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State of Knowledge on Chemical Dispersants for Canadian Marine Oil Spills

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Foreword

This series documents the scientific basis for the evaluation of aquatic resources and ecosystems in Canada. As such, it addresses the issues of the day in the time frames required and the documents it contains are not intended as definitive statements on the subjects addressed but rather as progress reports on ongoing investigations.

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ABSTRACT

Chemical dispersants represent one of many oil spill response measures. Following its large-scale application during response operations during the Gulf of Mexico Oil Spill in 2010 there has been significant advancement in the scientific understanding of dispersants. As a result, a large volume of literature has been produced detailing the results and findings of many studies and assessments.

A literature review was conducted to consolidate and evaluate the state of knowledge of chemical dispersants in a Canadian context. Specifically, the literature review investigates how dispersants interact with the fate, behavior, and transport of oil in the environment, pathways of effects of dispersed oil for marine biota, potential effects, and impacts of dispersed oil on biota. Furthermore, in light of environmental concerns, consideration is given to specific monitoring and oil trajectory modelling needs during response operations when dispersants are used.

The findings of the literature review suggest that chemical dispersants change the oil's transport, fate, and potential effects by changing the chemical and physical properties of oil. As dispersants enhance the movement of oil into the water column as small oil droplets, dispersants may alter the level of exposure for certain species. For example, dispersants may enhance the bioavailability of the oil to some species. However, based on the results of laboratory toxicity assessments, at oil loadings <100 mg/L (a common value for most oil spill scenarios), chemically-dispersed oil and untreated oil (without dispersant application) appear relatively similar in terms of their effects on marine biota.

A significant trade-off of dispersant use is that while dispersants may reduce impacts of oil slicks to wildlife at the water surface (e.g., marine mammals, seabirds), and the subsequent transport of oil to vulnerable and biologically rich coastlines and coastal habitats, they may increase impacts within the water column and sediments of the offshore environment. There are currently numerous ongoing studies focused on the evaluation of long term impacts of dispersant use on biota in the offshore marine environment to address knowledge gaps.

Proper use of dispersants within Canada must take into consideration the unique circumstances and conditions of each oil spill scenario, including the dynamic nature of the marine environment and the role of environmental, physiochemical, and ecological factors.

INTRODUCTION

CONTEXT

Canada has a strong marine safety system focusing around four major pillars: prevention, preparedness and response, liability and compensation, and recovery. In recent years, the Government of Canada has dedicated significant resources to further enhance specific aspects of the environmental protection and emergency response regime in Canada.

When spills occur into aquatic environments, Fisheries and Oceans Canada (DFO, which includes the Canadian Coast Guard), uses science-based evidence to make decisions that facilitate effective and sustainable management of Canada's fisheries, ensure that aquatic ecosystems are protected from negative impacts, and inform environmental response.

Following an oil spill, there is a need to assess and evaluate the effectiveness of all available response tools; this includes the consideration of dispersants as a response measure. Following historical oil spill incidents, such as the Torrey Canyon oil spill in the United Kingdom (1967) and the more recent Deepwater Horizon (DWH) spill in the Gulf of Mexico (2010), there has been extensive research and scientific advancement related to dispersant use. This information, available through various fora, has not yet been critically evaluated specific to its applicability within a Canadian context.

The scope of this peer review process is focused on the following:

- All oil pollution sources (e.g., offshore, ship, etc.);
- Marine (saltwater) use;
- Canadian environmental conditions (i.e., temperate and cold climate aguatic ecosystems);
- Non-specific dispersant formulation;
- Dispersed-oil mixture (rather than the dispersant itself);
- Routes of exposure and adverse effects (rather than the specific mechanisms for toxicity or effects);
- Broad considerations for impact, applicable to species groups (population/community level rather than individual species); and
- General recommendations for monitoring (rather than specific, detailed actions).

OBJECTIVES

The purpose of this document is to summarize the current state of knowledge on chemical dispersants to support discussions at the Canadian Science Advisory Secretariat science peer review meeting on the State of Knowledge on Chemical Dispersants for Canadian Marine Oil Spills held March 1–12, 2021.

The goal of the science peer review meeting is to consolidate, assess and critically evaluate the current state of knowledge on dispersants as it applies to a Canadian context. Specific questions to be addressed by this National peer review meeting include:

- 1. How does applying dispersants change the movement of oil and exposure to sensitive receptors (e.g., aquatic species, habitats, and other sensitive coastal or marine areas)?
- 2. What are the differences in exposure and effects between untreated oil and dispersed oil and their potential short- and long-term impacts on sensitive receptors?

- 3. What are the key considerations or recommendations for environmental monitoring after dispersant use?
- 4. What are the priority, outstanding science needs to support the regulatory regime and decision-making for the use of dispersants in Canada?

The outcomes from this process are expected to be used to:

- Efficiently inform critical and time sensitive spill response decisions (such as net environmental benefit determinations);
- Provide consensus-based, scientific advice to inform and support the communication of spill response decisions;
- Support and inform the development of regulations, policies, standards, and guidance for dispersant use; and
- Support various other Government of Canada initiatives related to spill response.

BACKGROUND

Dispersants are a blend of surfactants in solvent that enhance the natural dispersion of oil (EMSA, 2010). Dispersants facilitate the transfer of oil from the sea surface into the water column as small oil droplets which are diluted – and thus become more readily available for microbial degradation (Lee et al., 2015). While dispersants do not remove oil from the marine environment, they change its chemical and physical properties which will alter its transport, fate, and potential effects (NRC, 2005). For example, the potential enhancement of microbial biodegradation may reduce/eliminate components of oil that are of major environmental concern.

Dispersant use may effectively reduce the amount of oil present on the water's surface and the risk for surface and sub-surface species, including seabirds, marine mammals, and turtles. The dispersion of oil at sea from the water's surface helps reduce the likelihood of oil transport to more productive nearshore waters, shoreline marshes, estuaries, and beaches (Lee et al., 2015). From an ecotoxicological perspective, rapid dispersion and dilution of oil transported into the water column by natural processes, following the application of dispersants, will likely reduce oil concentrations to levels below toxicity threshold limits (Lee et al., 2015).

Dispersants represent one of many oil spill response options, including natural attenuation (monitored natural recovery – a recognized oil spill response option), shoreline clean up, physical/mechanical recovery, and in-situ burning (USGAO, 2012). Dispersants can be an effective method to mitigate spilled oil as has been demonstrated through numerous test applications and use on actual spills. A large-scale example of dispersant use (using airplane, boat, deep-water, and subsurface injection methods) in the marine environment was the DWH blowout in the Gulf of Mexico in 2010, the largest oil spill in U.S. history (BP, 2010; United States Congress, 2011; Lee et al., 2015). A variety of literature and research conducted post-DWH relating to chemical dispersants are discussed in this review.

DISPERSANT MODE OF ACTION AND TYPES

Generally, a chemical dispersant consists of three components: surfactants, solvents, and additives (USGAO, 2012). The surfactants serve as the active agents in the formulation. Surfactant molecules have a hydrophilic (an affinity for water) headgroup and an oleophilic (an affinity for oil) tailgroup (IPIECA, 2001) (Figure 1). The molecules orient themselves at the oil/water interface so that the tailgroup is in the oil and the headgroup is in the water, reducing

the surface tension so that when wave energy is added, small droplets break away from the slick, stay suspended, and spread beneath the surface (ITOPF, 2014). As a result of this process, the formation of these small droplets (stabilized micelles) decreases the adherence and re-coalescence of oil droplets which can have implications for oil spill response as oil is dispersed within the water column and less likely to adhere to biotic and abiotic features of the marine environment (Zhao et al., 2016a).

The surfactants used in dispersant formulations can be non-ionic (e.g., sorbitan oleate and polyethoxylated derivatives) or anionic (e.g., dioctyl sodium sulfosuccinate), and differ in their physicochemical properties (National Academies of Sciences, Engineering, and Medicine (NASEM), 2020). Surfactants which are non-ionic are less soluble in water, and generally less toxic than anionic surfactants (Porter, 1991; Myers, 2006). The comparative toxicity of non-ionic and anionic surfactants to aquatic species have been reviewed in several assessments (e.g., Rouse et al., 1994; Tözüm-Calgan and Atay-Güneyman, 1994; Mustapha and Bawa-Allah, 2020).

The solvent portion of a dispersant formulation reduces the viscosity of dispersants for application purposes (e.g., spraying) and can help the surfactant molecules and additives penetrate the oil slick (ITOPF, 2014). The solvents in current commercial formulations are largely hydrocarbon or glycol based (e.g., hydrotreated light distillates or glycol derivatives) (NASEM, 2020). Additives in a dispersant formulation may serve to improve the solubility of the surfactants or to increase the stability of the dispersant formulation (USGAO, 2012).

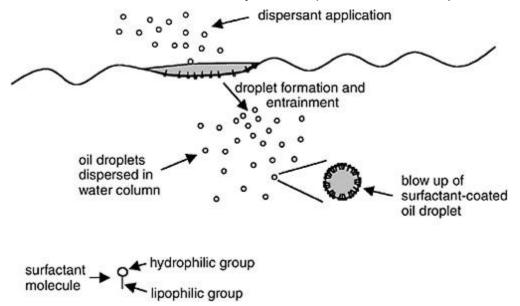


Figure 1: Dispersant mode of action (Adopted from NRC, 2005).

Improvements in dispersant formulations have been made since they were first used in the 1960s. The first generation of dispersants were similar to industrial cleaning agents and degreasers (ITOPF, 2014) and contained high levels of aromatic compounds that were very toxic in the aquatic environment (Lessard and DeMarco, 2000; NASEM, 2020). The use of first generation dispersants (e.g., industrial cleaners and degreasers) in the Torrey Canyon spill in the United Kingdom in 1967 resulted in significant ecological damage and amplified the scientific concern surrounding contamination of the sea (Wells, 2017). First generation dispersants are no longer used (ITOPF, 2014).

Advancements have been made to develop dispersant formulations with increased efficacy and reduced toxicity in the marine environment, including the development of second (Type I) and third generation (Types II and III) formulations (Table 1). Modern dispersants are typically formulated from chemicals used as food additives and/or cosmetics and they have acute toxicities that are similar to common shampoos and cleaning agents including those used to clean oiled sea-birds (Hemmer et al., 2011; DeLorenzo et al., 2018; Word et al., 2015; USFWS, 2003; NRC 1989; 2005). Dispersant effectiveness is customarily defined as the amount of oil that the dispersant puts into the water column relative to the amount of oil that remains on the surface (Chen et al., 2012).

Table 1: Comparative Summary Highlighting the Evolution of Dispersants (IPIECA, 2001; EMSA, 2010; ITOPF, 2014).

Dispersant Type	Approximate Timeline	Key Differences
First Generation	1960s	Similar to industrial cleaners and degreasersHigh aromatic content in the formulationHigh aquatic toxicity
Second Generation Type I	1970s	 Hydrocarbon solvent (low or no aromatic content) Surfactant concentration of 10–25% by weight Applied undiluted (neat) Application rate between 1:1 and 1:3 dispersant to oil Lower toxicity than First Generation dispersants More effective than First Generation Less toxic than First Generation
Third Generation Type II	1970s	 Concentrate Surfactant concentration in solvent between 25–65% (weight) Dilution with seawater, which serves as additional solvent, and wave energy for mixing Application rate of 2:1 to 1:5 (dispersant and sea water mix to oil) Designed for spraying from a vessel Seawater dilution decreases effectiveness More effective than First Generation Less toxic than First Generation
Third Generation Type III	1980s–1990s	 Concentrate Surfactant concentration in solvent between 25–65% (weight) Applied undiluted (neat) Application rate between 1:5 and 1:50 (dispersant to oil) Suited for both vessel and aerial application Most commonly applied formulation More effective than First and Second Generations Less toxic than First and Second Generations

OIL TYPES AND DISPERSANT USE

The type of oil and the chemical composition of oil affect the viability of dispersant use as a response option (NASEM, 2020). In the event of a spill and in determining the effectiveness of dispersants, the properties of oil to consider include the density (often expressed as American Petroleum Institute (API) Gravity or $^{\circ}$ API), volatility, viscosity, and pour point (ITOPF, 2018). The API Gravity is a number used to indicate the specific gravity (SG), or relative density, of oil compared to water and is calculated as API = (141.5/SG - 131.5). Generally, sea water has a

specific gravity of about 1.03; therefore, oils with an API number less than 10 will likely sink and those with an API number greater than 10 will float on water (USCG, 2003). Commonly transported oils can be classified into four standard groups with variable characteristics (ITOPF, 2018).

Table 2: Comparative Summary of Oil Types and Dispersibility (USCG, 2003; NOAA, 2013; Dillon, 2017a).

Group	API Number	Examples	Characteristics (USCG, 2003; NOAA, 2013)	Operationally dispersible? ¹
1	>45	Very Light Oils Gasoline, naphtha, kerosene	 Highly volatile and flammable; High rates of evaporation and dispersion; Rapid spreading; and Little emulsification. 	Unlikely
2	35–45	Light oils Diesel, Arabian Extra Light	 Moderate volatility, up to 40% volume loss through evaporation; Low to medium viscosity; and Potential for emulsions. 	Possibly
3	17.5–35	Medium Crudes Alaska North Slope, Arabian Light, Arabian Medium	 Moderate volatility, up to 40% volume loss through evaporation; Medium viscosity; and Generally forms stable emulsions immediately or after some evaporation. 	Possibly
4	<17.5	Heavy Crudes Medicine Hat Heavy, Nile Blend, Boscan, Pilon, Bunker C	 Low volatility; Medium to high viscosity; Little to no evaporation; Weathers very slowly; and Can form stable emulsions immediately. 	Unlikely

Group 1 oils are not good candidates for dispersant use as they readily evaporate and are not persistent, therefore reducing the need for a dispersant in the first place. Furthermore, Group 1 oils are likely to form sheens which are too thin for successful dispersant application. Group 2 oils, including light oils, may be possible candidates for dispersant use, if used before significant weathering and emulsification can occur. Group 3 oils may be candidates for dispersant use, depending on their physical and chemical properties, and if they are treated within a short

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¹Each spill scenario is unique. Determining whether an oil is a candidate for dispersant application in spill response operations (i.e., operationally dispersible) is contingent on many factors which are evaluated as part of a Net Environmental Benefit Analysis (NEBA). The suggestion of dispersibility above serves as a general assumption based on oil type and select characteristics alone. The physical properties of oil may limit the dispersibility of oil (e.g., viscosity, slick thickness), yet dispersibility may also be influenced by other factors (e.g., sea state, temperature) as well as the specific spill scenario (Mukherjee et al., 2011).

window of time before the effects of weathering and emulsification impact dispersibility. Group 4 oils are unlikely candidates for dispersant use as their physicochemical properties may exceed the effective range of dispersants (e.g., certain oils may sink and form stable emulsions immediately, decreasing the viability of dispersant use). Despite the general assumptions on dispersibility, on the basis of oil type and characteristics, a variety of studies have evaluated the efficacy of dispersants on viscous and weathered oils (see Martinelli and Cormack, 1979; Lewis et al., 1995; Strøm-Kristiansen et al., 1997; Daling and Strom, 1999; Lessard and DeMarco, 2000). Further, viscous oils have demonstrated degrees of dispersibility under simulated at-sea conditions (Trudel et al., 2011). Oils which are thicker and more viscous (e.g., lower API) are harder to disperse, while oils with low viscosity (e.g., higher API) are easier to disperse (Dillon, 2017a).

ENVIRONMENTAL CONSIDERATIONS FOR DISPERSANT USE

Oil weathering, primarily in the form of evaporation and emulsification, can negatively impact the dispersibility of oil as time passes after a spill. Some oils are prone to forming emulsions (i.e., oil-water mixture), which may be challenging for dispersants to break up and disperse. As oils weather over time and become more viscous, dispersants are considered most effective on oils that have been on the water surface for short periods of time and are less viscous – highlighting the need for timely decision-making processes (API, 2012).

Dispersants should not be used in shallow water, generally defined as less than 10 m (ARPEL, 2007), because the dispersed oil plume may contact sensitive nearshore species and features of the water column and sea-bed, potentially exposing organisms to high concentrations of dispersed oil (EMSA, 2010). As oil within a chemically dispersed oil plume penetrates down through the water column, water depth is a factor which must be considered in dispersant application tradeoff analyses and NEBA (NASEM, 2020).

Water depth and the rate of water exchange allow the dispersed oil to mix and dilute within the water column, further resulting in the formation of smaller oil droplets and dissolution. Mixing energy in the form of breaking or cresting waves has been thought to be required to facilitate the break-up of small droplets from the oil and their transport down into the water column (EMSA, 2010; Huber et al., 2014). However, dispersants in the field have been observed to be effective at lower energy dissipation rates (Huber et al., 2014). Rougher seas and higher wind speeds contribute to more rapid dispersion; however, there is an upper limit as the level of "sheer" mixing energy under high sea state conditions (e.g., storm conditions) will disperse the oil naturally without the addition of dispersants (NASEM, 2020). Under operational guidelines, dispersant spraying is generally deemed ineffective at wind speeds above 25 to 30 knots since the oil would be submerged much of the time (EMSA, 2010). High wind speeds can also increase wind drift, making accurate application of the dispersant to the oil slick difficult. High wind speeds may also limit the approval of flight operations due to wind-related safety concerns.

Most commercially available dispersants are specifically designed to be used in marine conditions with salinity of around 30 to 35 parts per thousand (ITOPF, 2014). While dispersants can be formulated for use in lower salinity waters, recommendations for their use in freshwater systems have been limited due to environmental concerns (e.g., inland waters affected by oil spills may be shallow, may have drinking water intakes, may have reduced circulation, or may have high sediment load (Lehtinen and Vesala, 1984; Payne et al., 1985; Blondina et al., 1999; George-Ares et al., 2001)). Commercial dispersants for fresh or low salinity water do exist, but have not been studied as extensively as marine dispersant formulations (SL Ross, 2010).

Advantages of Dispersants

The selection of an oil spill response measure considers and evaluates the benefits, limitations, operational requirements, and potential adverse impacts of each response option relative to the spill circumstances (Dillon, 2017a)². Prior to the use of a dispersant, a NEBA is conducted to evaluate and balance the tradeoffs associated with its application (Turner et al., 2010). This process requires an in-depth understanding of the relative impacts of spilled oil in the short and long term as well as the probable capabilities, limitations, and consequences of the different response options, including the potential impacts that dispersants may have on the environment to which it is being introduced. For additional information on the NEBA process please see DFO (2014). Despite the operational advantages of dispersants, a NEBA must be conducted to evaluate response options and their likely outcomes on people and the environment, relative to no response measure (Dillon, 2016).

Depending on the spill scenario, and contingent on a NEBA, dispersants may provide advantages over other response options, including physical/mechanical recovery, in-situ burning, and natural attenuation.

The range of environmental conditions under which dispersants can be applied is greater than those for mechanical recovery or in-situ burning operations, in terms of wind speed, wave-height, and oil thickness. Dispersants are the only effective option for spills at sea when slicks have spread very thin (< 0.1 mm) (SpillPrevention.org, 2014a). Dispersants may be a viable response option for larger spills that are far from shore, and far from stockpiles of recovery and containment equipment. While dispersants are generally considered to be most effective on oils that have been on the water for less than 72-96 hours, they can be rapidly applied from aircraft, which can travel to and between spill locations significantly faster than vessels. Arriving at the spill location quicker allows an effective response to start before slicks have a chance to spread, move, or break apart into smaller surface slicks. The effectiveness of dispersants is increased when mixing energy in the form of waves increases, since the greater the mixing energy, the smaller the resulting dispersed oil droplets. It is important to note that "encounter rate", which is the area treated over time, is orders of magnitude larger by aerial application relative to that which can be achieved from a surface vessel. Subsea injection of dispersants can also be used to treat oil releases from a point source (e.g., well blowout) before it reaches the surface and forms a widely spread slick (SpillPrevention.org, 2014a). Subsea dispersant injection (SSDI) has a maximized encounter rate as it applies dispersants directly at the oil release location (NASEM, 2020). Other advantages associated with SSDI are as follows:

- Reduces the need for surface recovery, in-situ burning, and surface dispersant operations, thereby reducing the potential for exposure and accidents during these operations;
- Reduces the potential for volatile organic compounds (VOCs) at surface (Gros et al., 2017);
- Reduces the potential of oil to reach the shoreline (French McCay et al., 2018);
- Large water volume is available for dilution;

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² An understanding of the physical and chemical properties of the spilled oil/hydrocarbon product, the degree of weathering, and the timelines for potential deployment are important for an initial consideration of chemical dispersant suitability and viability as a response option. Specific oil properties to consider include: density (often expressed as API Gravity), degree of weathering, viscosity, pour point, and slick thickness (important for surface application).

