panel produced its first report, *A Review of Canada's Ship-Source Oil Spill Preparedness and Response Regime — Setting the Course for the Future* (Houston et al. 2013). The report is a comprehensive summary and discussion of Canada’s existing spill response principles and practices (south of 60ºN latitude), and provides a number of recommendations for what can be done to improve upon them. One recommendation is that oil spill response plans should be developed to address specific risks within a geographical area. Because of the diversity of geography and climate within Canada, a single response plan would not sufficiently address the impacts and needs of a spill in all regions. The Panel recommended that a risk-based and strategic approach be used to develop Area Response Plans (ARPs) that consider geographic, industrial and environmental differences in preparing for the most probable types of spills and worst-case impacts in respective response areas (Houston et al. 2013).

Following the Panel's recommendations, the Government of Canada set out on a multi-departmental approach to establishing risk-based ARPs to spills from ship-based sources. Government departments have been working collaboratively with consultants and stakeholders in a pilot study to establish a methodology for risk assessment and development of specific response plans in four areas with the highest levels of tanker traffic (Figure 1):

- Saint John and Bay of Fundy, New Brunswick
- Port Hawkesbury-Canso Strait, Nova Scotia
- St. Lawrence Seaway, Montreal to Anticosti, Québec
- Strait of Georgia and the Juan de Fuca Strait, British Columbia



The Southern portion of British Columbia

The St. Lawrence (Montréal to Anticosti Island)

Saint John and the Bay of Fundy

Port Hawkesbury and the Strait of Canso

Figure 1. Maps showing the four ARP pilot areas

Oil spill preparedness and response activities in these areas would be selected based on consideration of geography, environmental sensitivities and traffic volumes. Based on the selected responses, plans would be developed to ensure that the required spill cleanup equipment is readily available, addressing a key recommendation to ensure timely responses to any spill. This initiative would draw on Aboriginal and marine stakeholder participation to strengthen spill preparedness and response plans. Lessons learned from these four areas will be used to refine area response planning models, and in the future, will allow the Government of Canada to consider options for implementing this spill-response planning approach in other locations nationally.

To support this study, a comprehensive search of relevant literature available in the public domain will be conducted for each response area and compiled into five volumes. This first volume provides a general overview of oil products applicable to all potential ship-based spills including:

- Types of petroleum products handled by each port
- Physical and chemical properties of the petroleum products
- Fate and behaviour of oil in aquatic environments

- Available oil spill countermeasures
- Use of modeling for oil spills preparedness and response.

Specific background information for each of the four pilot areas can be found separately in Volumes 2 to 5. In these volumes, information pertinent to developing a sound Area Response Plan is provided, including:

- Physical oceanography and climate
- History of oil spills in the area
- Previous oil spill modelling that has been applied to the area.

The knowledge acquired from this exercise will be integrated with other scientific documents to develop area response plans for the selected pilot ports.

2 OIL PRODUCTS HANDLED BY THE PORTS

In 2011, more than 80,000,000 metric tons of oil products moved through the four pilot areas selected for this study as cargo (Table 1). Reported volumes include refined and crude oil products.

Table 1. International and domestic imports and exports of petroleum products (thousands of metric tons) for the four pilot areas (Statistics Canada 2011)

		Saint John (NB)	Port Hawkesbury (NS)	Québec/Montreal (QC)	Vancouver (BC)
Unrefined products	Crude petroleum	15,415	18,542	9,989	2,198
Refined products	Gasoline and aviation fuel	4,998	826	7,284	1,960
	Refined petroleum and coal products	3,190	247	454	110
	Fuel oil	6,443	339	7,177	1,404
	Total	30,046	19,954	24,904	5,672

While the volumes above are classified according to the Statistics Canada classifications, for purposes of the current review, these oil products will be grouped into three categories based on their physical and chemical characteristics. The categories will include crude oil (include light, medium, heavy and extra heavy grades), refined light products (e.g. gasoline, diesel and jet fuel) and heavy fuel oils (e.g. Bunker C). Additionally, this review will include bitumen products. While data for volumes of bitumen products moving through the four ports is not available at this time, increased production of these products from Canadian oil sands is expected to result in increased export (Moritis 2007). In addition to the volume of imported and exported oil products, fuel oil is carried by all ships utilizing the ports and has the potential to be spilled and enter the environment. Vessels larger than 150 tons transited these 4 regions over 40,000 times from 2011-2012 (Genivar 2013), representing significant potential for fuel oil spills.

3 PHYSICAL AND CHEMICAL PROPERTIES OF OIL PRODUCTS

3.1 GENERAL CHARACTERISTICS OF OIL PRODUCTS

Oil, as a general description, encompasses a wide range of products with differing properties that result from different chemical compositions. All oil products are composed of four main types of molecules: saturates, aromatics, resins and asphaltenes, while some petroleum products also include gases such as methane and propane (American Society of Microbiology 2011). Within each of the four groups, there are a range of different individual molecules with varying chemical properties. Generally, smaller or 'lighter' molecules behave differently than the larger or 'heavy' molecules. The specific combination of these molecules, in differing amounts, dictates the physical and chemical characteristics of any given oil. In turn, these characteristics determine the fate and behaviour of oil spilled from ships into the marine environment (Head et al. 2006).