- High effectiveness treating fresh unemulsified oil at high turbulence (Brandvik et al., 2016; 2019);
- Injection at one manageable location with control and precision; and
- Can occur during most weather conditions resulting in 24/7 operations (IOGP-IPIECA, 2015).

Furthermore, while cold temperatures may hinder the operational feasibility of certain response options, assessments indicate that colder temperatures do not reduce the dispersibility of many oils or the activity of the dispersant (Brown and Goodman, 1996, Owens and Belore, 2004, Sørstrøm et al., 2010; Faksness et al., 2017). Thus, chemical dispersants are an effective oil spill response option in cold water conditions.

Challenges of Dispersants

Despite the advantages listed above, dispersants have limitations and should only be used when appropriate as determined by a NEBA.

In certain spill scenarios, there may not be a need to add dispersants given the fate and behaviour of the spilled oil and/or the environmental conditions (e.g., oil naturally disperses or evaporates, conditions do not permit).

As noted for all spill response options, a window of opportunity exists for dispersant applications and is contingent on oil weathering, slick thickness, and emulsification. The optimal use of dispersants is on freshly released, light crude oils (refer to Table 2). Dispersants are generally less effective on heavy crude oils and weathered oils with higher viscosities or those which are prone to form emulsions (Walker et al., 2003; ASTM International, 2013).

A common concern is the potential effects of the dispersants and the oil dispersed into the water column on the marine ecosystem. The use of dispersant in nearshore coastal areas, including wetlands or salt marshes, is limited by the presence of shallow water depths and limited wave energy (Lee et al., 2015). In addition, dispersant efficacy is reduced in brackish or freshwater environments as commercially available formulations in the majority of existing stockpiles are manufactured for salt water environments only (ITOPF, 2014).

The potential environmental effects of moving oil from the surface and into the water column for rapid dilution (which can change the exposure mechanisms for aquatic organisms) must be balanced with the consequences of leaving the oil untreated (this balance is the focus of the NEBA). A review of the potential ecotoxicological effects and impacts of dispersed oil on marine aquatic species is provided in subsequent sections of this report.

REGULATORY FRAMEWORK FOR DISPERSANT USE IN CANADA

In Canada, dispersants have been recognized since the 1960s as an effective oil spill counter-measure. Environment Canada's Environmental Emergencies Branch was established in 1972 and adopted "Guidelines on the Use and Acceptability of Oil Spill Dispersants" in 1973 (Environment Canada, 1973).

Under the Canada Oil and Gas Operation Act (the Act), Regulations Establishing a List of Spill-treating Agents were established in 2016. The term "spill treating agent (STA)" applies to a variety of products including dispersants. The deposit of STAs or any deleterious substance into Canadian waters is prohibited under a number of federal environmental statutes, including the Migratory Birds Convention Act, 1994, the Fisheries Act and the ocean disposal provisions of the Canadian Environmental Protection Act, 1999 (CEPA). Specifically, in the event of an oil

spill from an offshore platform, the Act lifts the legal prohibitions (Schedule 1 and 2 of the Act) that would otherwise prevent the use of a STA if:

- The STA is listed in a regulation made by the Minister of the Environment;
- The use of the STA is permitted for use under an authorization received from the relevant Board;
- In response to a spill, the relevant Board's Chief Conservation Officer determines that its
 use is likely to achieve a net environmental benefit in the particular circumstances of the spill
 and approves the use of the STA; and
- The STA is used in accordance with conditions stipulated by the Chief Conservation Officer at the time of the spill.

The STAs listed in the Regulations are Corexit® EC9500A (a dispersant) and Corexit® EC9580A (a surface-washing agent). Corexit® EC9500A, a Type III concentrate dispersant, is the only dispersant approved for use in Canada. Dispersants are not presently regulated for use in Canada for any spill context other than from offshore sources.

FATE AND BEHAVIOUR

PROPERTIES OF OIL THAT INFLUENCE FATE AND TRANSPORT

The laws of physics and chemistry guide the fate, behaviour, and transport of oil, yet oil fate and behaviour are also influenced by the oil type (and its properties), environmental conditions, biological processes, human activities, and time (Daling et al.,1997). The chemical and physical properties of oil will determine how the oil will be altered by environmental processes, including evaporation, aerosolization, photochemical oxidation, dissolution, biodegradation, aggregation, and adhesion (NASEM, 2020).

Chemical characteristics of oil, including the molecular weight of hydrocarbons, the abundance of elements (including nitrogen, sulfur and oxygen), and the relative abundance of saturates, aromatics, resins, and asphaltenes, can influence oil fate and transport (NASEM, 2020). Furthermore, oil properties such as density, volatility, viscosity, and pour point (ITOPF, 2018) are useful to understand how oil may undergo weathering and transport processes.

Oil droplet size is also an important factor governing the fate and behavior of oil in the marine environment (NASEM, 2020). Larger oil droplets are more buoyant and will rise to the surface faster than smaller oil droplets, which are expected to remain in the water column for a longer period of time (CRRC, 2017a). As smaller oil droplets (which have a greater surface area to volume ratio) rise to the surface at a slower rate, they are increasingly able to lose more soluble components and undergo biodegradation during this time, as compared to larger oil droplets, resulting in less VOCs at the water's surface (NASEM, 2020).

OIL FATE

This section describes typical fate processes for spilled oil (collectively referred to as "weathering") and how these processes may be altered by the use of chemical dispersants. It is important to acknowledge that environmental conditions, including (but not limited to) water and air temperature, water depth, presence of ice, mixing energy, and salinity, in conjunction with oil properties and type, can influence the weathering processes of oil (CRRC, 2017a). The review of fate processes presented below focuses on those processes most affected by dispersant use. Certain fate processes that are not relevant to dispersed oil are not addressed herein, but are addressed elsewhere (e.g., Lee et al., 2015; CRRC, 2017a).

Dispersion and Dilution

Oil spilled into the marine environment is generally dispersed and diluted over time (Lee et al., 2013). Contingent on mixing energy, the application of chemical dispersants on oil slicks can also enhance the movement of oil into the water column where it can be further diluted (NRC, 2005).

Evaporation

Evaporation involves the loss of lighter, water soluble, and volatile compounds present within oil after a spill (Stout et al., 2017). Evaporation occurs rapidly and plays a large role in changing the physical and chemical properties of the oil, and can hinder the efficacy of dispersants. Evaporation results in a remaining residue which is thicker, denser, and less soluble than the initially spilled oil. The use of chemical dispersants seeks to disperse the oil into the water column, thereby potentially reducing the evaporation of the volatile oil components into the atmosphere.

Aerosolization

Aerosolization of oil can occur in two different ways. It can occur when waves push air into the surface of the water column, resulting in bubbles. Bubbles then rise through the water column and burst at the surface. Bubbles containing oil compounds may then release these compounds into the atmosphere. A second way in which oil can undergo aerosolization occurs when evaporated compounds from oil oxidize and create secondary organic aerosols (SOAs). Aerosolized compounds from an oil spill can present challenges for air quality in the vicinity of an oil spill (Middlebrook et al., 2012). Natural dispersion of oil at sea has the potential to produce aerosols and is contingent on sea state and other environmental conditions (Deane and Stokes, 2002).

In theory, the use of chemical dispersants aims to disperse the oil into the water column, thereby reducing the formation of aerosols. However, there is also emerging evidence from laboratory studies which indicate that dispersants increase the aerosolization of oil compounds in the presence of breaking waves. The enhanced aerosolization of oil in the presence of dispersants in the laboratory assessments is deemed a function of both the dispersant's ability to disperse oil into the water column and the flotation capacity of oil-containing bubbles (Ehrenhauser et al., 2014; Afshar-Mohajer et al., 2018). The relationship between aerosolization and dispersant use, as well as the fate of any aerosolized droplets, requires validation in real-world scenarios and represents a future research need.

Photomodification

Photomodification is the alteration of oil components by sunlight and can occur via direct and indirect mechanisms, including photodegradation (decomposition caused by sunlight) and photooxidation (oxidation caused by sunlight) (see NRC 2005). When compounds within oil undergo photooxidation, the composition of the oil can change due to the generation of products not present in the initially spilled oil (NRC, 2005; Ward et al., 2018). Photomodification can occur rapidly following an oil spill and may reduce the window of opportunity for effective dispersant application (NASEM, 2020).

The rate of photooxidation is dependent on the amount of incident radiation, which may be affected by weather conditions and the time of year, and on the chemical composition of oil (NASEM, 2020). Furthermore, certain components of oil are more susceptible to photooxidation than others (Yang et al., 2015; Stout and Payne, 2016).

The results of photooxidation are variable depending on the oil spilled and environmental conditions. Based on the literature, photooxidation may contribute to the following (Chapelle, 2001; Wang and Fingas, 2003; NRC 2005; Yang et al., 2015; Lee et al., 2015):

- Potential for increased biodegradation rates due to increased hydrocarbon bioavailability.
- Potential for toxic by-products, especially as a result of polycyclic aromatic hydrocarbon (PAH) compounds undergoing photooxidation and/or photosensitization.
- By-products may include more water soluble products, or tar and gum-like residues, depending on the oil spilled.

Some studies have shown that dispersants may accelerate the photodegradation of oil components (Zhao et al., 2016b; Fu et al., 2017). In a laboratory assessment, Ward et al. (2018) demonstrated that dispersant efficacy was reduced for oil which had undergone photomodification relative to oil which had not been exposed to sunlight.

Dissolution

Oil is made up of many compounds, some of which may be soluble in water. Many factors influence the dissolution (solubility) of oil, including (but not limited to) temperature, salinity, pressure, and chemical and physical properties of the oil (Ryerson et al., 2011; Gros et al., 2017; Jaggi et al., 2017). The primary objective of dispersants is to create smaller droplets with increased surface area thereby promoting dissolution and other processes (e.g., biodegradation) (Atlas and Hazen, 2011; Ryerson et al., 2012; Bagby et al., 2017).

Dissolution is especially important for scenarios where oil is less readily available at the water's surface (e.g., subsea releases, oil release beneath ice) as the same compounds which are increasingly soluble in water can be volatile as well (Gros et al., 2016, 2017; NASEM, 2020). Weathering processes in the water column, including dissolution, can reduce the transfer of volatile oil compounds to the atmosphere (Gros et al., 2017). Dispersants increase the aqueous exposure of oil by increasing the surface area of oil exposed to water, thereby potentially enhancing the dissolution of oil (Reddy et al., 2012; Ryerson et al., 2012; NASEM, 2020).

Emulsification

When seawater and oil mix, water-in-oil emulsions form. Oil types are varied in their ability to form emulsions (please refer to the Oil Types and Dispersant Use Section). The properties of emulsified oil are different from the initial oil released, with the emulsified oil taking on semi-solid physical properties. Emulsified oil is more viscous than the initial oil, making it more difficult to disperse. Emulsification can also reduce the biodegradation rate of oil (Lee et al., 2011a).

The use of chemical dispersants may reduce or prevent water-in-oil emulsions (often referred to as mousse) as it reduces the presence of oil on the sea surface which is where emulsification most commonly occurs due to mixing. One of the purposes of subsurface dispersant injection is to reduce the mixing of oil with water as it rises through the water column, thus reducing emulsification. While chemical dispersants can be used on emulsified oil, they may not be as effective as their application on non-emulsified oil (Belore et al., 2008; NRC, 2014).

Hydrate Formation

Gas hydrates are crystals formed from water and hydrocarbon gases under specific pressure and temperature (Uchida et al., 2020). The formation of gas hydrates is most relevant for deep (> 300 m) subsea releases of hydrocarbons under high pressure and low temperature conditions. The formation of gas hydrates can have an impact on oil fate and transport

processes in the water column (see Johansen et al., 2003; Warzinski et al., 2014). Dispersants are not expected to greatly impact hydrate formation in a subsea spill scenario (NASEM, 2020).

Oil Particle Aggregates

Oil particle aggregates (OPAs) is a broad term that encompasses the interaction of oil with both inorganic and organic material in the environment, and includes oil-mineral aggregates (OMAs) and oil-sediment aggregates (OSAs), among others (Fitzpatrick et al., 2015; Zhao et al., 2016b, 2017). By definition, OPAs are small (20-100 μ m) and dominated by oil residue, alongside inorganic and organic matter (Quigg et al., 2020).

The formation of OPAs impacts the buoyancy of oil droplets, encouraging transport within the water column and sediments via currents (Lee et al., 2003a). The formation of OPAs can enhance dissolution and biodegradation of oil (Lee et al., 1997; Weise et al., 1999; Khelifa et al., 2002; Aveyard et al., 2003; Ajijolaiya et al., 2006; Gong et al., 2014). A positive relationship exists between the formation of OPAs and oil dispersion. First, the formation of OPAs enhances oil dispersion (Lee, 2002; Owens and Lee, 2003). Concurrently, the fragmentation of oil into smaller droplets through dispersion (natural or chemical) more readily supports the formation of OPAs (Gong et al., 2014; Gustitus et al., 2017). The literature indicates that the use of chemical dispersants is synergistic with OMA and OPA dispersion (Li et al., 2007; Khelifa et al., 2008; Wang et al., 2013).

The use of dispersants promotes the formation of smaller oil droplets which are more prone to the formation of OPAs (Quigg et al., 2020), which may result in enhanced dissolution and biodegradation of oil components.

Marine Oil Snow

Marine oil snow is a term used to describe the aggregate of oil with organic matter (e.g., bacteria, phytoplankton) (Passow et al., 2012; Fu et al., 2014; Daly et al., 2016; Passow and Ziervogel, 2016). Marine snow occurs naturally in the ocean due to the continuous shower of mostly organic detritus falling from the upper layers of the water column (Alldredge, 2001). Marine oil snow is formed when oil components (hydrocarbons) sorb to organic particles, or become caught in marine snow matrices (Wirth et al., 2018). By definition, in comparison to OPAs (oil-particle aggregates) marine oil snow is larger in size (>0.5 mm) and is dominated by organic particles (Daly et al., 2016; Passow and Ziervogel, 2016; Quigg et al., 2020).

In the aftermath of the Deepwater Horizon spill, marine oil snow was observed. It was hypothesized that marine oil snow was trapping additional particles and organic matter through a process called Marine Oil Snow Sedimentation and Flocculent Accumulation (MOSSFA) (Passow et al., 2012; White et al., 2012; Montagna et al., 2013; Kinner et al., 2014; Romero et al., 2015). This process led to increased sediment accumulation rates following the DWH spill (Brooks et al., 2015). Assessments following DWH also indicated that marine oil snow formation appears to be influenced by plankton dynamics, nutrients, and suspended minerals in the water column (Daly et al., 2016). Uncertainties exist for the relationship between chemical dispersants, the MOSSFA process, and the formation of marine snow (Passow et al., 2017). The significance of laboratory studies reporting a positive relationship between dispersants and marine snow formation has been questioned on the basis of the relevance of experimental conditions used relative to those likely to be encountered in the field during actual response operations (Lee et al., 2013; Prince et al., 2016; Brakstad et al., 2018). It currently appears that dispersants may increase or decrease the likelihood of a marine oil snow event following a spill depending on the environmental conditions and type/degree of weathering of the oil.

Dispersants may support the formation of marine snow and the transport of oil to ocean depths; further studies are ongoing to validate and assess the ecological significance of this phenomenon under real-world conditions (NASEM, 2020).

Biodegradation

Oil mixtures represent sources of energy for microbial communities (Prince et al., 2016). Aerobic biodegradation is expected to occur rapidly in real-world oil spill scenarios as oil naturally disperses and dilutes and is subsequently degraded by microbes (Brakstad et al., 2014). In order for biodegradation to occur, oil compounds need to encounter microbial consumers in the marine environment. Biodegradation of oil compounds can occur when compounds are in the aqueous phase or at the oil-water interface, making dissolved and dispersed fractions of the oil most susceptible to biodegradation (CRRC, 2017a; Brakstad et al., 2018).

Biodegradation rates are dependent on a variety of environmental and ecological factors. Microbial community structures are variable in marine environments across geographies (CRRC, 2017a), but oil degrading microbes are widespread globally and include bacteria, methanogenic archaea, and fungi (Head et al., 2003; 2006). Microbes capable of degrading oil have evolved and adapted over time in response to naturally occurring oil seeps (Atlas, 1995).

Temperature and water depth are two key factors related to biodegradation in the marine environment, as these factors influence the viability of microbial communities (CRRC, 2017a). Temperature is an especially important environmental condition related to biodegradation. Optimal temperatures for hydrocarbon degradation rates in the marine environment are in the range of 15–20 degrees Celsius (°C) (Das and Chandran, 2011). However, Hazen et al. (2010) measured biodegradation half-lives of n-alkanes of a few days in the dilute (2–442 parts per billion (ppb)) dispersed submarine plume from the Deepwater Horizon at 1100–1220 m and 5 °C. Cold water microbial communities, including those of the Arctic, have demonstrated similar biodegrading capacities as microbial communities residing in temperate seawater environments (Brakstad and Bonaunet, 2006; Brakstad et al., 2014; McFarlin et al., 2014).

Studies by Stewart and Marks (1978) and Yeung et al. (2015) demonstrated the widespread presence of oil-degrading microbes throughout water and sediment of the eastern coast of Canada, and Greer et al. (2014) described microbial communities capable of degrading oil in seawater and ice of the Canadian Arctic. To determine the significance of natural attenuation, the rates for oil degradation have been quantified for indigenous microbial communities in the Pacific and Atlantic Ocean waters of Canada (Tremblay et al., 2017; 2019).

The ability of dispersants to fragment oil into smaller droplets enables a greater amount of surface area for microbial colonization and supports biodegradation (Brakstad et al., 2014, Prince and Butler, 2014; Prince et al., 2016; Ribicic et al., 2018). In a laboratory assessment, the addition of a dispersant enhanced crude oil degradation rates in simulated conditions of near-surface seawater from the vicinity of crude oil and natural gas production facilities off Eastern Canada (Tremblay et al., 2017).

Dispersant formulations have also been shown to enhance biodegradation by serving as a food source for microbial communities (Lee et al., 1985; Varadaraj et al., 1995). In addition, the formation of OPAs enhances the biodegradation of oil – and dispersant applications support the formation of OPAs (Lee et al., 1997; Weise et al., 1999; Khelifa et al., 2002; Aveyard et al., 2003; Ajijolaiya et al., 2006; Gong et al., 2014).

The impact of chemical dispersants on biodegradation rates in laboratory assessments have elucidated variable results (Macnaughton et al., 2003; Kleindienest et al., 2015). The

discrepancies between the real world scenario outcomes and those determined in the laboratory are generally attributed to study design and laboratory methods which do not represent the realities of real world scenarios, particularly relating to oil concentrations and oil dilution (Lee et al., 2013; Prince et al., 2016).

The Relationship Between Weathering Processes and Chemical Dispersants

As noted in the Environmental Considerations for Dispersant Use Section, oil weathering processes can reduce dispersant effectiveness – operationally defined as the amount of oil transferred into the water column relative to that remaining on the surface. The efficacy of dispersant use in the event of an oil spill is reliant on a variety of factors, including oil composition, energy dissipation rate, oil weathering, type and amount of dispersant applied, temperature, and salinity of water (Chen et al., 2012). For example, as oil weathers, the viscosity of the oil increases, making it more difficult to chemically disperse. Generally speaking, the evaporation of volatile oil components results in an oil residue with higher viscosity, lower solubility, and a higher density, which is more difficult to disperse. Depending on the oil type, weathered oil may also form emulsions which are also difficult to chemically disperse. Based on reviewed evidence, dispersants may enhance oil dispersion, dilution, dissolution, photooxidation, biodegradation, the formation of oil-particle aggregates, and the formation of marine oil snow. On the other hand, by facilitating the transport of oil into the water column, dispersants may reduce evaporation and perhaps aerosolization of oil from the surface.

OIL TRANSPORT AND DISPERSANT USE

Surface Release

In the event of a surface release of oil, a slick or sheen will form on the surface of the water column. The unique characteristics and behavior of this slick depend on the type of oil released and the environmental conditions. Generally, oil will undergo natural dispersion and break up into smaller droplets of oil through wave energy and mixing. Smaller oil droplets will move from the water's surface and become entrained in the water column through wave energy, turbulence, and Langmuir circulation (NASEM, 2020). The application (spraying) of dispersants onto surface oil slicks from surface vessels and/or aircraft enhances the natural dispersion of oil, facilitating its transport from the sea-surface into the water column. Dispersants on the surface of oil droplets promote tip-streaming, which is the formation of microthreads due to the deformation of droplets from shear stress as they move through the water column, resulting in the formation of microdroplets (Zhao et al., 2017). While this reduces the presence of oil on the water's surface, it increases the concentration of oil in the water column. This can result in an increase in soluble oil components in the upper water column (CRRC, 2017b). Dispersed oil will undergo vertical and horizontal transportation in the water column as a result of waves, wind, and ocean currents (USGAO, 2012). Horizontal mixing is more significant than vertical mixing in ocean waters and can have implications for the transport of dispersed oil (CRRC, 2017b). The specific transport of dispersed oil as a result of surface dispersant use is highly dependent on the environmental conditions of the release location (CRRC, 2017b).

Subsurface Release

A subsea release of oil immediately causes oil to rise in the water column and creates a plume from the source up to the surface. As the plume of 'live oil' (a mixture of gas and oil components) rises through the water column, lower molecular weight oil components (e.g., <C10) dissolve into the seawater. SSDI serves as a delivery mechanism for dispersants directly in the water column. As observed during Deepwater Horizon, following SSDI, a lateral intrusion

layer may form in the water column whereby oil droplets (depending on droplet size) and dissolved gases become entrained and transported by underwater currents. The lateral intrusion layer can trap oil droplets and dissolved oil, reducing the potential for oil to reach the sea surface (NASEM, 2020). Environmental conditions, including currents, temperature, salinity, and depth, coupled with the oil type released and the pressure of the release, influence plume behavior and formation (USGAO, 2012).

SSDI was used in an oil spill response operation for the first time following the 2010 DWH spill. In contrast to the surface application of dispersants over a large area of a slick, subsea application of dispersants is focused at the release point of the oil where turbulence from the jet of oil and gas released can assist in the formation of a large range of oil droplet and gas bubbles (NASEM, 2020). Current research also indicates that SSDI effectiveness is not dependent on water pressure (at depth) (Brandvik et al., 2016; 2019). The encounter rate between oil and dispersant is higher for SSDI compared to aerial application on a surface oil slick, as the dispersant is applied directly to the oil stream at its point of release. SSDI can thus use a lower dispersant to oil ratio (DOR) than surface oil applications (a DOR of 1:100 has been demonstrated to be effective in the laboratory). SSDI is intended to reduce the droplet size and delay and/or arrest the ascent of the oil droplets, which facilitates biodegradation and reduces the extent of surface slicks.

Models and experiments show that the application of dispersants to a subsea oil release reduces the size of the oil droplets by 5–10 times (NASEM, 2020). Chemically dispersed oil in a subsea release is less likely to form into slicks on the water's surface due to smaller oil droplet sizes and the slow rise rates of smaller droplets in the water column, which become dispersed over a wider area (USGAO, 2012). For example, horizontal separation of dispersed oil in the water column may occur if a cross current is present (CRRC, 2017b). The increased residency of oil droplets during their vertical rise in the water column also provides a longer opportunity for weathering processes to occur, including (but not limited to) biodegradation, dissolution, and the formation of marine oil snow.

During the DWH response, measured dispersed oil concentrations were consistently below 5 ppm at a distance of 1 km from the wellhead (Coelho et al., 2011). The trajectory of the rising oil from SSDI is influenced by the ocean currents as well as the buoyancy of the dispersed oil droplets. An advantage of SSDI over surface operations is that it can be applied in almost any weather condition, operate 24 hours a day, use less dispersants, and can reduce operational requirements (including personnel and equipment). Gros et al. (2017) also reported that SSDI likely reduces the potential for responder exposure to hydrocarbon vapors at the surface.

A recent Comparative Risk Assessment concluded that SSDI resulted in a measurable decrease in the extent of surface slicks and shoreline oiling, increased biodegradation of oil at depth, and decreased VOC emissions to the atmosphere (French McCay et al., 2018).

COLD WATER ENVIRONMENTAL CONSIDERATIONS

The characteristics of cold water environments (inclusive of Arctic and subarctic regions), including lower air temperatures and the presence of ice, can influence the fate and behavior of oil (NRC, 2014). Collectively, cold water environment characteristics can influence the physical properties of oil, potentially resulting in an increase in the viscosity of oil and a diminished spread of oil, resulting in smaller contaminated areas (NRC, 2014). Pour point, the temperature by which liquid loses flow characteristics, may be more of an issue in cold temperatures, depending on the oil properties. Oil is less likely to evaporate, disperse, and emulsify when contained within ice which can lead to prolonged persistence of oil in the environment (NRC, 2014). This reduction in the weathering rate of the oil may extend the window of opportunity for

dispersant use (Brandvik and Faksness, 2009). Ice can behave as a natural barrier to oil transport and spread, reducing the likelihood that oil spilled offshore will reach shoreline environments. Ultimately, coldwater hydrodynamics can play an important role in the dispersion of oil.

In terms of dispersant use, both fresh and weathered Alaskan North Slope (ANS) crude oil has been demonstrated to disperse with Corexit 9500 and 9527 under cold water environmental conditions (Belore et al., 2009; Trudel et al., 2010). While extreme environmental conditions (short daylight hours, freezing temperatures, etc.) may reduce the operational feasibility of applying dispersants in remote areas of the Arctic, assessments indicate that colder temperatures do not reduce the dispersibility of many oils or the activity of the dispersant (Brown and Goodman, 1996; Owens and Belore, 2004; Sørstrøm et al., 2010; Faksness et al., 2017). While the presence of ice can reduce the efficiency of oil dispersant application on surface oil, due to its action as a natural boom to impede wave energy and mixing in cold water environments, there is evidence that small pieces of ice may also contribute to mixing and the dispersion process (Owens and Belore, 2004; Brandvik et al., 2010). Furthermore, field studies in the Arctic have validated the use of propeller wash from a vessel to provide the levels of mixing energy required for dispersant use (Daling et al., 2009). Studies have also indicated that icebreakers can effectively enhance the treatment of oil located in leads between ice floes, and on top of and beneath solid ice (Spring et al., 2006, Nedwed et al., 2007).

SUMMARY: HOW DISPERSANT USE INFLUENCES FATE AND BEHAVIOUR OF OIL

The application of dispersants on surface oil slicks facilitates the transport of oil from the surface of the water to the water column while simultaneously diluting oil – making it more readily available for microbial degradation (Lee et al., 2015). In terms of environmental protection, this reduces the risk of oil reaching nearshore coastal areas, marshes, estuaries, and shorelines and also reduces oil exposure for surface and subsurface dwelling species (additional details in subsequent sections) (Lee et al., 2015). While dispersants do not remove oil from the environment, they change its chemical and physical properties which then alter its transport, fate, and potential effects (NRC, 2005).

The concentration of dispersant associated with oil will change over time. There appear to be the following general scenarios affecting dispersant association and disassociation from oil: shedding of dispersants due to shear (i.e., tip-streaming); leaching of surfactant molecules from oil droplets; surface retention in oil slicks; and retention in ice. The specific mechanisms governing dispersant losses from dispersed oil are not well understood and additional research would be beneficial.

Subsea injection of dispersants seeks to expedite the dispersion and breakup of oil into smaller droplets at the source of a release. The increased surface area of smaller oil droplets, coupled with a longer residency in the water column, may also support increased biodegradation (NASEM, 2020). The subsea injection of dispersants can result in immediate dilution of the dispersant in the water column, with some of the dispersant remaining in the water column (e.g., intrusion layers) or held in sediments (NASEM, 2020). Dispersant use in the event of a subsea release enables currents to potentially transport oil droplets away from the release location (NASEM, 2020). The slow rise of smaller oil droplets as a result of dispersant use lends to a spatial dilution of the oil plume when it reaches the surface and a reduction in levels of VOCs (NASEM, 2020).

A summary of the fate, behavior, and transport characteristics of dispersed and non-dispersed oil is presented in Table 3.

Table 3: Summary of fate and behavior of oil with and without chemical dispersants.

Oil	Chemically dispersed oil
Slick on the surface Potential for weathering processes (e.g., natural dispersion, dissolution, dilution, evaporation,	Less oil at water surface as oil is transported from the surface into the water column or maintained in the water column (SSDI)
volatilization, aerosolization, biodegradation, formation of oil-particulate aggregates, and marine snow formation)	Increased rates of dispersion, dissolution, dilution, biodegradation, and oil particulate aggregate formations
Transport of oil mostly via wind, water currents, and wave energy	May increase the rates of aerosolization, marine oil snow formation, and photooxidation
Greater potential to impact species dwelling at or	Decreased evaporation
utilizing water surface Greater potential to migrate to and impact beaches, shorelines, coastlines, and nearshore sediments Potential for transport to sediments via MOSSFA	Transport of dispersed oil mostly via prevailing currents
	Potential for transport of oil to sediments via MOSSFA
	Greater potential to impact species that inhabit the water column (pelagic)
	Less potential to impact surface dwelling species
	Less potential to migrate to and impact vulnerable beaches, shorelines, and coastlines

PATHWAYS OF EFFECTS, BIOLOGICAL COMPONENTS OF CONCERN AND PATHWAYS OF EXPOSURE

Within DFO programs, pathways of effects (PoEs) are conceptual models that represent cause-and-effect relationships between human activities, their associated stressors, and their impacts (O et al., 2015; Hannah et al., 2020). PoEs are key features of DFO's ecological risk assessment framework (ERAF), as described in O et al., (2015). The ERAF notes that three categories of PoE models are under development within DFO programs but all consist of two principal components: a diagram that illustrates the relationships between human activities, stressors, and impacts on ecological components, and a supporting document that describes the predicted relationships among those elements along with the rationale and sources of information used for their selection (Government of Canada, 2012). Hannah et al., (2020) note that PoE models are primarily used in a scoping phase, prior to undertaking more comprehensive types of assessments such as ecological risk assessment, environmental impact assessment, and cumulative effects assessment, as the PoEs describe the potential stressors and effects that could be considered in such assessments, but do not include an assessment of relative or absolute impact, magnitude of change, or risk. Thus, in the context of understanding the effects of dispersed oil on marine biota. PoE models may best be used to provide initial direction to more comprehensive and/or location-specific types of studies.

With respect to PoE models, it is important to note the distinction between definitions of effect and impact that are common to DFO PoE development work. This work uses the definitions provided by Boehlert and Gill (2010), wherein: **effects** include "the broad range of potentially measurable changes that may be observed", while **impacts** are "effects that, with some certainty, rise to the level of deleterious ecological significance". In other words, effects are changes, while impacts are effects or changes that are adverse in their consequences. Thus,

while PoE models can describe how certain effects can potentially manifest from stressors, they do not determine if such effects are significant enough to become impacts. That determination occurs within risk or impact assessment studies. However, PoE models may initially inform such studies.

The development of PoE models for dispersed oil effects is not within the current scope of work but would be useful in providing direction to the development of assessment and monitoring tools and approaches that further the understanding of the effects and impacts of dispersed oil on marine biota. Following the current Canadian Science Advisory Secretariat (CSAS) process and state of knowledge review, sufficient information may exist to develop PoE models for dispersed oil in marine ecosystems. In addition, once developed, PoE models could be used to help inform the NEBA process, wherein they may improve understanding of the potential relationships or linkages between dispersed oil and effects or impacts on marine ecological/biological components and marine resources.

PoEs are not a term or concept that is used in standard chemical stressor ecological risk assessment (ERA) approaches that are applied to aquatic ecosystems (such as: Environment Canada, 2012 (and subsequent ERA guidance); CCME, 2020; Chapman, 2011; COA, 2008; Suter, 2007; U.S. EPA, 1998). As noted though, PoEs are a key feature of the DFO ERAF described in O et al., (2015). In terms of methodologies and tools, the ERAF (and the approaches upon which it is based) is quite different than the ERA approaches used to assess chemical exposures. The ERAF is primarily a qualitative scoring and ranking approach based on hypothetical exposure and consequence determinations for stressors and associated effects. In comparison, the ERA approach integrates estimates of chemical exposures in environmental media and biota with estimates of toxicity to identified biological components of interest.

Key concepts from chemical and contaminated aquatic site ERA that pertain to identifying receptors of concern (ROCs) and exposure pathways of concern, offer a useful frame of reference towards understanding the potential effects and impacts that relate to dispersed oil and marine biota (as summarized in subsequent sections herein). Prior to identifying potential effects and/or impacts of dispersed oil on marine biota, it is important to first determine the key marine biological components of concern (i.e., receptors), along with the means by which these biological components may come into contact with dispersed oil (i.e., exposure pathways). The potential effects and impacts of dispersed oil on marine biota, and their ecological relevance, are addressed in the Impacts Section.

IDENTIFICATION OF BIOLOGICAL COMPONENTS (RECEPTORS OF CONCERN)

In ERAs of chemical contamination, ROCs is the term used to describe the "key biological components" of the ecosystem that may be affected by chemical exposure and that may warrant assessment to determine if impacts will occur. For consistency with standard ERA terminology, ROCs is the term used herein to refer to key marine biological components of concern.

ROCs can be identified at many different levels of biological organization and potentially include individual organisms, species, populations, communities, habitats, or ecosystems (Environment Canada, 2012). The level of biological organization that applies to a given ROC links closely to, or aligns with, the desired ecological protection goals for the ROCs. For example, if the protection goal is to have a diverse benthic community that maintains ecological structure and function, then benthic invertebrates would be assessed at a community level of biological organization. For lower trophic level ROCs, such as benthic invertebrates, phytoplankton, zooplankton, and most fish and shellfish, the level of biological organization that is evaluated is generally community level (Environment Canada, 2012; Suter et al., 2000). The community level

is also considered the relevant level of biological organization when a ROC has limited ecotoxicity data available for the chemicals of interest. For higher trophic level receptors (typically birds and mammals), ROCs are usually evaluated at the population level³ of biological organization. Specific bird or mammal species are typically assessed as surrogates that represent a given avian or mammalian feeding guild or ecological niche. Individual organisms would be evaluated only if the ROCs are rare, threatened, or endangered species (Environment Canada, 2012).

In the context of dispersed oil impacts in the marine environment, most ROCs would be assessed at a population or community level, unless there are known to be species at risk present within an area of impact.

Consideration of potential ROCs is inherently site- or study area-specific and reflects an understanding of the specific ecological attributes of the area of interest. In ERA, numerous considerations are involved when identifying ROCs. For the scenario of a dispersed oil plume in the marine environment, key considerations related to identifying ROCs would include the following:

- General marine habitat type and habitat conditions of the impacted area. For example:
 - Open ocean.
 - o Estuary.
 - Coastal zone.
 - Salt marsh.
 - o Embayments such as bays, harbours, inlets, intertidal, and subtidal.
 - o Substrate conditions (hard versus soft bottom).
 - o Etc.

• The hydrodynamics of the marine impacted area (e.g., waves, currents, sea energy, wind energy, tides, and water depth).

- Known marine species inventories or surveys for the impacted area, including any existing studies of sensitive or vulnerable species (vulnerability assessments), species at risk, and/or resources at risk (i.e., RARs, which may include locations of resources that are of archaeo-cultural or socioeconomic importance, in addition to resource locations that are of ecological importance).
- Representation from the various trophic levels, habitats, and feeding guilds that are appropriate for the impacted area.
- Species that may provide critical habitat for other species (e.g., eelgrass beds or kelp forests).
- Data regarding the behavioural, physiological and life history characteristics of the potentially impacted biota that would increase or decrease the potential for exposure to dispersed oil. For example:
 - o Dietary and habitat preferences.
 - Habitat use characteristics.

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³ The definition of a "population" can vary greatly. In general, a population is a group of individuals of the same species that live together and breed amongst each other. Setting numerical limits on the number of individuals that comprise a population is inherently difficult and would vary greatly depending on the species and its life history characteristics.

- o Feeding behaviours/strategies.
- o Foraging/breeding ranges or locations.
- Reproductive strategies/modes.
- o Mobility.
- o Body weights.
- o Time likely spent in impacted area relative to other areas.
- Migratory versus transient versus resident biota unique behaviours related to grooming and foraging).
- The physical-chemical, environmental fate/behaviour, and toxicological properties of dispersed oil, including:
 - o The persistence of chemicals present within dispersed oil mixtures.
 - The potential for dispersed oil chemicals to bioaccumulate and/or biomagnify in marine aquatic food webs.
 - Any known sensitivity of certain marine species to chemicals present within dispersed oil mixtures).
- Availability of reliable marine ecotoxicological data on dispersed oil for the potentially impacted marine biota.
- Socioeconomic considerations (e.g., are commercially important or otherwise valued marine species present within the impacted area?).

Ultimately, the marine ROCs that would be identified in relation to dispersed oil impacts are those that are known or expected to occur within the impacted area, have a high potential to come into contact with dispersed oil (high exposure potential), and/or have a known sensitivity to the chemicals present within dispersed oil. ROCs that meet these general conditions have a greater likelihood to experience adverse effects relative to those that are less exposed or less sensitive.

As the characteristics of a dispersed oil plume may change quickly within a short period of time, the identification of ROCs should be flexible, iterative, and account for temporal and spatial factors that may affect the significance or sensitivity of certain ROCs relative to others.

The following broad categories of marine ROCs are of potential concern in relation to dispersed oil impacts on marine biota, and represent the main trophic levels within the marine food web. These categories are primarily based upon ROC identification considerations in ERA, NEBA, and Spill Impact Mitigation Assessment (SIMA). The categories presented below also reflect (in part) the grouping and subgrouping of marine biological components from Thornborough et al. (2017) (level 1 and 2 groupings and subgroupings), Hannah et al. (2017), and the valued ecosystem components (VECs) described in O et al. (2015).

- Microbial communities (pelagic and benthic);
- Phytoplankton;
- Algae/kelp (pelagic, benthic, attached to hard surfaces);
- Macrophytes and other marine vegetation (benthic vascular and non-vascular);
- Zooplankton (pelagic);
- Planktonic life stages (eggs, larvae) for fish and invertebrate species (meroplankton);
- Pelagic macroinvertebrates (including cnidarians, mollusks, crustaceans);

- Benthic invertebrates (rock/rubble-dwelling, infaunal and epifaunal, including macroinvertebrates);
- Finfish (pelagic, demersal, semi-demersal, sediment-dwelling);
- Marine birds;
- Marine mammals (including toothed and baleen whales (cetaceans), pinnipeds, and mustelids); and
- Marine reptiles (turtles).