One of the main factors affecting oil spill behaviour is the density of the oil. Fresh water has a density of 1.0 g/mL, while salt water has an average density of 1.03 g/mL. Low density oils will be <1.0 g/mL and tend to float on water, while high density oils may be more dense than water, resulting in sinking. The specific gravity and the API gravity value of an oil product are related to the density of oil. Specific gravity (SG) is commonly used to denote the ratio of the density of oil to the density of water, where an oil with SG>1 will tend to sink (Speight and Ozum 2001). The American Petroleum Institute (API) classifies crude oils according to their API gravity value, an inverse measure of how heavy crude oils are compared to water (Demirbas et al. 2015). Thus, low density oils have higher API gravity compared to high density oils. An oil product with an API gravity less than 10° would be predicted to sink (Demirbas et al. 2015).

The viscosity of the oil is a second factor that determines the behaviour of spilled oil. Viscosity is related to how easily a fluid will flow, highly viscous fluids tend to have a thick consistency and do not flow freely (National Academies of Sciences Engineering Medicine 2016). For oil spills, the viscosity of the oil will determine how easily a spill will be dispersed (National Academies of Sciences Engineering Medicine 2016). Low viscosity oils will easily spread across a water surface and more easily mix with the water, whereas high viscosity oils will resist spreading and mixing.

Surface tension is another factor which influences the fate of spilled oil, it is a measure of how strongly the molecules in a fluid will hold together, usually at the surface-air interface (US Geological Survey 2016). An oil with a high surface tension will resist spreading, while a low surface tension oil will more easily spread. The surface tension of any single oil will depend on the chemical composition, but also the temperature (Lee et al. 2015). At warmer temperatures, the surface tension decreases along with viscosity, increasing spreading rates at higher temperatures.

An important factor in determining density, viscosity, and surface tension of a spilled oil product is temperature; all three of these factors will change as the temperature of an oil changes. As temperatures rise, oil will become less viscous, decrease in density, and have lower surface tension. Alternatively, as temperature decreases, density, viscosity, and surface tension increase (National Academies of Sciences Engineering Medicine 2016). In the case of an oil spill, the temperature of the ocean may be one of the largest factors determining the behaviour of the oil, and thus the area and extent of any impact (Atlas 1975).

The four oil types addressed in this report are grouped based on physical and chemical characteristics. General properties of these four oil types are discussed in the following subsections. However, it is important to note that differences exist within an oil category depending on the specific oil that is present.

3.2 CRUDE OILS

Crude oil refers to unrefined oil products and encompasses a range oil types based on the overall physical and chemical properties (American Society of Microbiology 2011). Crude oil is usually divided into categories based on API gravity (density), which tends to reflect the chemical composition. Light crude has an API >38°, medium crude has an API of 22° - 38° and heavy crude has an API < 22° (U.S. Energy Information Administration 2018). Heavy crude oil can be further divided with extra heavy crude defined as oil with an API <10° (Meyer and Attanasi 2004). Because of their densities, the majority of crude oils will float on water, with only the extra heavy crudes likely to sink.

3.3 REFINED LIGHT PRODUCTS

The oil-based products used for fuel or manufacturing are a result of a refining process that fractionates crude oil, usually through distillation (Doerffer 1992). These refined products include gasoline, diesel and jet fuel as well as the heavier fuel oils. The heavier fuel oils will be discussed separately due to differences in their physical and chemical characteristics.

Lighter refined petroleum products have low densities and viscosities compared to the crude oil they are generated from. Their APIs are >10° (Doerffer 1992), indicating that these products will float if spilled in fresh or salt water. These refined products tend to have more of the lighter aromatics such as benzene, toluene, ethyl-benzene and xylene (BTEX), small polycyclic aromatic hydrocarbons (PAHs), and light saturates, while the heavier resins and asphaltenes are significantly reduced (Curl and O'Donnell 1977). Because light aromatics are volatile, refined petroleum products can evaporate rapidly (Curl and O'Donnell 1977).

3.4 HEAVY FUEL PRODUCTS

Heavy fuel products (e.g. Bunker C), while also refined, have significantly different physical and chemical properties than the refined light products described above, thus their behaviour following a spill will be quite different. Generally speaking, heavy oils have higher densities and those “extra heavy” crude oils with API <10° would tend to sink if spilled into water (Environment Canada 2001). Heavy fuel products also have more heavy saturates, resins and asphaltenes compared to the light refined products, with smaller concentrations of the volatile aromatics (CONCAWE 1998). The viscosity of heavy fuel oils is relatively high, which combined with their higher density affects how the fuels interact with water (CONCAWE 1998). As well as moving through the four ports of interest as cargo, heavy fuel oils are used to power the vessels themselves, thus heavy fuel products may be spilled from any ship transiting the areas of interest.