Further subgrouping and categorization is certainly possible if necessary, as these categories are general, and broadly applicable to most locations in Canadian waters. Modifications to the categories and any associated grouping or sub-grouping scheme would be specific to the locations of oil spills and the spatial and temporal boundaries of dispersed oil plumes. Depending on the specific dispersed oil impact scenario, further subgrouping and categorization of ROCs could also consider (or further consider) feeding guilds, feeding strategies, reproductive strategies, migration patterns (diel, seasonal), and behavioural stressor response strategies (e.g., avoidance, burial, shell closure).

IDENTIFICATION OF EXPOSURE PATHWAYS TO DISPERSED OIL FOR KEY RECEPTORS OF CONCERN

The means by which an organism comes into contact with a chemical in an environmental medium are referred to as exposure pathways. The means by which a chemical enters the organism from the environmental medium are referred to as exposure routes. The potential for adverse health effects to occur as a result of exposure to chemicals, in any medium, is directly related to the exposure pathways. If there is no possible pathway of exposure to a chemical, regardless of its toxic potency or its concentration within a given medium, there is no potential for the development of adverse health effects from that chemical. Thus, if there are no possible exposure pathways that link marine ROCs to chemicals in dispersed oil, there can be no potential for adverse effects from those chemicals.

Table 4 describes the most likely exposure pathways and routes for the marine ROCs that may come into contact with dispersed oil. The relative significance of these exposure pathways and routes will vary substantially across the species that are represented by the ROC groupings. It should be recognized that the exposure pathways between marine biota and dispersed oil are the same as the pathways that exist between marine biota and non-dispersed (untreated) oil. However, the use of chemical dispersants may alter the relative significance and magnitude of the main exposure pathways when compared to a scenario of marine biota exposure to untreated oil.

Table 4: Main Exposure Pathways and Routes that Link Untreated Oil and Dispersed Oil to Marine Receptors of Concern.

Receptor Group	Main Exposure Pathways and Routes
Microbial communities (pelagic and benthic)	Direct absorption across cell membranes from direct sea water, sediment, droplet contact (during microbial respiration, decomposition and other microbial processes)

Receptor Group	Main Exposure Pathways and Routes
Phytoplankton and algae (pelagic and benthic)	Direct absorption across cell membranes/cell walls from direct sea water, sediment, droplet contact
Macrophytes and other marine vegetation (benthic vascular and non-vascular)	Direct absorption across cell membranes/cell walls in foliar tissues from direct sea water, porewater sediment, droplet contact; root uptake from sediments and sediment porewater
Zooplankton (pelagic)	Direct absorption across cell membranes from direct sea water, sediment, droplet contact; food/prey/water/detritus/droplet ingestion; direct contact of gills and other respiratory surfaces with water and sediment
Planktonic life stages (eggs, larvae) for fish and invertebrate species (meroplankton)	Direct uptake and/or absorption across membrane surfaces from direct sea water, sediment, droplet contact; food/prey/water/detritus/droplet ingestion; direct contact of gills and other respiratory surfaces with water and sediment; uptake via the micropyle during and shortly after fertilization
Pelagic macroinvertebrates (including cnidarians, mollusks, crustaceans)	Direct uptake and/or absorption across membrane surfaces from direct sea water, sediment, droplet contact; food/prey/water/detritus/droplet ingestion; filter-feeding of sea water; respiration via gills or other respiratory surfaces
Benthic invertebrates (rock/rubble-dwelling, infaunal and epifaunal, including macroinvertebrates; includes such benthic organisms as: bivalves, other molluscs, crustaceans, worms, echinoderms, cnidarians, poriferans, corals and ascids)	Filter-feeding of sea water; sediment/water/food/ prey/detritus/droplet ingestion; respiration via gills or other respiratory surfaces; sediment porewater ingestion; direct sediment/seawater/pore water contact; uptake via the micropyle during and shortly after fertilization
Finfish (pelagic, demersal, semi-demersal, sediment-dwelling)	Respiration via gills; dermal contact with sea water, sediment, droplets; food/prey/water/detritus/droplet/sediment ingestion
Marine birds	Feather and dermal contact (including adhesion) with dispersed oil droplets, as well as impacted water and sediments; ingestion of dispersed oil via preening behavior; food/prey/water/droplet ingestion; inhalation of aerosols and volatile substances present in dispersed oil; aspiration of dispersed oil at water surface; incidental sea water and sediment ingestion; or oil transfer from feathers to developing eggs
Marine mammals (including toothed and baleen whales (cetaceans), pinnipeds, and mustelids)	Dermal and/or fur contact (including adhesion) with dispersed oil droplets, water, sediment;

Receptor Group	Main Exposure Pathways and Routes
	ingestion of dispersed oil via preening/grooming behavior; food/prey/water/droplet ingestion; inhalation of aerosols and volatile substances present in dispersed oil; aspiration of dispersed oil at water surface; incidental sea water and sediment ingestion
	Marine mammal species with smoother skin are less likely to experience dermal adhesion of dispersed oil relative to species that are rougher-skinned, furred, or lacking blubber layers (Engelhardt 1983; Lee et al., 2015).
Marine reptiles (turtles)	Dermal contact (including adhesion) with dispersed oil droplets and impacted water and sediments; food/prey/water/droplet ingestion; inhalation of aerosols and volatile substances present in dispersed oil; aspiration of dispersed oil at water surface

Sources: <u>U.S. EPA Ecobox</u>; Suter II, 2007; Schoof, 2003; Environment Canada, 2012; BC SAB, 2008; Hannah et al, 2017; Thornborough et al., 2017; Boehm and Page, 2007; Dupuis and Ucan-Marin, 2015; IPIECA, 2016a,b; Lee et al., 2015; Rosenberger et al., 2017; NASEM, 2020; Harris et al., 2011; Geraci and St Aubin, 1988; Law et al., 2011; Hook et al., 2016; Engelhardt, 1983; NOAA, 2019; 2020.

In general, the direct absorption of oil substances across cell membranes in many types of ROCs is facilitated by the lipophilic/hydrophobic properties of the substances within both untreated oil and dispersed oil, and the fact that cell membranes are composed of lipid-rich structures.

For many marine vertebrate and invertebrate species, there is a potential that some substances present in chemically dispersed (and untreated) oil (particularly lipophilic substances with a tendency to bioaccumulate in the parent organism) may transfer to eggs or embryos, depending on the reproductive strategy that is employed.

HOW CHEMICAL DISPERSANTS AFFECT POTENTIAL EXPOSURE PATHWAYS BETWEEN DISPERSED OIL SUBSTANCES AND RECEPTORS OF CONCERN

Exposure pathways between marine biota and dispersed oil are the same as the pathways that exist between non-dispersed oil. However, the use of chemical dispersants may alter the relative significance and magnitude of the main exposure pathways when compared to a scenario of marine biota exposure to non-dispersed oil.

In comparison to non-dispersed oil plumes or slicks, the use of chemical dispersants would be expected to result in relatively higher amounts of oil droplets (and dissolved or water-accommodated oil-associated substances) in the water column and relatively lower amounts of oil at the water surface. Dispersant use may also enhance or increase the formation of oil particle aggregates and marine oil snow which mediate the transport of oil-associated substances from the water column to the sediment (NASEM, 2020; Daly et al., 2016). This fate process may be most significant in the case of a sustained subsea oil release, and subsea dispersant application scenario (NASEM, 2020).

Dispersants will also result in a generally larger spatial extent of oil plumes relative to non-dispersed oil plumes or slicks, although the concentrations of oil droplets and oil-associated substances are typically lower in a dispersed oil plume than in a non-dispersed oil plume.

In general, chemically dispersed oil (relative to non-dispersed oil) would be expected to affect exposure pathways between oil-associated substances and marine biota in the following ways:

- A reduced significance and/or magnitude of exposure pathways related to contact with oil-associated substances at water surface. This would be expected to include:
 - o A reduced significance of the volatile substance inhalation pathway;
 - A reduced significance of the oil aspiration pathway;
 - o A reduced significance of the dermal contact and dermal adhesion pathways;
 - A reduced significance of bird and mammal oil ingestion pathways related to preening and grooming behaviors.
- A potentially increased significance and/or magnitude of exposure pathways related to water column exposure of pelagic organisms or life stages to dissolved and water-accommodated oil substances, and oil droplets. This would be expected to include:
 - An increased significance of dermal or membrane direct contact with impacted seawater pathways as well as dermal/membrane contact with droplets;
 - o An increased significance of the gill/other respiratory surface respiration pathway;
 - An increased significance of the pelagic food/prey/water/detritus/droplet ingestion pathways;
 - o An increased significance of filter-feeding pathways.
- A potentially increased significance and/or magnitude of exposure pathways related to sediment exposure of demersal and benthic organisms or life stages to sediment and/or pore water-associated oil substances, and oil droplets. However, this would only be the case if conditions supported marine oil snow formation and relatively high rates of settling onto marine sediments. This would be expected to include:
 - An increased significance of dermal or membrane direct contact with impacted sediment and pore water pathways, as well as dermal/membrane contact with droplets;
 - An increased significance of the prey/sediment/pore water/droplet/detritus ingestion pathways;
 - An increased significance of sediment to macrophyte root uptake pathways (if marine snow deposition occurs in shallow enough water for macrophytes to be present);
 - o An increased significance of benthic filter-feeding pathways.
 - There may also be an increased significance and/or magnitude of ingestion-based exposure pathways for diving mammals and birds that feed on benthic organisms.

It must be recognized that dispersant-induced alterations to exposure pathways between marine biota and oil-associated substances may be numerous and highly variable, and greatly dependent on numerous complex and interrelated factors related to the marine biophysical conditions, marine habitat characteristics, marine hydrodynamics, the nature/type of oil spilled, and changes in its potential bioavailability. Dispersant effects on the bioavailability of oil-associated substances are addressed in the Impacts Section.

With respect to inhalation exposure pathways for marine mammals, birds, and reptiles, how dispersant application to oil affects aerosol formation is not well understood. Because dispersants cause oil to enter the water column, it would be expected that surface oil and aerosol formation potential would be reduced relative to non-dispersed oil. However, some laboratory studies indicate that dispersants may temporarily increase the aerosolization of oil

substances, which may lead to a subsequent increase in the significance of inhalation exposure pathways during the period(s) of time when aerosol formation is occurring (e.g., Ehrenhauser et al., 2014; Afshar-Mohajer et al., 2019; Sampath et al., 2019; Afshar-Mohajer et al., 2020).

The ecological relevance of the ways by which dispersants may alter the relative significance and magnitude of exposure pathways between marine biota and oil-associated substances is not well understood. Nonetheless, the general reduction in the significance and magnitude of exposure pathways related to oil at the water surface with the concurrent increased significance and magnitude of water column-based exposure pathways would shift the bulk of exposures to oil substances from organisms that interact with the water surface to organisms that are pelagic for some or all of their life cycle. However, this would be expected to be a temporary and short-lived exposure event, given the substantial and rapid dilution of oil substances that occurs with dispersant use under field conditions (e.g., Bejarano et al., 2014a,b; Lee et al., 2013).

IMPACTS

INTRODUCTION

This section compiles available information that seeks to address the question of whether chemically dispersed oil is more or less toxic than untreated oil to marine biota.

To facilitate addressing this fundamental question, specific definitions of effect and impact were adopted based on Boehlert and Gill (2010) (as presented previously in the Pathways of Effects Section), wherein: effects include "the broad range of potentially measurable changes that may be observed", while impacts are "effects that, with some certainty, rise to the level of deleterious ecological significance". In other words, effects are changes, while impacts are effects or changes that are adverse in their consequences.

In the event of a marine oil spill event, the potential use of dispersants is carefully evaluated within the context of site-specific characteristics through the NEBA process. Subsequently, the potential for effects and/or impacts of oil (and dispersed oil) to marine biota is entirely contingent on the conditions of the spill location and the numerous environmental and hydrodynamic factors, as well as the ecology of the area where the spill occurred.

When considering the impacts of dispersed oil relative to untreated oil, it is important to bear in mind some key fate and behaviour characteristics of dispersed oil (explained in the Background Section). Dispersants do not remove oil from the marine environment; rather, dispersants modify the fate, transport, and bioavailability of substances present within an oil mixture (NRC, 2005).

From an ecological vulnerability perspective, all components of the marine environment are assumed to be vulnerable to a certain degree in an oil spill scenario (Thornborough et al., 2017). The framework by Thornborough et al. (2017) lays the foundation for assessing the vulnerability of marine biota to oil spills based on exposure, sensitivity, and recovery criteria among biological component groupings. The criteria for exposure and sensitivity to spilled oil, as outlined by Thornborough et al. (2017), were considered in the discussion of the effects and impacts of dispersed oil. Recovery considerations are addressed in the Recovery Section of this document.

The framework developed by Thornborough et al. (2017) establishes criteria that evaluate the mechanical and chemical sensitivity of species on the basis of physiological characteristics. Mechanical sensitivity criteria include the loss of insulation and reduction in feeding/photosynthesis, while chemical sensitivity criteria include impairment due to toxicity. This framework is based in part on the National Oceanic and Atmospheric Administration

(NOAA) Environmental Sensitivity Index (ESI), which supports the identification of vulnerable biological components. The NOAA ESI indicates that the risk to biological components from oil is greatest when:

- Many individuals are concentrated in a small area, such as a seal haul out area or a bay where waterfowl concentrate during migration.
- Early life stages are present in certain areas, such as seabird rookeries, spawning beds used by anadromous fish, or turtle nesting beaches.
- Oil affects areas important to specific life stages or important for migration, such as foraging or over-wintering sites.
- Specific areas are critically important for propagation of a species (e.g., nursery areas, preferred egg-laying areas).
- A particular species is threatened or endangered.
- A substantial percentage of an animal or plant population is likely to be exposed to oil.

Species which are more sensitive to oil substances are more likely to experience such impacts as reproductive failure, inability to feed, neurological impairment, and mortality (Reich et al., 2014).

Many of the same features that relate to sensitivity are considered when identifying biological components of concern in a marine receiving environment (See Pathways of Effects Section).

In general, the effects and impacts of oil and chemically dispersed oil on marine biota are highly variable and are a function of the exposure pathways, degree and duration of exposure, the concentrations of oil substances in the exposure media, the bioavailability of the oil-associated substances to the exposed marine organisms, and the sensitivity of the species (CRRC, 2018; NASEM, 2020). The potential for impacts of dispersed oil on marine biota is unique to the conditions of each oil spill and dispersant application scenario. As described in subsequent sections herein, marine organisms respond the same and show the same range of effects following exposure to dispersed oil as they do following exposure to untreated oil.

BIOAVAILABILITY

The bioavailability of a given substance(s) is an important toxicological property as it determines the actual amount of a substance that may enter an organisms' cells and tissues from the exposure medium that the organism has contacted. Bioavailability can be a key variable influencing the quantity of the exposure or dose that is received by the organism, along with the variables of exposure frequency and exposure duration.

Since dispersants break up oil into smaller droplets and microdroplets, which have a larger surface area to volume ratio than untreated oil droplets, the bioavailability of oil-associated contaminants to marine organisms is potentially increased when dispersants are applied (USGAO, 2012). In addition, as the concentration of microdroplets increases, the amount of oil-associated substances that enter the water-accommodated fraction (WAF) (which includes microdroplets) and the dissolved fraction may also increase (Ramachandran et al., 2004a; Lee et al., 2011b). It is well established that dissolved oil substances are of highest bioavailability to aquatic organisms, relative to particulate-bound substances or oil droplets (Dupuis and Ucan-Marin, 2015). However, small droplets and particulates may be readily ingested by certain pelagic organisms. Droplets also act as a source of dissolved oil substances and sustain dissolved hydrocarbon concentrations via equilibrium partitioning between droplets and the dissolved phase.

There can be substantial variability in the concentration of microdroplets in various WAFs, depending on dispersant efficacy and local marine mixing dynamics. NASEM (2020) reports that a number of studies have found that the majority of the oil substances present in dispersed WAFs are not dissolved, and therefore it cannot be reliably assumed that the WAF of dispersed (or untreated oil) is entirely bioavailable. In other words, the WAF does not equal the bioavailable fraction. However, the presence of droplets and microdroplets drive and sustain the dissolved hydrocarbon fraction via equilibrium partitioning.

EXPOSURE TIME CONSIDERATIONS

It is well known that increasing the length (duration) of exposure typically increases the toxicity of a given aqueous concentration of a substance. Variations in exposure times and exposure concentrations can be extreme during oil spills and dispersant application scenarios. The water-accommodated and dissolved fractions of oil substances in the water column that dispersants facilitate typically dilute substantially and rapidly (often within a few hours), to concentrations below toxicity thresholds and within the low parts per million (ppm) range (Lee et al., 2013; Bejarano et al., 2014a,b).

The significance of oil dilution at sea following an oil spill incident has been well documented by Wade et al., (2016). This study compared pre-spill background concentrations of total petroleum hydrocarbons (TPH) and PAH in water samples from the Gulf of Mexico to samples recovered during and after the Deepwater Horizon incident (over 20,000 samples from 13,000 stations located from within a few meters to over 800 km in all directions from the wellhead). As expected, the highest concentrations of TPH and PAH were generally in surface waters due to slicks, in the deep water layer or in the proximity of the wellhead. Of the 13,172 water sample TPH concentrations reported, 84% were below 1 μ g/L (background). Of the 16,557 water sample PAH concentrations reported, 79% were below 0.056 μ g/L (the median field blank and background). The percentage of samples below background levels increased rapidly after the well was capped.

AQUATIC TOXICITY OF UNTREATED AND DISPERSED OIL

There are numerous papers in the literature covering various aspects and issues related to standard aquatic toxicity testing methods and protocols, that create challenges in differentiating the biological effects of an oil spill with and without dispersant use under field conditions, and in extrapolating laboratory-based toxicity outcomes to the complex field conditions that exist in an oil spill scenario, where dispersants may be applied. While a detailed exploration of these issues and challenges are not within the scope of this CSAS Research Document, it is important to acknowledge that there are many laboratory aquatic toxicity studies of chemically dispersed and untreated oil that yielded conflicting or contradictory outcomes to other similar studies. Thus, when evaluating such studies, it is important to apply a weight of evidence approach and a quantitative and/or qualitative assessment of reliability and ecological relevance (e.g., Moermond et al., 2016; Hanson et al., 2017). Such an approach would enable the identification of studies that may have had such flaws as inappropriate experimental designs, lack of reported measured chemistry data, or other methodological issues that may make a study less reliable for use in considering whether or not dispersants should be applied to an oil spill.

Many of these same issues and challenges complicate communications about the toxicity of oil to marine biota to decision-makers and the public. For example, there has been a lack of consistency in the communication of dispersed oil toxicity and impacts wherein some toxicity studies report measured exposures over time but others only report nominal exposures. This can impede study comparability. How oil exposure is represented and reported is a critical consideration when examining and interpreting dispersed and untreated oil toxicity studies.

NASEM (2020) and Adams et al. (2017) recently reviewed the various methodologies and protocols used in laboratory experiments on the toxicity of hydrocarbons in water. Particular reference was given to the use of the CROSERF (Chemical Response to Oil Spills: Ecological Research Forum) standard protocol (Aurand and Coelho, 2005) and various revisions of this procedure used by a multitude of investigators for the production of the laboratory toxicity test solutions WAF with oil, and CEWAF (chemically enhanced water accommodated fraction) with oil and dispersant.

Outcomes of both the NASEM (2020) and Adams et al. (2017) surveys showed that the reviewed studies employed a wide diversity of toxicity test methods and displayed substantial differences in test media preparation methods, test species, exposure methods, exposure durations, nominal water concentrations of oil or dispersed oil, dispersant to oil ratios, chemical analyses, experimental conditions (such as temperature, salinity, pH), and the toxicological endpoints that were evaluated. Many reviewed studies also suffered from a lack of detailed reporting of methods, lack of reported measured analytical chemistry data for tested solutions (as also noted by Coelho et al., 2013), the use of inappropriate methods in some cases, lack of rationale for modifications to standard protocols, and inconsistent terminology use. The majority of existing published toxicity studies tend to be 24 to 96 hours in duration, which are reflective of experimental designs to generate standard aquatic toxicity values such as EC50s (50% effective concentration) and LC50s (50% lethal concentration), but are not reflective of the duration that dispersed oil levels remain elevated in sea water. A number of existing studies only tested single exposure levels rather than multiple exposure levels, which precludes the ability to determine exposure-response relationships. Such factors hinder direct comparisons between studies with respect to the toxicity of oil to marine organisms. They also confound the ability to use the published aquatic toxicity data to determine if chemically dispersed oil is more or less toxic than untreated oil. Furthermore, it was apparent that many laboratory studies were conducted using oil concentrations much higher than those that would be expected in actual oil spill response operations. As highlighted by Coelho et al., (2013), toxicity testing of dispersed oil (and untreated oil) requires adherence to standardized protocols in order to be able use toxicity study outcomes to evaluate potential "real world" effects of oil and dispersed oil in marine ecosystems.

In their evaluation of the pros and cons of various methodologies used by investigators to prepare the WAF and CEWAF of oil in toxicity tests, NASEM (2020) and Adams et al. (2017) provided a number of insights on the influence or role of microdroplets on the WAF/CEWAF and dissolved fractions of oil substances. Key findings included the following:

- The concentration of microdroplets does not affect the resulting dissolved concentration of oil substances at equilibrium. In other words, separating the WAF from bulk oil does not markedly affect the dissolved concentrations of oil-associated substances.
- Different WAF types will have the same dissolved concentrations because if a portion of the
 oil phase is removed, it does not affect the equilibrium dissolved concentration. However,
 different types of WAF can have different total concentrations of oil substances if the
 concentration of microdroplets is higher in one type of the WAF than the other (e.g., CEWAF
 versus WAF).
- Thus, dissolved concentrations of oil substances may not decrease when a WAF undergoes serial dilution. This poses a problem in variable dilution toxicity tests when a dilution factor of the WAF is assumed to apply equally to the concentrations of substances in the dissolved fraction. Oil microdroplets may act as a source of dissolved constituents that reach equilibrium after each dilution. This results in the dissolved concentrations at equilibrium being higher than can be predicted by the dilution factor alone.

NASEM (2020) and Adams et al. (2017) recommended further research to improve standardized methods for the preparation and characterization of test solutions, analytical chemistry protocols to fully characterize hydrocarbon composition and concentrations in the tested exposure media, and toxicity testing experimental designs. NASEM (2020) concluded that variable loading toxicity test designs are the most robust and reliable method for laboratory investigations of oil and dispersed oil toxicity, when compared to variable dilution-based toxicity test designs. The NASEM review concluded that variable dilution test designs cannot unambiguously determine if dispersed oil (as represented by the CEWAF) is more toxic than untreated oil (represented by the WAF). This is largely due to the influence of microdroplets on dissolved concentrations of oil substances, as noted above. Various other studies have also reviewed the methods and conditions used in aquatic toxicity tests of oil and have reached similar conclusions (e.g., Aurand and Coelho, 2005; NRC, 2005; Coelho et al., 2013; Bejarano et al., 2014b; Redman and Parkerton, 2015).

Laboratory studies that test environmentally representative concentrations of oil substances are frequently unable to produce an exposure-response relationship. Thus, higher than environmentally realistic or relevant exposure levels must often be used in laboratory experiments to be able to generate information on exposure-response. To address this issue, the application of aquatic toxicity models for hydrocarbons (with experimental laboratory data used to support modelling efforts and to calibrate and validate model outcomes), using environmentally realistic concentrations, was proposed by NASEM (2020) as the most robust and reliable approach towards understanding the toxicity of dispersed oil and determining whether dispersed oil is more or less toxic than untreated oil. Coupled with environmental fate models to evaluate the exposure associated with various response options, including dispersant use, this approach was deemed to be more practical and achievable relative to attempting to design laboratory toxicity studies that strive to represent or reproduce oil and dispersed oil exposure conditions that occur in the field.

Following a review of the models used for predicting the aquatic toxicity of hydrocarbons (including PAHs), NASEM (2020) advocated the use of a toxic unit (TU) approach coupled with a target lipid narcosis model (TLNM) to predict the toxicity of oil substances. However, it should be recognized that TU's are most commonly applied when the endpoint is acute lethality or narcosis. TU's may be less applicable to other types of endpoints and may oversimplify the expression of aquatic toxicity when applied to other acute effects, chronic effects and delayed onset effects (e.g., Greer et al., 2012; McIntosh et al., 2010). It was noted that the PETROTOX model (Redman et al. 2012; 2017) has utilized TUs and the TLNM for a number of years in various hydrocarbon assessment frameworks and benchmark development programs within Canada (e.g., CEPA Petroleum Sector Stream Approach; Atlantic Risk-Based Corrective Action).

Summary of Experimental Aquatic Toxicity Study Data on Dispersed Oil – Is Chemically Dispersed Oil More Toxic than Untreated Oil?

A key outcome of the NASEM (2020) review of the available laboratory toxicity data was the conclusion that at oil loadings below approximately 100 mg oil/L, when the solutions are at equilibrium, toxicity of the WAF (untreated oil) is equivalent to the toxicity of the CEWAF (dispersed oil). While the CEWAF solutions reached equilibrium faster than WAF solutions because of the larger surface area of oil microdroplets and the increased microdroplet concentrations, at loadings less than 100 mg oil/L, at equilibrium, the addition of dispersant does not affect the toxicity of oil. It was also noted that field measured concentrations of oil in water during spills are typically well below 100 mg/L. When oil loadings are greater than 100 mg oil/L, the CEWAF toxicity is higher than the WAF by at least a factor of 3. This increased toxicity

of the CEWAF was attributed to either the presence of higher microdroplet concentrations in the CEWAF relative to the WAF, or potential toxicity of the dispersant itself (i.e., at loadings >100 mg oil/L and assuming the highest dispersant:oil ratio from the reviewed studies (1:20), the dispersant concentration would be above the estimated acute hazard concentration 5% (HC5) for currently approved dispersants). At oil loadings much lower than 100 mg/L, which are common in oil spill scenarios, the potential toxicity of the dispersant would generally be lower than the acute HC5 values for the dispersants.

The NASEM (2020) conclusion aligns with the conclusions of previous reviews of the toxicity of dispersed oil relative to untreated oil. For example, Lee et al., (2015) concluded that the toxicity arising from dispersed oil mixtures is deemed to be a function of the oil and is not a result of the addition of a chemical dispersant. Dispersants (at the concentrations used in response operations (i.e., 1 to 5 mg/L)) do not change the toxicity of the substances within oil; rather, they modify the exposure potential and bioavailability of oil substances. Dispersants do not act synergistically or additively with the oil substances, nor do they alter the chemical toxicity of the substances present within the oil (Adams et al., 2014; Hemmer et al., 2011).

KEY BIOLOGICAL ENDPOINTS FOR DISPERSED OIL IMPACTS

The main biological endpoints of interest with respect to chemically dispersed oil and marine biota are growth, reproduction, and survival (mortality). These endpoints reflect what are typically the relevant levels of biological organization for ERAs of chemical stressors, and typical ecological protection goals when assessing environmental contamination (i.e., protection of populations and communities, unless species at risk (SAR) are being assessed, in which case individual organisms and/or their critical habitat are typically the focus). Considering dispersed oil impacts to sensitive receptors, such as SAR, is important for decision-making and should include the examination of potential impacts to both the SAR and their critical habitat.

These biological endpoints are also reflected within DFO's ERAF (O et al., 2015), and are consistent with the definitions of direct effect categories from a recent DFO document describing biological/ecological PoE conceptual models for marine commercial shipping in Canada (i.e., Hannah et al., 2020).

The endpoints of survival, growth, and reproduction have traditionally been and continue to be the biological endpoints of greatest focus in ERA, largely because these types of endpoints are most easily and intuitively extrapolated to estimating potential effects on populations or communities (Dillon, 2013). In other words, these endpoints have a sufficiently severe consequence such that the implications of impaired growth, reproduction, or increased mortality could potentially be observed in affected populations or communities. Conversely, the biological significance of less severe endpoints (e.g., biochemical, physiological, or behavioral changes in individual organisms), is much more difficult to extrapolate to higher levels of biological organization, as the consequence of such effects (which are not necessarily adverse effects, but may simply be contaminant-induced changes) at a larger biological scale is more uncertain (Dillon, 2013). However, such less severe endpoints as biochemical, physiological, and behavioral responses should not necessarily be discounted, especially if they may directly or indirectly lead to responses that affect the survival, growth, reproduction, or immigration of organisms (Allard et al., 2010). Such lower severity endpoints may have the potential to result in adverse consequences to a population if many individual organisms are exposed and affected.

Carcinogenic endpoints are not considered herein (even though tumors are often noted in fish following exposure to PAHs, which are among the substances of concern in dispersed oil mixtures), and cancer is also typically not considered to be an endpoint of interest in ERAs. Cancer is generally only considered relevant as an endpoint if it has impacts on reproduction

(with the possible exception of threatened or endangered species). In addition, due to the short lifespans of many marine organisms, other types of adverse effects may be manifested before carcinogenic effects occur. Behavioral endpoints are also not considered herein. While chemical-induced behavioral changes may impact marine biota populations, standard measurements for these types of effects at a population level are generally not available.

KEY AREAS OF UNCERTAINTY REGARDING THE IMPACTS OF DISPERSED OIL ON MARINE BIOTA

While the previous subsections herein have noted major areas of uncertainty pertaining to laboratory toxicity testing of oil and dispersed oil, there are many other areas of uncertainty that also confound the ability to extrapolate dispersed oil impacts information from a laboratory to a marine setting, and to make confident inferences about the likelihood and significance of potential impacts of dispersed oil on marine biota.

Often, these numerous uncertainties preclude the ability of laboratory toxicity data to accurately predict what may occur in the field. Also, the uncertain ecological relevance of many laboratory study outcomes limits their application towards predicting or understanding the impacts of dispersed oil in the marine environment. Ecological relevance uncertainty is not unique to the study of oil and dispersants; rather, it is a common issue affecting the use of most ecotoxicological data (e.g., Moermond et al., 2016; Hanson et al., 2017). In general, toxicity studies reported in the literature should undergo an evaluation of relevance and reliability prior to their use in determining if dispersed oil differs in toxicity from untreated oil.

While a discussion or review of general ecological relevance considerations for ecotoxicological data is not within the scope of this CSAS review, it is important that whenever ecotoxicological data are being used to make inferences about the likelihood and significance of dispersed oil impacts on marine biota, the ecological relevance of the data should be carefully considered.

Selected additional key areas of uncertainty include the following:

- There is a general lack of directly comparable examples in the literature where oil spill impacts were measured and documented in the field under conditions where spilled oil was not treated with dispersants, and where spilled oil was treated with dispersants.
- The extrapolation of data from laboratory studies (typically focused on exposure to the WAF or CEWAF) to marine environmental conditions where exposure is not limited to the WAF or CEWAF, but may include a number of additional water, sediment, and food-based exposure pathways (Lee et al., 2015; NASEM, 2020).
- The complexity and variability of oil chemical and toxicological properties. Oils are a complex mixture of thousands of compounds of widely varying physical, chemical, and toxicological properties (Lee et al., 2015). For many substances in oil, these properties are not well understood or characterized.
- There is a lack of data derived from exposure conditions that capture the environmental realism of most oil spills and account for the dominant fate processes occurring in sea water, including, at a minimum, the processes of dilution, mixing, transport, and biodegradation (e.g., Aurand and Coelho, 2005; Bejarano et al., 2014a,b).
- Exposure durations to dispersed oil in the marine environment are believed to be generally short (Lee et al., 2013; Bejarano et al., 2014a,b), and are likely to be highly variable across exposed marine species. This poses challenges in extrapolating laboratory toxicity test results (which typically evaluate 24 to 96 h durations) to the marine environment.

- With the exception of relatively few species, the sensitivity of potentially exposed marine species/life stages to both untreated and dispersed oil is not well understood.
- It is not well understood if the avoidance behaviour that many marine organisms display (particularly certain pelagic organisms with chemosensory capabilities) to oil spills occurs to a similar degree under a dispersed oil scenario.
- Dispersant application to an oil spill would be expected to increase the concentration of oil
 droplets and microdroplets in the upper few metres of water, where PAHs would dissolve
 from the droplets and microdroplets to increase the dissolved PAH concentrations that may
 be available for photochemical reactions (NASEM, 2020). However, the increased presence
 of oil droplets and microdroplets may also alter ultraviolet penetration and attenuation in the
 water column, which may alter the potential for phototoxicity (NASEM, 2020).
- While there are numerous reports suggesting that PAHs are the likely cause of much of the toxicity of oil and dispersed oil mixtures (e.g., Gulec and Holdway, 2000; Ramachandran et al., 2004b; NRC, 2005; Couillard et al., 2005; Milinkovitch et al., 2011; Adams et al., 2014), a number of other hydrocarbon compounds are also likely contributing to the aquatic toxicity of oil (NRC, 2005; Lee et al., 2015).
- Dispersant use has been reported to increase the mass of oil reaching the sediments through formation of oiled marine snow (Daly et al., 2016; Vonk et al., 2015). The bioavailability and toxicity of hydrocarbons to benthic organisms is dependent on a number of environmental factors such as sediment organic carbon content and the pore water concentrations of the oil-associated substances (USEPA, 2003; 2010; 2016a,b; Di Toro et al., 1991; Redman et al., 2014). Advances in the development of environmental fate models that can estimate the deposition of oil droplets onto sediment with reasonable confidence are required to evaluate the effect of dispersants on benthic communities (NASEM, 2020).
- The potential for, and environmental significance of, the impacts of photosensitization of PAHs (including photodegradation processes) and the resultant effect on toxicity to aquatic life from exposure to the photosensitized PAH compounds and/or their photodegradation products, is not well understood. Phototoxicity of certain PAHs is well documented, including in some studies that assessed dispersant use (e.g., Incardona et al., 2012; Alloy et al., 2017; Barron, 2017; Barron et al., 2020; Bridges et al., 2018; Finch and Stubblefield, 2016; Finch et al., 2017a,b, 2018; Nordborg et al., 2018; Overmans et al., 2018; Salvo et al., 2016); however, few studies to date have been conducted in a marine setting.
- The potential for PAH phototoxicity (due to photosensitization and/or photodegradation reactions) associated with dispersant use cannot currently be accounted for with existing hydrocarbon fate and toxicity modelling approaches or current aquatic toxicity test experimental approaches (NASEM, 2020). However, there are some models, such as the Phototoxic Target Lipid Model (Marzooghi et al., 2017; 2018), which is based on the TLNM used in PETROTOX, which show some promise in being able to address the potential for PAH phototoxicity in untreated and dispersed oil mixtures.
- There is concern that current field assessment methods may be inadequate in detecting the significance of potential delayed effects, due to dispersal and the extended time between exposure of sensitive life stages and changes in population characteristics that may be measured in older organisms.

The general issue of toxicity extrapolation merits some discussion in the context of dispersed oil impacts. The issues that affect extrapolation of dispersed oil toxicity data are the same as those that affect toxicity extrapolation in ERAs.

The vast majority of toxicity data for marine biota and dispersed oil represents potential effects that may occur in individual organisms or groups of organisms. These data must then be extrapolated to a population or community scale to assess the potential impacts and risks of dispersed oil to marine biota. However, measured or predicted impacts on individuals cannot be assumed to result in adverse changes at a population or community level, due to numerous compensatory mechanisms that are present in ecological systems (Fairbrother, 2001), including acclimation and adaptation processes, but also natural redundancies in ecological structure and function, and in and outmigration of individuals into a given population.

A number of inherent uncertainties exist in the interpretation and extrapolation of toxicity data for marine biota and chemically dispersed oil, including (Allard et al., 2010):

- Extrapolation from high dose exposures used in toxicity tests to lower exposures encountered in the marine environment:
- Extrapolation of toxicity test results in common laboratory test species (under controlled laboratory conditions) to those anticipated in free-living species in a multiple stressor environment;
- Extrapolation from results in homogenous test populations to those in more variable wild populations;
- Interspecies and inter-taxa variations in response;
- Acute to chronic toxicity extrapolation; and,
- Difficulties in measuring or confirming changes in the field with those that are predicted based on the extrapolation of laboratory toxicity test outcomes.

SUMMARY OF IMPACTS OF DISPERSED OIL

The following brief summary is largely based on the meta-analysis provided in NASEM (2020). This effort vetted a large number of laboratory toxicity studies for minimum quality requirements and sought to carefully identify publications that supported an understanding of the toxicity of chemically dispersed oil, relative to untreated oil (e.g., studies were original publications, contained complete descriptions of testing procedures and analytical methods, utilized appropriate biological endpoints, and reported toxicity values as measured concentrations).

Figure 2 (from Beyer et al., 2016) provides an illustrative summary of the types of impacts that may occur in marine biota following exposure to untreated and dispersed oil. This figure is based on the findings of numerous studies conducted after the DWH event.

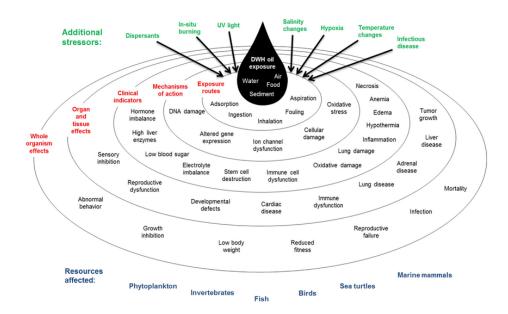


Figure 2: Potential impacts of oil on marine biota.

Many of the types of effects illustrated in Figure 2 would not be expected to occur immediately or even shortly following marine organism exposure to dispersed oil. Some types of effects in some organisms may be delayed and manifest at variable times following exposure. The potential for delayed effects is species and effect-dependent and is highly variable across marine biota.

Arctic/Cold Water Species and Deep Water Species

It appears that cold water species have generally similar sensitivity as temperate species to oil-associated substances (in both untreated and dispersed oil) in relation to acute effects (chronic effects are less well characterized between cold water and temperate species) (de Hoop et al., 2011; Norwegian Research Council, 2012; Gardiner et al., 2013; Bejarano et al., 2017; Frometa et al., 2017; Knap et al., 2017; McConville et al., 2018).

However, some studies have found that cold water species may take longer than temperate species to exhibit the effects of oil or dispersed oil exposure (Chapman and Riddle, 2005; Gardiner et al., 2013; Hansen et al., 2013; Olsen et al., 2011). This is believed to be due to morphological and physiological adaptations for cold water survival such as increased lipid stores and lower metabolic rates (de Hoop et al., 2011). Where differences in species sensitivity to chemically dispersed oil in arctic or other cold water environments have been observed, relative to species in more temperate environments, the differences are believed to be more a function of exposure-related factors rather than a higher sensitivity to the toxic effects of oil substances (Lee et al., 2015; CRRC, 2018).

With respect to deep water species, even basic information on species physiology and ecology is lacking for most species. However, limited empirical data suggests that the sensitivity of deep water species to oil-associated substances is comparable to the sensitivity of temperate and shallow-water species (e.g., Frometa et al., 2017; Knap et al., 2017; McConville et al., 2018).