3.5 BITUMEN PRODUCTS

Bitumen products are also transported through the four Canadian ports. These high density oil products (API ~8°) are extracted from the oil sands in northern Alberta (Crosby et al. 2013). Because of the high viscosity of bitumen, it cannot be transported directly and is modified through dilution with other petroleum products (King et al. 2014). Diluted bitumen (dilbit) is a mixture of bitumen and condensates, with the condensates making up 20-30% of the final product (Crosby et al. 2013). When diluted with synthetic oil, the product is called synbit (King et al. 2014). These diluted products have an API gravity of 20.6° (King et al. 2017). The reduced viscosity of dilbit and synbit allows these products to be transported by pipeline to facilities where they can be loaded on tankers for export. Railbit, a third type of diluted bitumen is transported via rail and usually has lower amounts of diluent added (Nimana et al. 2016). The amount and type of diluent varies seasonally, with bitumen source and among producers (Crosby et al. 2013). The behaviour of diluted bitumen products in aquatic systems is an area of active research (e.g. behaviour of dilbit in flume tanks (King et al. 2014). Because of the mixture between a high density, high viscosity product and the low density, low viscosity diluent, the rates of spreading and likelihood of sinking is a current area of study, but will depend on the environmental conditions where the spill occurs (King et al. 2014).

4 FATE AND BEHAVIOUR OF PETROLEUM PRODUCT SPILLS

When oil is spilled from a ship, the fate and behaviour of the oil is affected by the type of oil spilled, the location of the spill and the environmental conditions in the area. The combination of these factors, along with the volume of the spill, will determine the overall impact of a spill, which will affect decisions regarding the best approach for mitigation.

When oil is spilled into the marine environment, the characteristics of the oil immediately begin to change as a result of exposure to the environment (Figure 2). Through a series of different mechanisms, the oil undergoes chemical and physical changes, collectively called ‘weathering’ (Mishra and Kumar 2015). These processes alter the density and viscosity of the oil, altering how the oil moves across or through the water with winds and waves, as well as how long oil will persist in the marine environment (Mishra and Kumar 2015). Non-persistent oils will be rapidly lost through weathering, resulting in short-term exposure and impacts (National Research Council 2003). Conversely, persistent oils, while still undergoing weathering, can remain in the environment for long periods and generally require substantial mitigation efforts (National Research Council 2003). In general, non-persistent oils have larger proportions of the lighter molecules (e.g. BTEX, PAHs), as found in the light refined products (Mishra and Kumar 2015). Persistent oils tend to have higher proportions of the heavy compounds including asphaltenes and resins (Mishra and Kumar 2015). Crude oils, heavy refined products and bitumen products are classified as persistent oils.

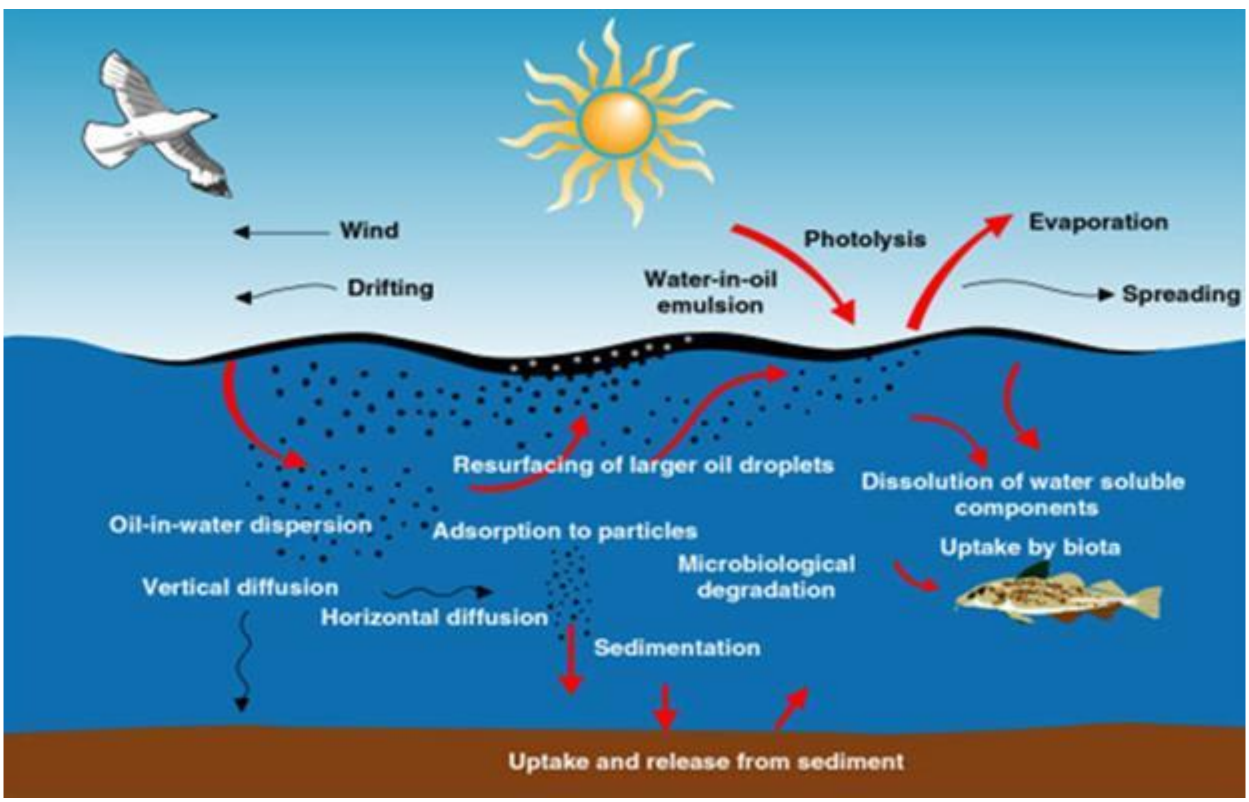


Figure 2. Oil weathering processes (Sorheim and Andreassen 2011)

4.1 ENVIRONMENTAL VARIABLES AFFECTING SPILLED PRODUCTS

When a spill occurs, the location, season and local weather patterns will interact to affect how the oil behaves in the marine environment (Lee et al. 2015). These impacts will depend on the type of oil spilled. With a ship-based oil spill, location can vary from a ship sitting at a dock to and open ocean environment, and thus occur at varying distances from shore. Mitigation and clean up techniques in open or coastal waters will differ dramatically from techniques applied to shorelines. One of the main goals of a mitigating an open water spill may be to prevent the oil from reaching shore where it may interact with the substrate resulting in longer persistence (Nuka Research and Planning Group 2012).

The interaction between oil products and shorelines alters the fate and behaviour of oil following a spill. The type of oil and the type of shoreline can increase or decrease the rates of different weathering processes (Lee et al. 2015). Wave energy, tidal action, vegetation, substrate (e.g. sand, gravel, mud) and even the slope of the shoreline combine to create environments where surface area of oil exposed to air and water can be reduced, slowing weathering through evaporation, dispersion or biodegradation (National Research Council 2003). Alternatively, these same factors could result in an environment where removal rates are increased.

Regardless of the distance from shore, water is in constant motion. Currents, wind-driven waves and tidal flow can all contribute to the transportation and weathering of spilled oil (Lynagh 1985). Local weather patterns at the time of a spill will determine the wind speed, which in turn determines the wave height and frequency (NOAA 2017). Winds, along with currents and tides, will affect transportation of oil and determine the size and location of the area impacted.

Seasonal patterns determine the temperature of the water at the spill site, which can have a significant effect on the density and viscosity of the oil (National Research Council 2003). In winter, several of the large ports in Canada experience ice cover, which adds an extra variable in the interaction between oil and environment (Transportation Research Board and National Research Council 2014). While all of the ports in the pilot study are marine, some of the areas have significant inputs of freshwater due to river flow. Melting ice in spring may also contribute freshwater to a region. Freshwater will alter the salinity of the port water, and thus the density of the medium into which an oil is spilled. While some oils may float on both freshwater and saltwater, others may have API values close to that of water (10°) and may sink under freshwater conditions (Demirbas et al. 2015). Freshwater inputs from rivers are also often associated with increased concentrations of nutrients, which are necessary for marine microorganisms to grow (Smith 2002). These nutrients may affect growth rates of species that are capable of growing on oil products, impacting rates of biodegradation.

Another consideration associated with river flow is sediment load. Some river systems may carry large concentrations of suspended particles. This may occur seasonally, often associated with periods of high flow in spring and early summer (French McCay et al. 2016). Sediment particles can interact with oil and alter its fate and behaviour by increasing the formation of tar balls or increasing rates of sedimentation (Lee 2002; Warnock et al. 2015).

4.2 TRANSPORTATION

*4.2.1 **Spreading***

When oil enters the water, it tends to spread out over a larger surface area, decreasing the overall thickness of the spill (Fay 1969). Higher viscosity oils will resist spreading relative to low viscosity oils, which will rapidly spread to form a large, thin sheen (Njobuenwu and Abowei 2008). The surface tension of an oil also affects the speed at which it spreads, with low surface tension oils spreading more quickly than those with high surface tension.

*4.2.2 **Advection***

Because of currents at the surface of the ocean, oil spilled in one location will quickly begin moving. In areas where tidal forces are high, the oil may move first in one direction and then back as the tides ebb and flow. The surface of the ocean is not smooth, and wind and wave action will also affect the horizontal transport of oil. The prevailing wind will drive waves and other turbulence at the ocean's surface causing 'windrows' in the oil (Lee et al. 2015). These are narrow bands of oil which form parallel to the wind. The actions of the wind may counteract spreading, resulting in thicker, smaller slicks than in the presence of spreading alone (Lee et al. 2015). Advection can move an oil spill from an area of open water towards shorelines, so understanding patterns of local currents is important in developing a mitigation strategy.