Marine Birds

The impacts of oil on marine bird species are well documented in the literature (e.g., Duerr et al., 2011; Jenssen, 1994; Jenssen and Ekker, 1991; NRC, 2005; O'Hara and Morandin, 2010; Whitmer et al., 2017). Oil fouling of feathers is of particular concern as it can negatively influence the ability of a bird to fly, remain buoyant, and to thermoregulate (Lee et al., 2015). Oiled birds are also at risk of drowning, starvation, and hypothermia (NASEM, 2020). Ingested oil can cause anemia, pneumonia, intestinal irritation, kidney damage, altered blood chemistry, decreased growth, and reproductive-related problems for many marine bird species (Lee et al., 2015).

Chemical oil dispersants are generally thought to reduce the impact of oil spills to seabirds by reducing the area of surface oil slicks to which birds may be attracted. However, studies in the literature indicate that should birds become exposed to chemically dispersed oil, the effects may be similar to that of physically dispersed or untreated oil, as the chemically dispersed oil also reduces the waterproofing properties of feathers, which can affect buoyancy and thermoregulation (Duerr et al., 2011; Whitmer et al., 2017). Whitmer et al. (2017) determined a lack of significant differences in waterproofing of feathers between oil-exposed and dispersant-and oil-exposed Common Murres (*Uria aalge*).

For many marine bird species that interact with the water surface, dispersant use may result in physical/mechanical effects that are of greater biological significance than toxicological effects of the dispersed oil.

Marine Reptiles (Turtles)

Oil can have physical and toxicological effects on sea turtles (Wallace et al., 2020), with physical effects being the most commonly studied and reported within the literature (Wallace et al., 2020). Oil exposure has been associated with increased hatchling mortality, smaller hatchings, and increased rate of respiration in sea turtles (RPI, 1991).

Some studies have documented oil exposure in turtles, but did not report toxicological effects or other impacts. Oil was present in the nose, mouth, and digestive tract of sea turtles following both the Ixtoc I and DWH spill event (Hall et al., 1983; Mitchelmore et al., 2017). Following the DWH spill, visibly oiled turtles had higher concentrations of PAHs in tissues than un-oiled turtles (Ylitalo et al., 2017).

A very limited number of studies on turtles have considered the effects of dispersants or dispersed oil (Wallace et al., 2020). In one laboratory assessment, Harms et al. (2019) found that loggerhead turtle hatchlings demonstrated greater acute clinicopathological abnormalities, including failure to gain weight, when exposed to crude oil-dispersant combinations relative to oil or direct dispersant exposures separately.

Marine Mammals

There is a large body of knowledge about the effects of untreated oil on marine mammals, largely stemming from research conducted after large oil spill events (e.g., Exxon Valdez). However, very little information appears to exist in the literature regarding the impacts of dispersed oil on marine mammals. The DWH incident (which used large volumes of dispersant) has provided some insights on potential impacts. For example, chemically dispersed oil was cytotoxic and genotoxic to sperm whale skin cells (Wise et al., 2018). Sublethal effects of oil exposure were observed in two studies of bottlenose dolphins (*Tursiops truncatus*) following the DWH spill event. The DWH spill event was implicated as contributing to increased mortality of dolphins in Louisiana, Mississippi, and Alabama from 2010 to 2014. (Schwacke et al., 2014;

Mullin et al., 2017). Other large oil spill incidents such as the Exxon Valdez provide some incident specific insights regarding impacts to marine mammals, but did not involve the use of dispersants.

It is well known that many mammal species display avoidance behaviour (where possible) to untreated oil slicks. However, little is known about the avoidance behavior of marine mammals to dispersed oil plumes. This is a knowledge gap that could be further examined in the field following a major oil spill event where dispersants are applied. Priority research is warranted for vulnerable mammal species that are frequently in areas with a high probability of an oil spill event occurring.

Marine Fish

Marine vertebrates, such as fish, tend to have a greater capacity to metabolize and eliminate oil substances (such as PAHs) relative to invertebrates, and therefore tend to bioaccumulate such compounds to a lesser relative degree (Rust et al., 2004; Murawski et al., 2020).

The impacts of untreated oil on marine fish species has been well studied. Generally, oil exposure can result in a variety of lethal and sublethal impacts for fish, including mortality, reduced growth rates, increased rates of infectious disease, and reproductive impairments (Dupuis and Ucan-Marin 2015). Some oil components, especially those which are low molecular weight (e.g., BTEX, short chain alkanes), have been shown to cause acute lethality in fish species (Lee et al., 2015). Fish embryos appear to be the life stage that is most sensitive to oil exposure (Lee et al., 2015; Hodson et al., 2017).

Embryo toxicity for fish species appears to strongly correlate with the dissolved phase of oil substances rather than oil droplets or particulates (e.g., Carls et al. 2008; Olsvik et al. 2011). However, oil droplets may adhere to the gills and eggs of certain fish species and may contribute to oil exposure (Ramachandran et al. 2004a; Sørhus et al. 2015).

A study evaluating the toxicity of chemically dispersed oil on Atlantic herring embryos (*Clupea harengus*) indicated that the effects of chemically dispersed oil included blue sac disease and a reduced number of normally hatched embryos (Greer et al., 2012). Chemically dispersed oil reduced the growth of larval spotted seatrout (*Cynoscion nebulosus*) (Brewton et al., 2013).

In a study with juvenile lumpsucker (*Cyclopterus lumpus*), EC50s (narcosis) for chemically dispersed oil were the same as EC50s for mechanically dispersed oil, but acute mortality was more apparent in the chemically dispersed versus mechanically dispersed oil treatments (Frantzen et al., 2015). There were no significant differences between chemically dispersed and mechanically dispersed oil treatments with respect to gill lesions, swimming, or feeding behaviours.

Gardiner et al., (2013) measured LC50 values of 80 ppb for PAHs in Arctic cod juveniles exposed to physically dispersed oil (WAF), and 1640 ppb for PAHs in juvenile cod exposed to chemically dispersed oil (CEWAF), indicating a lower acute toxicity of the chemically-dispersed oil treatments.

Higher mortality was observed for juvenile thin-lipped grey mullets (*Liza ramada*) when exposed to chemically dispersed oil, relative to the water-soluble fraction of untreated oil (Milinkovitch et al., 2011).

Marine Invertebrates (Benthic and Pelagic, Non-planktonic)

Marine invertebrates more readily bioaccumulate oil components as compared to vertebrates, as invertebrates inefficiently metabolize oil components relative to vertebrate species (Rust et al., 2004; Murawski et al., 2020).

In general, dissolved phase oil substances appear more bioavailable for invertebrates (depending on the feeding strategy) as compared to oil droplets or particulate oil (Dupuis and Ucan-Marin, 2015). Similar to fish, the embryo life stage of invertebrates is suggested to be the most sensitive to oil exposure (NASEM, 2020). Studies on invertebrates following the DWH spill did not indicate direct negative effects for blue crab and oyster species (Fulford et al., 2014; La Peyre et al., 2014). Impaired growth, settlement success, and survival were observed in oyster (*Crassostrea virginica*) larvae following exposure to chemically dispersed oil (*Vignier et al.*, 2016). Growth rates of barnacle nauplii (*Amphibalanus improvisus*) were reduced after exposure to chemically dispersed crude oil at concentrations commonly found in the water column after dispersant application in crude oil spills (Almeda et al., 2014). Exposure to the combination of oil and dispersant resulted in marked mortality and abnormalities of jellyfish *Aurelia spp.* (Echols et al., 2016).

Oil deposited onto sediments has been shown to negatively affect benthic species and coral species (e.g., White et al., 2012; Montagna et al., 2013; Fisher et al., 2014; van Eenennaam et al., 2018).

Lower survival rates, reduced feeding rates, and slower larval development were observed for Northern Shrimp (*P. borealis*) larvae following a 24-hour exposure to chemically dispersed oil, relative to mechanically dispersed oil (Arnberg et al., 2019). A study with juvenile mud crabs (*Rhithropanopeus harrisii*) indicated that the acute mortality of crabs was increased with exposure to chemically dispersed oil relative to non-dispersed oil (Anderson et al., 2014).

Differences were not observed in sublethal short- or long-term responses among Icelandic scallops (*Chlamys islandica*) when exposed to chemically dispersed oil and mechanically dispersed oil (Frantzen et al., 2016). Cohen et al., (2014) found that the toxicity of crude oil and chemically dispersed crude oil was similar for the copepod, *Labidocera aestiva*, and that acute exposure to crude oil and/or dispersed crude oil resulted in impaired swimming for this species.

Pelagic Planktonic Marine Organisms

Exposure to chemically dispersed oil may cause sublethal and lethal effects for planktonic pelagic species (Ozhan et al., 2014; Garr et al., 2014; Almeda et al., 2013; 2014), yet the toxicity varies markedly across species and is dependent on many factors. Select examples from the literature are briefly described below.

Phytoplankton appear to be impacted through a similar mode of action by both dispersed oil and untreated oil, where genes regulating the cell membrane are affected by oil exposure (Hook and Osborn, 2012).

Garr et al., (2014) investigated the acute toxicity of oil (tar mat and MC252 crude oil), dispersant (Corexit 9500A), and dispersed oil on growth inhibition (IC50) and motility of two marine microalgal species, *Isochrysis galbana* and *Chaetoceros sp.* There was no significant impact on cell division (growth) or motility in either species when exposed to both untreated oil types. Exposure to dispersed oil caused an inhibition of cell division and motility within 24 hours, with *Chaetoceros sp.* being more sensitive to dispersed oil than *I. galbana*.

Growth rates of tornaria larvae (*Schizocardium sp.*) were reduced after exposure to chemically dispersed crude oil at concentrations commonly found in the water column after dispersant application in crude oil spills (Almeda et al., 2014).

Exposure to oil components and dispersants can result in a variety of effects in marine copepods, including narcosis and effects on feeding, reproduction, and development (e.g., Suderman and Marcus, 2002; Barata et al., 2005; Bellas and Thor, 2007; Calbet et al., 2007; Saiz et al., 2009; Seuront, 2011). A study using Calanoid copepods (*C. glacialis*) found that lethality (based on PAHs) was similar following exposure to both chemically dispersed oil and physically dispersed oil (Gardiner et al., 2013). However, physically dispersed oil was more toxic than chemically dispersed oil (based on total petroleum hydrocarbons) (Gardiner et al., 2013).

Corals

Public concerns over the potential impact of oil and chemically dispersed oil on corals has been raised following the Deepwater Horizon oil spill. While healthy coral communities were observed at all sites >20 km from the Macondo well, at one site 11 km southwest of the Macondo well, coral colonies presented widespread signs of stress, including varying degrees of tissue loss, sclerite enlargement, excess mucous production, bleached commensal ophiuroids, and covering by brown flocculent material (floc). Analysis of hopanoid petroleum biomarkers isolated from the floc provided strong evidence that this material contained oil from the plume released from the Macondo well (White et al., 2012).

Adverse effects have been observed for deep water coral species when exposed to chemically dispersed oil in laboratory studies. Frometa et al. (2017) evaluated the vulnerability of *Swiftia exserta* octocorals to oil and dispersants using 96 hour laboratory toxicity assays of surrogate DWH oil water-accommodated fractions (WAF), Corexit® 9500 dispersant, and the combination of both oil and dispersant (CEWAF). Fragment mortality occurred within 48 hours for some fragments in the dispersant-alone and oil-dispersant (CEWAF) treatments, while the WAF group remained relatively unaffected. This study indicates that combinations of oil and dispersants are more toxic to octocorals than exposure to oil alone. These results are consistent with previous studies by Goodbody-Gringley et al. (2013) which found that Deepwater Horizon source oil and the chemical dispersant, Corexit® 9500, reduced settlement and survival of *P. astreoides* and *M. faveolata* larvae.

Epstein et al. (2000) assessed the effects of third-generation oil dispersants (Inipol IP-90, Petrotech PTI-25, Bioreico R-93, Biosolve and Emulgal C-100) on planula larvae of the Red Sea stony coral *Stylophora pistillata* and the soft coral *Heteroxenia fuscescense* in short-term (2–96 h) bioassays. While oil WAF treatments resulted in reductions in planulae settlement only, treatments by all dispersants tested caused a further decrease in settlement rates. Dispersed oil exposures resulted in a dramatic increase in toxicity to both coral larvae species. Furthermore, the combined dispersant and WAF treatments caused larval morphology deformations, loss of normal swimming behaviour, and rapid tissue degeneration. The authors suggested avoidance of the use of chemical dispersants for oil spills near or within coral reef habitats.

Many species of cold-water corals are common throughout Atlantic Canada, in both shallow and deep waters. The large deep channels of the continental slope off both Nova Scotia and Newfoundland are home to the greatest abundance and diversity of deep-water corals in Atlantic Canada. Given the depth of these species, corals are unlikely to be exposed to chemically dispersed oil as a result of surface applications. However, corals may experience exposure to oil and dispersed oil from a subsea blowout event.

RECOVERY

Oil spill recovery is dependent on many factors, including the type of oil spilled and the environmental conditions present in a spill scenario. Oil spill response methods, including dispersants, are considered as part of a NEBA in a spill scenario. Previous oil spill events and experimental studies in Canada and abroad have led to advancements in understanding the fate and effects of oil spilled in cold water environments and the impacts of dispersant use (Lee et al., 2020). The lessons learned from these events contribute to a more robust understanding of the recovery potential of ecosystems following an oil spill and can be used to inform a NEBA when evaluating the use of dispersants as a response measure.

ARROW SPILL

The Arrow spill of 1970 off the coast of Nova Scotia resulted in the release of 9500 tonnes of Bunker C oil from a tanker, resulting in widespread oiling of shorelines in the Chedabucto Bay area. It was clear from existing reports that the Bunker C oil in cold coastal waters was too viscous for effective chemically-enhanced dispersal. As one area of the Chedabucto Bay (Black Duck Cove) was not remediated and monitored over time, the Arrow oil spill response has become a classic case study to demonstrate the critical role natural attenuation can play in remediating oiled shoreline and beach environments (Lee et al., 2020).

In the decade following the spill, differences in biological effects were observed for intertidal biological communities between the remediated and control sites (See Thomas 1977; 1978, Gilfillan and Vandermeulen, 1978). The recovery assessments indicated that the concentration of hydrocarbons in the water returned to pre-spill levels within a year of the spill event. Oil was cleaned from shorelines through remedial activities and via natural attenuation (Owens, 2009), yet oil has persisted in sediments of the Chedabucto Bay decades following the spill (Vandermeulen and Singh, 1994; Owens et al., 2008). Differences in biological effects were still observed for intertidal biological communities between the remediated and control sites a decade later (see Thomas 1977; 1978, Gilfillan and Vandermeulen, 1978). Residual oil is still present in sediments of Black Duck Cove fifty years after the spill. Despite the persistence of oil in areas of Black Duck Cove, the benthic communities have demonstrated recovery (Lee et al., 1999; 2003). The oil which is present in sediments has undergone weathering processes, especially biodegradation, and is of low aquatic toxicity (Lee et al., 1999; 2020; Prince et al., 2003). For oil spills at sea, the application of dispersants could reduce the landfall and persistence of oil on shorelines.

THE BAFFIN ISLAND OIL SPILL (BIOS) EXPERIMENT

The Baffin Island Oil Spill (BIOS) experiment conducted in the Canadian Arctic investigated the ecological impacts of crude oil on the shoreline and nearshore areas with and without dispersant use. An evaluation of water, sediment, and benthic fauna before the deliberate release of crude oil determined that hydrocarbon concentrations were at very low background levels (Cretney et al., 1987 a,b,c). In the nearshore study, oil concentrations were diluted to background levels within a few days after the release. The exposure to chemically-dispersed oil resulted in acute behavioural and physiological effects in a variety of species, including a short-term reduction in abundance (Sergy and Blackall, 1987). Responses of benthic fauna included the emergence from the sediment and/or immobilization of infaunal and epibenthic invertebrates which ceased within two weeks. Ultimately, few changes were observed in the populations and community structure among infauna, epifauna, and macroalgae two years following the spill event (Cross and Thomson, 1987; Cross et al. 1987a; Cross et al. 1987b).Oil persisting in sediments from both undispersed and dispersed oil was attributed to sublethal effects observed in specific species over a period of 1–2 years (e.g., the condition in the bivalve *Macoma*

calcaerea and decreased density of the polychaete *Spio spp.* (Cross and Martin, 1983). In certain locations and in the presence of contaminated sediment, deposit feeding benthos had elevated body burdens two years after the spill (Humphrey et al., 1987).

This experiment indicated that the impacts of dispersed and non-dispersed oil were minor and short term for a variety of benthic organisms. The subsurface injection of dispersed oil resulted in short term responses among benthic organisms, with recovery occurring within two weeks. Longer term responses among species were sublethal and only observed in a few species. Overall, findings of the BIOS experiment supports the notion that the use of chemical dispersants is not anticipated to result in major population or community level consequences when used in the nearshore area.

Sea Empress

On February 15th 1996, the Sea Empress oil tanker grounded in Southwest Wales, United Kingdom. The damage from the grounding resulted in the release of 72,000 tonnes of Forties Blend crude oil and 370 tonnes of Heavy Fuel Oil into the sea. Spill response options at sea utilized included dispersants, mechanical recovery, and protective booms. Mechanical recovery of the oil at sea only removed 1–2% of the oil released as operations were hampered by high winds (>15 knots) during much of the recovery period. A decision was made to spray dispersants from aircraft on surface oil slicks targeted by remote sensing systems to ensure maximum encounter rates with the oil (Lunel et al., 1995). An extensive post spill monitoring program concluded that the targeted use of dispersants probably prevented 57,000 to 110,000 tons of emulsion from impacting the shoreline and potentially resulting in greatly increased impacts on sea birds, coastal waders, intertidal vertebrates and invertebrates, and amenity areas (Lunel et al., 1995, 1997). It was deemed that the benefits from dispersant use outweighed the potential disadvantages associated with elevated oil concentrations in the water column.

Biological impacts were evident following the Sea Empress spill. Hydrocarbon concentrations in seawater were elevated relative to background levels after the spill event. Shortly after the spill, molluscs, crustaceans, and certain fish species demonstrated elevated hydrocarbon levels, with molluscs expressing the most elevated levels; however, mass mortality of fin-fish, crustaceans, and molluscs from the oil spill were not recorded following the spill event (Edwards and White, 1999). It was acknowledged that large numbers of dead or moribund bivalve molluscs, starfish, and heart-urchins did wash up on shore near the spill event and exhibited high tissue concentrations of hydrocarbons, suggesting this outcome was a result of the spill. A variety of sublethal and chronic effects were assessed among a variety of species (e.g., mussels, fish species, lugworms, amphipods). Studies with fish species (dab, plaice, shanny) showed that while the induction of high levels of DNA adducts at highly polluted sites soon after the spill, the effects did not persist into 1997.

A year following the spill, communities of amphipods and crustaceans were sparse near the grounding site, yet appeared to have recovered at most survey locations. Benthic sampling indicated the biological effects were limited to an absence of amphipods at many sites (Edwards and White, 1999). The cushion starfish, a rare species, demonstrated a reduction in population relative to pre-spill populations, yet the recovery of this species was deemed virtually complete by 1998. Certain rocky shore species were adversely affected, especially those in highly contaminated areas; however, surveys in March 1997 indicated the general recovery among crevice, holdfast, and algal-turf fauna (Edwards and White, 1999). Recovery among salt marsh vegetation was variable with certain species recovering while others experienced die-backs (Edwards and White, 1999).

The spill impacted important bird habitat as a large number of bird species, including the common scoter (*Melanitta nigra*) which used the site as a wintering site, exhibited lethal effects. It is assumed that the majority of the common scoters inhabiting the spill site died at sea or washed ashore. The population of common scoters was reduced in the years following the spill. A comparison of data collected following the spill to pre-spill counts of bird species and breeding success suggested that bird populations and nesting success were not reduced as a result of the spill (Edwards and White, 1999). Monitoring did not suggest any adverse impacts to marine mammal species, including cetaceans and grey seals (Edwards and White, 1999).