4.3 EVAPORATION

Ship-based spills will tend to release oil products at the surface-air interface. Under these conditions, loss of light, volatile components, such as BTEX and small PAHs, can occur rapidly (Douglas et al. 2002). At higher temperatures, this evaporation can be enhanced. For some oil products, especially light refined products, the majority of the oil can be lost through evaporation (Fingas 2000). This rapid loss of compounds to the air, along with dissolution, contributes to the non-persistent behaviour of light refined products (Lee et al. 2015). In a spill, little clean-up is required for these products. An additional benefit to evaporation is that the most volatile components tend to be the most toxic (Lee et al. 2015). Evaporation removes these toxic compounds from the water, decreasing the potential toxic impacts of a spill (Lee et al. 2015).

In contrast to light refined products, evaporation of heavy refined products, crude oils or bitumen products can increase the density of the remaining oil (Lee et al. 2015). The loss of the volatile components of the oils leaves the heavier compounds (e.g. asphaltenes, resins), which are considered more persistent. These remaining components are then subjected to further weathering through mechanisms described below.

An important factor affecting the rate of evaporation is the thickness of the slick. When spreading occurs quickly, the oil forms a thin slick with a large surface area from which evaporation can occur (Lee et al. 2015). The higher viscosity crude oils, refined products and bitumen products tend to form thicker slicks. This decreases the surface area over which evaporation can occur. Surface resins and asphaltenes can also undergo oxidation, forming a 'skin' over the remaining oil products (Bauget et al. 2001). Thus, even if some compounds are volatile, their evaporation may be prevented by being partitioned away from the surface-air interface (Bauget et al. 2001).

4.4 DISSOLUTION

Instead of moving into the air, some compounds in oil will dissolve into the water column. The same fraction that is easily volatilized, the short chain saturates and BTEX, are the components with the highest solubility in water (Singass and Lewis 2011). While most of these compounds will be lost through evaporation, some will enter the water column. Once these compounds are dissolved in the water column, they represent potential toxicity to organisms (Peterson et al. 2003). High molecular weight compounds including larger PAHs, asphaltenes and resins are insoluble in water (Singass and Lewis 2011). Instead, they undergo alternative weathering processes. Dissolution differs from dispersion, as dissolution involves single hydrocarbon molecules being surrounded by water molecules, while dispersion results in droplets of multiple oil molecules surrounded by water (National Research Council 2003).

4.5 DISPERSION

Dispersion of oil into the water column is driven by turbulent mixing due to wind and waves (National Research Council 2003). During dispersion, the oil is broken up into droplets of varying sizes (National Research Council 2003). Small droplets can be entrained into the water column and remain below the surface. Larger droplets tend to be buoyant, and will float back to the surface where they can coalesce and reform a slick (National Research Council 2003). Dispersion works with spreading to increase the surface area of a spill, but vertical dispersion increases the volume of water affected by the oil (American Society of Microbiology 2011). Well dispersed oil can increase the surface area available for biodegradation as well as dissolution, which can increase the rate at which oil compounds are removed from the environment (American Society of Microbiology 2011). The use of chemical dispersants in response to oil spills is intended to increase dispersion and decrease droplet size, thus augmenting natural dispersion (American Society of Microbiology 2011).

4.6 EMULSIFICATION

Waves and wind can also mix the oil with water as an emulsion, without forming small droplets as during dispersion. The ratio of water to oil in an emulsion and the overall stability of the mixture depend on the type of oil and previous weathering (National Research Council 2003). Emulsions increase the volume of the spilled oil, as the water content of stable emulsions are 60-85% (National Research Council 2003). Additionally, the viscosity of the oil is increased (Mishra and Kumar 2015), reducing the surface area and decreasing evaporation, dispersion and biodegradation. Emulsions may float on the surface or sink, depending on the overall composition. The stability of emulsions is thought to be due to interactions among asphaltenes, resins and potential microbial cells (National Research Council 2003). Regardless of the mechanism, emulsions can be stable for days to months, but can be broken up, exposing the oil to other weathering pathways and organisms to potential toxicity (National Research Council 2003).

4.7 SEDIMENTATION

Sedimentation involves the interaction between oil compounds and sediment particles, mixing at shorelines or in the water column. At the shoreline, fine particles mixed with oil may be re-suspended through wave or tidal action (Gong et al. 2014). Where sediment loads in the water column are high, oil can interact and mix with fine particles (Stoffyn-Egli and Lee 2002). In both these instances, the oil-sediment particles, or oil mineral aggregates (OMAs), may remain suspended in the water column or sink, depending on the density (Stoffyn-Egli and Lee 2002) (Figure 3).

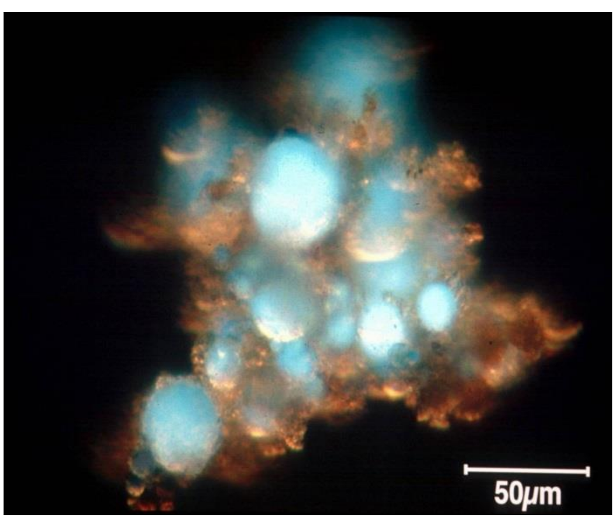


Figure 3. Oil-sediment aggregate, also known as oil-mineral aggregate or oil-particle aggregate

Other interactions between oil and particles involve organic or biological particles. Oil may become part of zooplankton fecal pellets after ingestion (Prahl and Carpenter 1979), interact with microscopic cells, or dissolved organic matter (Stoffyn-Egli and Lee 2002). These oil particle aggregates (OPAs, which includes OMAs) may be 'sticky' and clump together, forming larger particles that can sink (Zhao et al. 2016). Oil products that reach the sediments as OPAs are likely to persist if the sediments have low oxygen concentrations due to low rates of biodegradation.

4.8 PHOTO-OXIDATION

In surface spills, oil can be exposed to ultra-violet (UV) radiation in sunlight. This radiation can cause chemical changes in hydrocarbon molecules through oxidation (Lee 2003). The hydrocarbon molecules or molecules in the surrounding water absorb the energy in the sunlight which can then alter the chemical bonds in the oil compounds (NRC 2003). The rate of photo-oxidation is slow in the environment, with little of the oil being removed through this process (National Research Council 2003). Photo-oxidation can result in crusts forming on floating oil emulsion or suspended oil, enhancing the formation of tar balls or patties (Bobra 1989). These tar balls can persist for long periods of time and can often be found on beaches (Kiruri et al. 2013).

4.9 BIODEGRADATION

Oil products represent a large organic carbon source for microbial species in aquatic environment. Under oxygen rich environments, microbial organisms are present in most environments that can rapidly oxidize hydrocarbons (American Society of Microbiology 2011). Working as a consortium, multiple species of microbes (mainly Bacteria and Fungi) can degrade hydrocarbons to CO_2. Degradation rates are higher for short-chain saturates and PAHs compared to rates for larger molecules such as asphaltenes and resins (Brakstad and Bonaunet 2006). Because of the high amount of carbon in oil products, availability of other nutrients, such as nitrogen and phosphate, may limit the rate and extent of biodegradation in aquatic environments (American Society of Microbiology 2011). Oil in the water column, either dissolved or dispersed in small droplets, is relatively accessible to microbes (American Society of Microbiology 2011). OMAs, oil in sediments or oil attached to shorelines, all have reduced surface area for microbes to colonize (Zhao et al. 2016). In some cases, sediment may also have low oxygen concentrations (Niu et al. 2011). Although anaerobic biodegradation does occur, it occurs at a much slower rate than aerobic degradation, resulting in the persistence of oil in sediments (Ghattas et al. 2017).

The microbial community present at any single location will vary based on the temperature, salinity and nutrient state of the environment (American Society of Microbiology 2011). Generally, degradation rates will be higher with increased temperatures, as microbes are able to grow faster at higher temperatures (American

Society of Microbiology 2011). However, because microbial communities are adapted to the temperatures where they live, degradation can still occur at significant rates even at low temperatures (American Society of Microbiology 2011).

5 OIL SPILL COUNTERMEASURES

There are multiple different approaches to mitigating the impacts of an oil spill, from trying to recover the oil from a point source or from open water to trying to remove it from or prevent it from reaching sensitive environments. There are costs and benefits to the different approaches and not every approach will be effective in all circumstances. The actual approach will vary depending on the type and volume of oil, the mechanism and location of the spill, local environmental conditions and the predicted fate and behaviour of the oil (Doerffer 1992). To predict how oil might behave in the environment, most oil spill planning uses modelling. Based on all of these factors, a response plan is developed which aims to maximize recovery and minimize impact.

5.1 NATURAL ATTENUATION

In some instances, mitigation approaches may not be feasible due to the location of a spill or the impact of clean-up efforts outweighing the benefits. In these cases, monitored natural attenuation (MNA) may be the optimal response (Transportation Research Board and National Research Council 2014). MNA allows natural weathering processes, mainly biodegradation along with evaporation, dissolution and photo-oxidation, to remove the oil products from the environment (Esquinas et al. 2017). This approach may be appropriate for spills of light refined products, where natural evaporation will occur rapidly and remove the majority of the oil compounds within hours to days (Gallego et al. 2006).