The key finding derived from this spill event is the reduction of oil which reached the shoreline and nearshore sediments as a result of natural and chemical dispersion. It is understood that the use of dispersants, along with optimal environmental conditions (e.g., high winds) and other spill response operations, greatly reduced the estimated volume of oil capable of reaching the shoreline.

DEEPWATER HORIZON

The DWH spill is the largest accidental marine oil spill in history. The event led to a discharge of approximately 500,000 tonnes of Macondo light crude oil into the Gulf of Mexico (Fingas, 2013). Multiple response measures were utilized including surface applied and sub-surface injected dispersants, Corexit 9500 and Corexit 9527. The magnitude of effects on marine biota were variable.

In the review of species impacted by the DWH spill conducted by Schwing et al. (2020), a summary of recovery rates for biological groupings studied during and post DWH was developed by the Gulf of Mexico Research Initiative (GOMRI) as a function of various impact types (Schwing et al., 2020) (Table 5). Recovery in this assessment is defined as the length of time for each group to either recover to pre-DWH status or reach a steady state ("new normal" status) (Schwing et al., 2020). The study concluded that microbes are likely to exhibit the shortest resilience period following an oil spill, while corals are likely to exhibit the longest recovery period. (Schwing et al., 2020). These findings are in alignment with other literature, specifically in that recovery times for the deep sea are anticipated to be slow given lower recruitment levels and the slower growth rates of biota present (Hook et al., 2016; Rohal et al., 2020), and that regardless of exposure or sensitivity of specific species, phytoplankton generally appear to have high recovery rates when exposed to oil (Hannah et al., 2017).

In addition, larger organisms, especially marine mammals, have long lifespans and grow slowly at the community level. These characteristics suggest a longer recovery period in the event of an oil spill event (Schwing et al., 2020).

Table 5: Resilience rates for deep benthic marine biota in the Gulf of Mexico (Adapted from Schwing et al., 2020).

Group	Resilience (Years)	References
Microbes	<2	Mason et al., 2014; Overholt et al., 2019
Foraminifera	<3	Schwing et al., 2015, Schwing et al., 2017, 2018; Schwing and Machain-Castillo, 2020
Meiofauna	<4	Montagna et al., 2017; Schwing and Machain-Castillo, 2020
Macrofauna	<4	Montagna et al., 2017; Schwing and Machain-Castillo, 2020
Megafauna	<7	Mcclain et al., 2019
Corals	10-30	Girard et al., 2018

VULNERABILITY OF BIOTA

Ecosystems are subjected to both natural and anthropogenic disturbances, including oil spills (NRC, 2013). As detailed previously, all components of the marine environment are assumed to be vulnerable to a certain degree in an oil spill scenario, yet the vulnerability of marine biota is dependent on the exposure, sensitivity, and recovery factors for species. The scale of impacts and speed of recovery varies depending on the spill size and the magnitude of response actions or treatment intensity (NASEM, 2020). The level of biological relevance is an important recovery consideration (e.g., species, community, population). Protection at the species level is most relevant for endangered, rare, or federally protected species (Environment Canada, 2012). Long term recovery (or adaptive capacity or resilience) of a population following an oil spill is dependent on a variety of species-specific factors, including (Thornoborough et al., 2017):

- Sensitivity of individual organisms;
- Habitat health;
- Population status;
- Reproductive capacity;
- Geographic range within the region;
- Ability to metabolise, excrete, or otherwise remove hydrocarbons; and
- Close association with sediments.

Brief exposures to oil components can cause acute and delayed effects for marine biota following a spill event (see NASEM, 2020). Determining the resilience or recovery of a species,

community, or population upon exposure to oil or dispersed oil is difficult without adequate baseline information. In many instances, the presence of baseline data is limited or missing for spill locations, making response considerations and tradeoffs increasingly difficult (Lee et al., 2015).

The ability of a community/population to recover following an oil spill event is dependent on many factors, and may be influenced by the presence of other additional stressors occurring in the environment (Lee et al., 2015). Limited information exists in detailing the differences in recovery potential among biota exposed to dispersed oil relative to non-dispersed oil. However, general conclusions can be drawn from literature, previous spill events and experimental studies, and inferences made based on the broad relative impacts of oil and dispersed on the various habitats and species of marine environment (Law et al., 2011; Azimuth and SNC Lavalin, 2019).

IMPACTS AND RECOVERY

In an oil spill scenario, impacts are most commonly associated with oil present on the water's surface and oiled shoreline areas. Oil at the water's surface especially increases the risk to surface-dwelling species, including sea birds and mammals. Nearshore habitats, including wave sheltered habitats or subtidal areas, demonstrate environmental characteristics which may support the persistence of oil for long periods of time (e.g., oil stranded within sediments). The limited wave energy of sheltered nearshore habitats also limits the washing and dilution of oil and may lead to oil persistence. Substrates of the intertidal area (e.g., rock pools, rocks, crevices) may also trap oil and contribute to oil persistence. An extensive investigation by the Aberdeen University Research and Industrial Services (AURIS) indicated that the recovery time period of rocky shores was up to three years, while for salt marshes it was up to five years (Sell et al., 1995).

The persistence of oil in shoreline areas has been observed decades following oil spills (e.g., the Arrow oil spill off the coast of Nova Scotia and the Exxon Valdez spill in Alaska). The persistence of oil along shorelines and in sediments is of concern because it can impact sessile and slow moving invertebrates and potentially consumers of higher trophic levels (Peterson et al., 2003; Ballachey et al., 2014). Furthermore, oil which persists can represent a chronic source of oil for various nearshore species; organisms with increased exposure to oil contaminated sediments or shorelines, especially in early life stages, are at a higher risk of adverse effects (Lee et al., 2015).

Historical oil spills and models demonstrate that the application of dispersants (surface and subsea) can help to reduce the surfacing of oil and the transport of oil to shorelines, which can reduce the potential for exposure for surface dwelling species and vulnerable nearshore coastal habitats, including shorelines (NASEM, 2020). Chemical dispersants, by enhancing the dispersion and dilution of oil, alter the relative significance and magnitude of the main exposure pathways to biota when compared to untreated oil. In short, they reduce the potential for exposure for surface dwelling species and nearshore environments (e.g., shorelines), while potentially increasing the exposure for biota within the water column or on the seafloor.

Impacts of oil in the deeper ocean are generally more acute and less common as oil rapidly dilutes and this process can be enhanced by dispersants. However, dispersants can increase the short term exposure (and potentially the toxicity) of oil by making the oil components more bioavailable for species residing in the water column or on the seafloor.

Concern exists for benthic organisms residing on the seafloor as benthic organisms have an increased probability of exposure to oil residues through the formation of marine snow (MOSSFA material) which transports oil to the seafloor (Vonk et al., 2015; Daly et al., 2016). In

the case of a subsea blowout, benthic organisms may also be exposed to oil residues and have short-term exposure to elevated concentrations of water soluble oil compounds. (Lee et al., 2013). As toxicity is primarily associated with the oil itself rather than the dispersants added, research studies have been largely focused on the persistence and effects of residual oil rather than the long term potential impacts of chemically dispersed oil (Lee et al., 2015).

SUMMARY

- Dispersants alter the fate, transport, and exposure of oil in the marine environment which influences the effects and impacts oil may have on marine biota.
- Oil residues can persist for long periods of time in shoreline and intertidal areas which may chronically affect marine organisms.
- Dispersants support the rapid dilution of oil in the water column, reducing the potential for oiled shorelines, nearshore sediments, and subsequent biological effects in these environments.
- The rapid dispersion of oil in surface waters may increase the risks of exposure to toxic concentrations of petroleum hydrocarbons for species that frequent those waters. These species include planktonic and fish embryos, raising the potential for delayed effects on recruitment and year class strength.
- The key takeaway is that dispersants support the dilution of oil in the water column, speeding up biodegradation and reducing the potential for some long term impacts in the marine environment.

MONITORING

The purpose of monitoring is two-fold, to evaluate the effectiveness of the applied dispersant on dispersing the oil and to evaluate the environmental effects of the dispersed oil on water quality and aquatic life. The monitoring associated with evaluating the effectiveness of dispersant application is referred to as operational monitoring while the monitoring associated with the environmental effects is referred to as environmental monitoring. The parameters for use of dispersants and the conditions to use dispersants are discussed in the Background Section. Information on how to develop and execute an oil spill monitoring program are summarized in Law et al., 2011, 2014; AMSA, 2016; and IPIECA, 2020. These reports make it clear that a good monitoring program contains the elements in Figure 3. It is beyond the scope of this report to detail all the necessary steps and phases of an oil spill monitoring program.

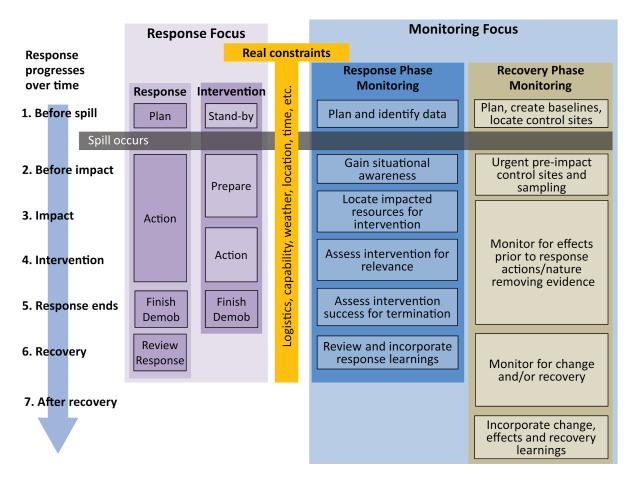


Figure 3: Description of monitoring program for an oil spill (Source: AMSA, 2016). Operational monitoring is equivalent to Response Phase Monitoring and Environmental Monitoring equates to Recovery Phase Monitoring in the figure.

OPERATIONAL MONITORING

Operational monitoring or response phase monitoring is required to determine the effectiveness of the dispersant application. One of the most widely recognized methods of monitoring dispersant application is a protocol designed by the United States Coast Guard (USCG), National Oceanic and Atmospheric Agency (NOAA), United States Environmental Protection Agency (US EPA), Centers for Disease Control and Prevention (CDC) and Bureau of Safety and Environmental Enforcement (BSEE) (NOAA, 2006; 2019).

The result of these agencies working together was the development of the Special Monitoring of Applied Response Technologies (SMART) protocol. The SMART protocol uses three tiers of monitoring (Walker et al., 2003; SpillPrevention.org, 2014b):

- Tier I Visual observations (fly-overs) by trained observers.
- Tier II Tier I plus real-time sampling in the water column at a single depth.
- Tier III Tier I and II plus monitoring in the water column at multiple depths from 1 to 10 meters below the water surface.
- The SMART protocol was first envisioned for limited geographic scope and duration but it has evolved over time (BenKinney et al., 2011; Bejarano et al., 2013).

Following the Deepwater Horizon blowout, subsea application of dispersant was used for the first time and in large amounts. Based on the lessons learned, the National Response Team developed a guidance document to be used by Regional Response Teams (RRT) and responsible parties (RP) entitled Environmental Monitoring for Atypical Dispersant Operations: Including Guidance for Subsea Application and Prolonged Surface Application (NRT, 2013). In addition, the American Petroleum Institute – API (2020) has also developed a "model plan" for subsea dispersant monitoring that could be used by its member companies as the basis for facility response plans, or Incident Action Plans, for a spill event. This guidance is intended to be used by RRTs, but also contains specific guidelines for use by the RP. Both of these documents provide standard methodologies for monitoring the efficacy of subsea dispersant injection to inform operational oil spill response decision-making by the Unified Command (UC).

Pre-Dispersant Application Survey

The pre-dispersant application surveys are designed to confirm that there are no sensitive ecological receptors or species in the vicinity of where the dispersants are to be applied, conduct baseline sampling of water and receptors, and to document the environmental conditions in the area where dispersants are to be applied (PWS RCAC, 2016). This survey is conducted before any dispersants are applied (e.g., as part of preparedness planning efforts) to help inform decision makers on the net benefits of dispersant use. As such, it is often conducted in a very limited time frame. Additional details on pre-spill monitoring are presented in the next section (Environmental Monitoring). This survey must be completed by trained observers and they should document the presence, location, and abundance of biological resources in the vicinity of the proposed dispersant application locations. Water sampling should be conducted, if feasible, to collect data on water quality (including pH, salinity, temperature, etc.) as well as petroleum hydrocarbon concentrations within the water column. Documenting this information is important as it will allow for the characterization of potential biological resources that could be impacted by dispersant applications.

Tier I

Tier I monitoring involves visual monitoring of the dispersant application and the visual assessment of the dispersant effectiveness. The observers use photography and advance remote sensing instruments to assess dispersant efficacy. For dispersant application to be considered effective, a change in appearance of the slick should be visible to the trained observers. If there is no change in the appearance or coverage of the oil, or if the dispersant runs off the oil and forms a milky white plume in the water, then the dispersant application is considered ineffective (ITOPF, 2014). Guidance on Tier I monitoring is provided within NOAA's Dispersant Job Aid, the SMART Protocol. Included in the NOAA's Dispersant Job Aid are standard reference figures, showing examples of effective and ineffective dispersant applications. One of the findings from the Deepwater Horizon is that the observers must be trained to the same standard and undergo regular refresher training to maintain this perishable skill set (Fingas and Banta, 2014).

Tier II

The Tier II monitoring involves Tier I monitoring plus using towed instruments to measure the effectiveness of the dispersant application and collecting water samples for later laboratory analysis. One or multiple fluorometers are towed behind a sampling boat or boats at depths greater than 1 meter under the slick. The fluorometers are used to measure the variation in subsurface oil concentrations. Dispersion is measured by a large increase in the measured concentration of oil detected by the fluorometer relative to the measured concentration in the

water column prior to the dispersant application. The fluorometer measurements can only provide relative measurements and cannot provide quantitative measures of the concentration of oil dispersed into the water column. Therefore, it is recommended that water samples be collected during the measurement for analysis.

In their 2014 paper, Fingas and Banta propose a new methodology for Tier II monitoring that includes towing a measurement and sampling array under pre-application and post-application slicks at depths of 2 and 5 meters. They recommended that the measurement array consist of both a particle measurement unit and a fluorometer. The use of a particle measurement unit addresses some of the limitations identified in solely relying on fluorometers which only respond to PAHs. Data from DWH suggested that a high fluorometer reading did not equate to a high dispersion. During DWH it was discovered that particle size (Li et al., 2009; Li et al., 2011) is a key parameter for evaluating the effectiveness of dispersant application, the potential for oil resurfacing, and distinguishing between physical entrainment and chemical dispersion.

Tier III

The SMART protocol defines the Tier III monitoring as the Tier I and II suite of monitoring plus monitoring in the water column at multiple depths from 1 to 10 meters below the water surface and a portable laboratory to provide data on water temperature, pH, conductivity, dissolved oxygen (DO), and turbidity. Tier III is used to collect information on transport and dispersion in the water column, verifying that oil is dispersing to background water levels. In addition to the water quality data, the water samples collected should be analyzed for petroleum hydrocarbons and PAHs and can also be used to conduct toxicity testing. As well, the water should be analyzed for concentrations of dispersants alone (if the dispersant chemistry is known and analytical methods exist for the dispersant substances).

ENVIRONMENTAL MONITORING

Environmental monitoring or recovery phase monitoring involves activities that collect and compile environment data over a period of months or years and that characterize the conditions in a region where dispersants may or have been applied.

Environmental monitoring will be presented in three stages including:

- 1. Pre-spill monitoring;
- 2. Time of Spill Monitoring; and
- 3. Post Spill monitoring.

Pre-spill monitoring is conducted to collect baseline environmental, ecological, and biological data for a specific region. The data should not just consider ecological and biological data but also include economic, social, recreational, and indigenous data in order to get a better understanding of what resources are in the region (NRC, 2013). Scientific and technical expertise is available from government, academia, and resource management experts who are engaged in research and monitoring (IPIECA, 2020). Their engagement at this stage in pre-spill monitoring, their awareness of spill response data needs, and their involvement in spill-response exercises can greatly enhance spill management decisions (IPIECA, 2020).

Taking an ecosystems services approach is also recommended as it helps focus what goods and services provided by the ecosystem affected are at risk (NRC, 2013). As part of the Regional Response Planning initiative under the Ocean Protection Plan, a portion of this data is being collected by DFO and Environment and Climate Change Canada (ECCC). DFO has developed a framework for assessing the vulnerability of biological components to ship-source

oil spills that could provide direction on pre- and post-spill monitoring (DFO, 2017). Pre-spill monitoring recommends collecting baseline data on hydrocarbon concentrations within the water. For areas where subsea dispersant application could be considered, pre-spill monitoring should consider what resources (e.g., recreational, economic, biological, ecological) are potentially at risk in areas where subsea dispersant use may be or may not be considered to inform trade-offs.

Time of spill monitoring has a very limited window of opportunity as data is needed for decision-making on the use of dispersants based on the evaluation of potential impacts from the dispersed oil. Bejarano et al. (2014) outlines three priorities that an effective monitoring strategy should have:

- 1. Identify, access, and review pre-existing baseline data and identify any potential gaps in baseline data:
- 2. Collect time of spill data (e.g.: samples of spilled oil for analysis); and
- 3. Collect additional baseline data (e.g.: water, sediment, biota, and shoreline samples) from selected locations. This would include sites that are likely to be exposed to the released oil and reference sites.

Post-spill monitoring would be conducted to assess the ecological sensitivities and other factors related to dispersant effectiveness and/or effects on the environment and aquatic life (Law et al., 2011). Based on the review of literature and an understanding of the mode of action of dispersants, the impacts of dispersed oil on marine biota are anticipated to be acute and short term, yet delayed effects resulting from oil exposure may also occur. Further, oil which persists in the environment in sediments, for example, may also serve as a chronic source of oil exposure for organisms, leading to a greater potential for long term effects. Less information is available for assessing the long term impacts of dispersed oil in the marine environment. This presents a challenge for monitoring the long term impacts post spill. Compounding this issue, long term monitoring may be further impeded by the potential lack of baseline data for species and the potential for exacerbated impacts by other stressors in the environment. The presence of baseline data at the population level and/or species level (for endangered or protected species) is especially useful for both short and long term environmental monitoring.

The post-spill monitoring program is highly dependent on the products spilled, nature of the spill, response measures used (including surface and subsea dispersant application), and resources within the area. Furthermore, it is dependent on what biological components of concern have been identified during the baseline monitoring. In addition, post-spill monitoring should consider what, if any, baseline data is available to allow for comparisons of the pre and post data sets. For subsea, a post-spill monitoring plan should include site characterization, source oil sampling, water sampling and monitoring, and sediment sampling and monitoring.

Boehm et al. (2013) outlined the questions that can assist in the definition of monitoring objectives:

- 1. What is the rate and extent that the spilled oil will weather?
- 2. What are the concentrations of oil to which ROCs are exposed in water, shoreline, and sediments? Do these exposure levels exceed reference/baseline concentrations or toxicological benchmarks?
- 3. What habitats have been impacted by the spill and to what extent?
- 4. What aquatic life has been affected and how severely?

- 5. At what rate do the concentrations and related toxicity decline either due to natural attenuation or recovery efforts?
- 6. By what measures should effects and recovery be assessed?

Finally, post-spill monitoring should be cognizant of monitoring endpoints. Monitoring endpoints should be determined by the impacts and recovery of marine life in the area along with the details involved around the spill scenario.

A detailed example of monitoring requirements in the context of dispersant use as an oil spill response is presented in Figure 4 (Adopted from IPIECA, 2020).