5.2 CONTAINMENT AND RECOVERY

When a ship-based spill occurs, the first response is usually to minimize the impacted area by containing the spill. This can be accomplished by deploying booms, or floating barricades, which prevents spreading from occurring (Lee et al. 2015). Boomed oil can then be recovered and removed from the environment using devices such as skimmers (Al-Majed et al. 2012). Booms and skimmers work well in calm waters, but rough seas caused by high winds reduce their ability to work (Al-Majed et al. 2012). Turbulence from rough seas also increases dispersion and emulsion, which can reduce the oil at the surface that can be skimmed or the ability of the skimmers to work. Different skimmer designs work best at different oil viscosities (Al-Majed et al. 2012), thus the type of oil must match the available skimmer. Additionally, weathering of the oil may change the viscosity enough that available skimmers may no longer work (Nordvik 1995). Thus, clean up may work best if carried out immediately. Even under ideal situations, containment and recovery is not highly effective and tends to result in removal of only 10-30% of spilled oil (Vodyanoy et al. 2013).

Along with skimmers, sorbent material may be used to remove oil products following a spill (Al-Majed et al. 2012). These materials can be used on shorelines or in open water, in conjunction with booms. Sorbents may be made from minerals or biological material as well as synthetic polymers and are designed to bind the hydrocarbons (Al-Majed et al. 2012). A potential downside to deploying sorbent materials is the need to dispose of contaminated materials after use.

5.3 PHYSICAL REMOVAL FROM SHORELINES

Once oil has reached the shoreline, physical removal of materials may be the only clean-up option. MNA may be a better option if a contaminated shoreline is considered to be composed of sensitive habitat (e.g. marsh) (National Research Council 2013). Physical collection of contaminated rocks, sand or other materials (e.g. debris, logs) from a spill area can quickly remove oil, but results in large volumes of contaminated waste for disposal. In wetlands or kelp beds, contaminated vegetation may be removed and disposed of (Pezeshki et al. 2000). This may have a large short term impact, but longer term benefits (Baker 1995). In some cases, washing oil off the shoreline into a contained area of water may provide the opportunity to clean the shoreline and recover some of the spilled oil (Baker 1995). The decision to use any shoreline clean-up is usually based on a Net Environmental Benefit analysis, as increased activity and removal of materials can cause larger disruptions to an environment compared to a MNA approach (Baker 1995).

5.4 IN SITU BURNING

In conjunction with booming, *in situ* burning (ISB) can be used to remove oil from open water environments (van Gelderen et al. 2015). After oil is trapped in a fire resistant boom, the material is ignited and allowed to burn until no more fuel remains (van Gelderen et al. 2015)(Figure 4). ISB effectively removes oil products from the environment without generating contaminated waste; however, ISB results in 1-5% of the oil remaining as residues (Mullin and Champ 2003). ISB works best under calm seas, where the thickness of slick is > 1-2 mm and under higher temperatures (Mullin and Champ 2003). Under low temperatures, little volatilization occurs, reducing the material that can be burned (Al-Majed et al. 2012). Also, emulsions with high water content burn poorly (Al-Majed et al. 2012).


Figure 4. Ships towing booms feed oil into an *in situ* burn (Allen et al. 2011)

5.5 SPILL TREATING AGENTS

While natural dispersion will occur with most oil spills, the addition of chemical dispersants can increase the rate and effectiveness of the natural process (American Society of Microbiology 2011). Dispersants can be sprayed by airplanes or boats on water surfaces when slicks have been identified (Flaherty 1989). While the composition of individual products varies, they are generally surfactants dissolved in solvents (Brandvik and Daling 1998). Chemical dispersants have different effectiveness depending on the type of oil and the ratio of oil to dispersant. The aim is to disrupt surface slicks by generating small droplets that will enter the water column and become available for biodegradation (American Society of Microbiology 2011). Waves provide mixing to enhance the activity of dispersants, making them useful in weather conditions when booming and skimming cannot be used (International Tanker Owners Pollution Federation 2014). Most regulations regarding chemical dispersants prevent them being used close to shore (International Tanker Owners Pollution Federation 2014), thus they are mostly used in open ocean environments. Use of chemical dispersants is limited when oil at the surface is weathered, as emulsions and tar balls are resistant to dispersal (International Tanker Owners Pollution Federation 2014). Additionally, the effectiveness of current available dispersants in fresh or brackish water environments is limited.

5.6 HERDING AGENTS

Similar to dispersants, herding agents are chemicals that can be applied to an oil spill to alter the oil's behaviour (Buist et al. 2011). In contrast to dispersants which disrupt a slick, herding agents are designed to collect the slick (Buist et al. 2011). In calm waters, herding agents can increase the thickness of slicks, enabling skimmers and other equipment to collect and remove the oil (SL Ross Environmental Research 2012). A potential use for herding agents is in regions with some ice cover where traditional booming is not possible. Herding agents could be deployed in irregular open water areas to collect oil, which would then be removed through ISB (Buist et al. 2011).

5.7 BIOAUGMENTATION AND BIOSTIMULATION

Microbes with the capacity to degrade hydrocarbons exist in most aquatic environments; however, the effectiveness of biodegradation varies depending on local conditions (Head et al. 2006). One approach to mitigating an oil spill is to allow the natural community to degrade the hydrocarbons under natural conditions. For example, in warm weather with a light crude oil, this process may occur rapidly. In other instances, with lower temperatures or a different oil type, the rates may be low. Bio-augmentation consists of the addition of microbial organisms to the environment (Head et al. 2006). Either pure cultures or mixtures of oil degrading organisms would be added to the water or substrate where the oil is present (Tyagi et al. 2011). Bio-augmentation has not been shown to increase rates of degradation significantly under field conditions (Lee et al. 1997), but increased understanding of how microbes interact to degrade oil may lead to improvements in this area (Heinaru et al. 2005).

Bio-stimulation aims to improve rates of degradation by stimulating the naturally occurring microbial community (Nikolopoulou and Kalogerakis 2009). This may take the form of adding nutrients (e.g. nitrogen and phosphate) to an oil spill to stimulate growth of biodegrading organisms (Nikolopoulou and Kalogerakis 2009). In some instances, increasing oxygen availability through aeration can increase biodegradation rates (Nikolopoulou and Kalogerakis 2009). Bio-stimulation requires identifying what factor is limiting the rates of biodegradation and then alleviating that limitation.

5.8 OIL SPILL MODELLING

As mentioned in Section 4, designing an oil spill response plan and identifying the appropriate mitigation techniques requires predictions about the fate and behaviour of oil once it is spilled. These predictions are derived from models which use our understanding of oil properties, weathering processes and oceanography to estimate how the oil will change and where it will move. Models are mathematical descriptions of natural processes, where the processes are simplified as much as possible. Most models are based on empirical data collected through laboratory and field studies and verified by follow up studies. Models are constantly being updated and modified to incorporate new understanding of processes. For oil spills, several different models focus on different aspects of a spill. These may include transport models, weathering models and biodegradation models (Reed et al. 1999).

5.9 APPLICATION OF MODELS

One of the main applications of models in designing an oil spill response is to predict where the oil will go (Spaulding 1988). Knowing that oil will tend to move in a particular direction based on local water currents, tides and winds provides responders with information crucial to making decisions regarding personnel and equipment deployment. Other models can predict what types of toxic exposure organisms may receive (French-McCay 2004). This can be used to make decisions regarding fishery closures or deployment of resources for wildlife care.

5.10 TYPES OF MODELS FOR OIL SPILLS

There are a wide range of models available for oil spills. These models include weathering models that predict how different weathering processes will affect the oil (Daling et al. 1997). Models also address transport of the oil including spreading and advection as well as how oil will interact with shorelines (Reed et al. 1999). For all of the models, a variety of parameters are needed to generate a prediction. Some parameters are associated with the oil, such as knowing the viscosity, density and composition as well as the volume and type (Spaulding 1988). Other parameters are associated with the environment in which the spill occurred. These may include the water temperature, salinity, sediment load, oxygen concentration, wind speed, wave height and current direct and speed (Reed et al. 1999). Together, the different models can provide a projection of what is likely to happen in the event of an oil spill. By modifying the parameters entered into a model, different scenarios can be generated providing response planners with a range of potential events to prepare for.

5.11 LIMITATION OF MODELS

Because models are simplified representations of a process, they have some errors and do not perfectly predict what will happen. Researchers design models by identifying the most important aspects of the process and choose which parameter to include and which ones to leave out. In some cases, models may be too simple and need to incorporate more complex representations of processes. In other cases, the models are well developed, but the parameters needed for the model are not well known. Models, especially those that incorporate local processes such as currents and shorelines, may work well in one region, but not in other areas.

6 CONCLUSIONS

This first volume (Introduction) aims to present general information about the various oil products transported in Canada today. Relevant information is also provided with regard to the fate of oil, and operational response techniques in the context of ship-based spills in order to aid in understanding the four following volumes which focus on individual ports. All four ports included in this pilot study have large volumes of oil products moving through them as cargo, although volumes of bitumen products are unknown as of 2011. Along with the cargo, high volumes of tanker traffic in the ports represent potential spills of fuel oil from the ships tanks.

Understanding different types of cargo oils, and the ships fuel is important as different oil products behave differently in the environment. Differences in chemical composition between light refined products, heavy refined products, crude oils, and bitumen products result in unique physical and chemical properties for each oil. The behaviour of each oil interacting with local environmental conditions will determine which of the available mitigation techniques should be incorporated as part of an area response plan.

To incorporate local environmental conditions into response planning, predictive models can be used. These models can integrate knowledge about different oil types and how they are affected by weathering with the local climate, habitats, and oceanography to predict the fate and behaviour of oil following a spill. This information can then be used to evaluate the potential effectiveness of different oil spill countermeasures to develop a comprehensive regional response plan.

Volumes 2, 3, 4 and 5 of this report will provide information on the hydrography, oceanography, climate, past oil spills in the area, and, where available, spill modelling for each of the four selected pilot ports. This will provide an overview of the information needed to develop a sound Area Response Plan for ship-sourced spills in each area.

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