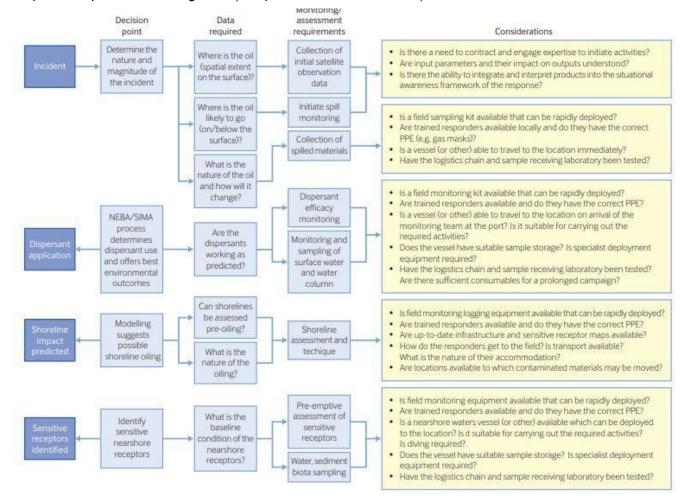


Figure 4: Monitoring requirements and considerations when using dispersants (adopted from IPIECA, 2020).

SUBSEA DISPERSANT INJECTION

Following the Deepwater Horizon spill, additional guidance was developed on subsea dispersant application (NRT, 2013). The first step in subsea dispersant injection is similar to surface dispersant application, in that pre-spill baseline data needs to be collected. For subsea dispersant monitoring, additional effort is required to collect the correct baseline data as it is required not just for the water surface but the entire water column.

According to the NRT (2013) a monitoring plan for subsea dispersant application should include the following:

- Site Characterization.
- Source Oil Sampling.
- Water and Sediment Sampling and Monitoring.
- · Sediment Sampling and Monitoring.

Site characterization includes determining the oil spill flow rate and re-evaluating it at periodic intervals. Preparing and approving the NEBA process to make the determination to use subsea dispersants. As part of the NEBA process, the application plan on how, type of, and quantities of dispersants to be used will be documented.

Source oil sampling involves collecting samples and then analyzing the source oil. Source oil samples should be collected to determine the chemical properties of the oil and for developing a fingerprinting profile. Additional information collecting source oil samples and analyzing them are detailed in NRC, 2013.

One of the key reasons to monitor subsea dispersant applications is to understand the fate and behavior of the dispersed oil. That is where water and sediment sampling and monitoring come into play. In order to meet the requirements of the response, a combination of oil spill fate and trajectory modeling, real time data collection, and water sampling is required. Oceanographic data is required to be collected in order to run and calibrate fate and trajectory models. The necessary information to collect is outlined in the Trajectory Modelling Section. For subsea dispersant applications, Oil Droplet Size Distribution is an indicator of dispersant effectiveness. Using various droplet size analyzers, the relative changes in the droplet size compared to pre-dispersant application provide an indication of dispersant effectiveness.

Collecting water column data, both continuous and discrete, is a requirement for subsea dispersant monitoring. At a minimum, conductivity, temperature, and depth, along with fluorometer data, should be collected. The fluorometer provides data on the possibility of a dispersed plume and the conductivity, while temperate and depth provides additional information for use in the oceanographic, fate, and trajectory models. Discrete water samples should be taken at specific depths throughout the water column and analyzed in a lab to determine concentrations of oil and dispersed oil within the water sample. These samples could also be used to determine the effects the dispersed oils have on marine life.

Sediment monitoring and sampling should be collected in certain situations to evaluate dispersant effectiveness and oil sedimentation. Any sediment sampling and analysis should also include benchmark sites in order to compare areas near the release source and areas far away from the source.

TRAJECTORY MODELLING

Oil spill fate and trajectory models are complex tools that must integrate several different processes to predict where the oil will go when released and how it will behave. The prediction of where the released oil will go is based on currents, wind, waves, properties of the oil, and other environmental factors (Drozdowski et al., 2011). This can be further complicated in the Canadian arctic due to the presence of ice, limited observational data on ocean currents, and difficulty in monitoring the spill in real time. Deep-sea blowouts also pose a difficulty to model as there can be different currents within the deep-sea environment compared to the water surface and these can affect both the fate and trajectory of spilled oil.

Trajectory models use a "scenario" to define the location, volume, type of product released, and other parameters as inputs to a spill simulation. Trajectory models can be used during oil spill preparation and planning, including risk assessments, to determine where a hypothetical spill could go given certain conditions, as well they are used when an oil spill has occurred to determine potential impacts and response measures. There are two main types of models that are used: deterministic and stochastic models.

Deterministic modelling is used for a specific scenario, a known date, time, and location. During an actual oil spill deterministic modelling is used to determine the fate and trajectory of the oil. For risk assessments and spill preparation and planning, where a spill could occur on various dates and environmental conditions, the scenarios are run using a stochastic model. The stochastic approach is a statistical analysis of results generated from many different individual trajectories of the same spill event with each trajectory having a different spill start time selected at random from a multi-year period. The random start times allow for the same spill scenario to be analyzed under varying wind and current conditions (Creber et al., 2017).

TRAJECTORY MODEL CONSIDERATIONS

The inputs into trajectory models include the scenario, environment data, the properties of the oil spilled, and the oil thresholds used to determine impacts (Dillon, 2017b). The majority of the input data for trajectory models are fairly specialized and require the understanding of complex data files formats, scientific conventions, and preparation. Each trajectory model as well could have requirements for different file inputs. Trajectory modelling that integrates the use of dispersants is important to inform decision-making. Additional information on trajectory model considerations can be found in French McCay, 2004, Drozdowski et al., 2011 and for subsea oil spills in Murray et al., 2020.

Oil Spill Information

In an oil spill fate and trajectory model, the oil spill information contains the details on the location, date, volume, and type of oil spilled. Early on in an oil spill, there could be several challenges associated with getting oil spill information, including limited information on the volume of oil released and detailed analysis of the oil released. During the Deepwater Horizon spill, the volume of oil released remained unknown throughout the response and oil spill trajectory modelling (Lui et al., 2011).

Specifying the physical and chemical properties of the spilled oil in a trajectory model is critical to achieving accurate and reliable oil fate predictions in any trajectory model. To have accurate simulation of evaporation, dispersion, and dissolution of the spilled oil, an accurate quantification of the oil components is required. The components of oil can be categorized into four groups based on their chemical composition: saturates, aromatics, resins, and asphaltenes. The saturates and aromatics are the greatest concern in terms of human and ecological toxicity while the asphaltenes play a large role in the emulsification of oil as the lighter ends are lost.

The saturate and aromatic fractions are more soluble and mobile in the water and more susceptible to degradation. Resins and asphaltenes are generally insoluble in water and less likely to degrade (Murray et al., 2020).

One of the best resources for physical and chemical parameters describing crude and refined petroleum products is the <u>Environment Canada Crude Oil and Petroleum Product Database</u> which has recently been updated. In addition, there have been several recent studies of the fate and behavior of oil published by DFO's Centre for Offshore Oil, Gas and Energy Research.

Oil Droplet Size Distribution

Oil droplet size distribution (DSD) is an important consideration for the transportation and the fate of spilled oil (NASEM, 2020). Increasing the proportion of small droplets increases the surface area per unit of mass of the spilled oil and can lead to enhanced dissolution of the oil within the water column (Zhao et al., 2014). Oil spill fate and trajectory model calculations in both surface spills and deep-sea blowouts are impacted by DSD and accuracy of the model depends on how well the model can represent oil droplet size (Nissanka and Yapa, 2018). The first oil spill fate and trajectory models developed did not take into consideration the importance of DSD. The early models used a limited number of experimentally measured DSD or simple empirical formulas, without taking into account droplet breakup and coalescence. DWH generated considerable interest on DSD, and since then there has been improvement in DSD calculations, especially as it relates to subsea blowouts.

The calculations of DSD in surface releases and subsea blowout models differ as the surface slicks are exposed to breaking waves as well as surface wave dynamics which alters DSD in comparison to subsea releases. However, several recent studies illustrated that methods used to calculate DSD in subsea spills can be adapted for use on surface oil slick models (Johansen et al., 2015; Nissanka and Yapa, 2017, 2018). For example, Socolofsky et al. (2015) compared oil spill prediction models for accidental blowout scenarios with and without subsea chemical dispersant injection and indicated that the volume median droplet diameter at the oil source was lower with dispersant (0.01 to 0.8 mm) as compared to without (0.3 to 6 mm).

Historically, most surface oil spill models have used the Delvigne and Sweeny (1988) model. One of the limitations of the Delvigne and Sweeny model is that it considers viscosity; it doesn't take into account the oil water interfacial tension (IFT) (NASEM, 2020). IFT is a key consideration of dispersed oil. Recently population balance models have been developed to determine the DSD. These models take into account the mechanisms that break oil up into small droplets while also considering the forces that resist the breakup (Zhao et al., 2014). A recently developed numerical model, VDROP, is capable of simulating both transient and steady state oil droplet size distribution of dispersed oil (Zhao et al., 2014). The model takes into consideration both the resistance due to the viscosity of the dispersed plume and the interfacial tension. The developers of the VDROP model validated its output with experimental results from 25 different studies that were summarized in literature (Zhao et al., 2015). The authors noted that the VDROP model results showed good agreement with the experimental data.

For subsea oil releases, experimental and field studies have shown that underwater oil jets/plumes form droplets (Wang et al., 2018; Nissanka and Yapa, 2018). During a subsea release the oil is initially broken up into smaller droplets due to instability and they then continue to break up and amalgamate due to turbulence in the jet/plume until they reach a steady state distribution (Bandara and Yapa, 2011). In a deepwater subsea spill, droplets will move in three dimensions as they ascend in the water column (NASEM, 2020). Models for droplet transportation and fate have been developed to gain an understanding of how these processes work and how better to predict the trajectory and fate of the released oil. Subsea fate and

trajectory models have two main methods to calculate oil DSD which are equilibrium models and population dynamic models.

Equilibrium models determine a single distribution which is considered the steady state oil DSD. Equilibrium models are generally derived by fitting a statistical distribution to experimentally observed oil DSD. Unlike the equilibrium model, the population dynamic (also known as phenomenological) model calculates changes to the oil DSD based on droplet breakup and coalesce dynamics. The advantage is that population dynamic models can determine intermediate oil DSD that then lead to an equilibrium DSD. Zhao et al. (2015) modified their VDROP model (called VDROP-J) that can be used to simulate the DSD from a subsea release.

While the experimental data is important to understand droplet formation and break characteristics, caution should be taken when using the data. Most of the experimental data is from laboratory experiments and only provides qualitative data (Nissanka and Yapa, 2018). Field experiments for subsea oil spills are difficult to conduct and gaining regulatory approval to perform them is unlikely. The best field experiment conducted related to deepwater subsea oil spills was the Deepspill experiment (Johansen et al., 2001). During the experiment, oil and gas was released from a depth of approximately 850 m and the transport of the oil and gas from the release was measured. The results of the experiment have been widely used to calibrate and validate deepwater subsea oil spill models. Little data exists on oil DSD from the Deepwater Horizon oil spill (Zhao et al., 2015). Additional research is required in order to calibrate oil droplet size for subsea release models.

A recommendation from the National Academy of Science (NASEM, 2020) is to consider undertaking real-time measurement of DSD at the source in the event of a subsea release.

Current

In order to adequately model an oil spill, hydrodynamic or ocean circulation information is required. Ocean currents vary both in time and space and therefore current information at one location or one time step is not sufficient for tracking an oil spill for more than a couple of kilometers or a few hours (Drozdowski et al., 2011). For surface releases, an adequate surface hydrodynamic model is all that is required, but for sub-surface releases (including subsea blowouts) a deep ocean current and surface current model is required.

Simulating the trajectory and fate of oil spills requires a definition of the currents over the entire area where oil may potentially travel. Current observations, such as those collected by instruments deployed in the field, do not have sufficient spatial coverage to adequately drive an oil spill model. In addition to complete spatial coverage, when modelling a spill over a long time period, a current field extending over a long time period is required in order to capture the variability that occurs on monthly, seasonal, annual, or decadal time scales. A hydrodynamic model applied to the area of interest is the best solution for meeting the spatial and temporal requirements of the spill modeling tasks.

One common approach in hydrodynamic modeling is to hind-cast a recent multi-year period and use current data collected by instruments in a data assimilation process to improve the hydrodynamic model accuracy. These types of hydrodynamic model products are not readily available for many parts of the world. Another approach to modeling the hydrodynamics in a region, particularly where tides or strong seasonal freshwater inflows are important drivers, is to use a hydrodynamic model to simulate currents for a one-year period based on tides and river inflows. This approach is more easily achieved than the long-term model hind-cast and it provides hydrodynamics well suited to the stochastic modeling approach because they vary by month and seasonally and have contiguous spatial coverage (Dillon, 2019).

Other oceanographic processes that drive current in a region may be important and should be included in the hydrodynamic model if possible. An example of this kind of process is a current generated by the difference in density of water masses where density differences drive the water movements.

Wind

Simulating the trajectory and fate of oil spills requires a definition of a highly dynamic and variable wind field over the entire area where oil may potentially travel. Observations from experiments and actual spills indicate that wind drift can range from 1 to 6% of the wind speed, with 3% being the mean (NOAA, 2002; Drozdowski et al., 2011). There are public sources for wind data maintained by Canadian and U.S. government agencies that provide the necessary inputs for trajectory modeling. In order to output accurate fate and trajectory models of oil on the water surface, effective representation of the wind within the model is required. Due to the limited availability of offshore wind datasets, ocean models rely on outputs from atmospheric models that can provide forecasts (from now out to 10 days) or hind-casts that can go back several decades.

The wind forecast data provided by Canadian and U.S. government agencies is adequate for the first few days of a spill but modellers should understand that the forecasts change, they all have errors that will grow with time (Lui et al., 2011), and have limited coverage areas (e.g., inlets and bays).

The data come from buoys or fixed instruments where wind speed and direction have been recorded for multiple years or from output from meteorological models that generate wind speed and direction on a regular grid from a multiple year simulation. This multiple year simulation is suited for longer term oil spill fate and trajectory models where releases could occur over days or weeks (Dillon, 2019).

Waves

Waves breaking on the surface of the ocean are important in oil spill modelling as they can drive oil on the surface into the water column. Field trials indicate that the optimum wind speed for dispersant application is between 4–12 m/s, or a wave height of 0.3 to 2.5 m. Anything higher than this and the oil will predominately be submerged (ITOPF, 2014). Depending on the droplet size generated by the entrainment process, the oil could remain submerged in the water for some time or it could resurface (Creber et. al., 2017). Any oil that is entrained in the water column will also not undergo evaporation. There are several methods to generate wave data including using wave models (e.g. Simulating Waves Nearshore model (SWAN) (Dillon, 2019)) or methods created by the United States Army Corps of Engineers (US COE) (US COE, 2002).

Ice

The presence of ice has a significant and direct effect on the transport and fate of spilled oil. Ice can shelter the oil from wind and wave actions which can slow down spreading and weathering of the oil. When oil is released in the presence of sea ice, several interactions can occur, including (Drozdowski et al., 2011):

- Oil deposition onto the ice surface;
- Oil absorption into snow;
- Oil encapsulation into the ice;
- Oil becoming trapped in leads or in open water fields between floes:

- Oil becoming trapped under ice in ridges and keels; and
- Oil building up along and becoming trapped in landfast ice edges.

When modelling oil spills in ice covered waters, it is critical to use a coupled hydrodynamic ice model. The Canadian Ice Service of ECCC provides daily ice charts. These charts have a resolution of 10 to 100 kilometers and simulate the average thickness of ice and concentration for various categories of ice. For modelling of oil-ice interactions, a model with 100 m or less resolution of ice is ideal (Drozdowski et al., 2011).

The modelling of oil droplets in the water column has been generally performed using a Lagrangian approach, where each droplet is tracked individually as it moves through the water column .Boufadel et al. (2018) reviewed available information and discussed modelling approaches to model oil droplets under ice. The study found that the boundary layer between the water and ice produces a downward velocity that can reach up to 0.2% of the horizontal current speed and is generally greater than the rise velocity of smaller droplets. This suggests that previous oil spill models could have overestimated the number of small oil droplets (<70 µm) at the water-ice interface.

Temperature, Salinity and Total Suspended Particles

The temperature and salinity of the water are important parameters that are used by oil trajectory models in various oil fate calculations. Oil entrained in the water column in the form of droplets is carried upward by buoyant forces acting on each individual droplet, and the density of the water (determined by the temperature and salinity) is a key component of the calculation (Creber et al., 2017). Both water temperature and salinity vary both horizontally, vertically, and temporally within the water column. Temperature and salinity data are available from DFO (DFO, 2009) as well as the World Ocean Atlas (Locarnini et al., 2013; Zweng et al., 2013) but have limited spatial resolution.

A primary mechanic for oil to deposit onto the sea floor is through adhesion or sorption onto suspended particles or detrital material and then the incorporation of sediment into oil. Sedimentation of the oil droplets occur when the specific gravity of oil increases over that of surrounding water.

AVAILABLE OIL SPILL AND TRAJECTORY MODELS

There are a number of available oil spill and trajectory models available for use in Canada. This review focused on existing models that have been used within Canada and where information on the model could be found and the details of the trajectory models that have been published.

Oil Spill Contingency and Response (OSCAR)

The Oil Spill Contingency and Response (OSCAR) is an oil spill fate and trajectory model and simulation tool developed by SINTEF and available for commercial use. Details of the OSCAR model are found in Aamo et al., 1997 and Reed et al., 1995. OSCAR can model an accidental release of oil from an offshore platform or a vessel or can be used for contingency planning (stochastic approach). Response strategies, including dispersant application, can be simulated within the OSCAR model.

The model accounts for oil weathering (using a database), a chemical fates model, an oil spill response model, a biological exposure model for fish and other marine species, and a three-dimensional advection model (Drozdowski, et. al., 2011). OSCAR simulates the following oil fate processes, including surface spreading and advection, entrainment within the water

column, emulsification, volatilisation and interaction with the shoreline. The oil weathering model within OSCAR has been refined with experimental results conducted at SINTEF.

OSCAR does incorporate ice into the model simulation. Ice coverage affects weathering, spreading, evaporation of surface oil, and drifting of the spilled oil with ice (Daae et al., 2011). OSCAR can simulate oil being trapped under ice, oil within ice floes, and free floating surface oil. The drift rate of the oil with the ice includes modifications to adjust for Coriolis effect. OSCAR has a DeepBlow model that simulates the fate and transport of oil from a subsea release. It can simulate the multiphase plume trajectory including both oil and gas.

OSCAR is currently the oil spill fate and trajectory planning model being used by Oil Spill Response Limited (OSRL) who hold the world's stockpile of oil spill dispersants (OSR, 2021) OSCAR is used for development of oil spill contingency plans and Environmental Impact Assessments.

OILMAP and SIMAP

OILMAP is an oil spill fate and trajectory model developed by the RPS Group that is used for oil spill response and contingency planning. OILMAP is used by ECCC as well as accredited Canadian oil spill response agencies (e.g., Point Tupper Marine Services, Atlantic Environmental Response Team, Western Canada Marine Response Corporation) and OSRL on a global scale. OILMAP includes algorithms for spreading, evaporation, emulsification, entrainment, oiled shoreline, and oil-ice interaction. In addition to the oil spill fate and trajectory model, OILMAP has a back track function which enables to track oil slicks backwards in time to determine where a slick could have originated as well as a stochastic modelling function for contingency planning (RPS, 2016). OILMAP incorporates response efforts including placement of booms, mechanical recovery, in-situ burning, and dispersant applications.

OILMAP is a three-dimensional fate and trajectory model that can track both surface and sub-surface movements of oil and determine the oil's distribution on the water surface, atmosphere, water column, and shoreline. OILMAP can track oil within the water column that is entrained and can predict and track if the oil resurfaces. OILMAP can simulate both surface spills and submerged spills.

Ice is incorporated into OILMAP using geographic information system based polygons designating percent ice coverage. With ice coverage less than 30%, no impacts to the fate and trajectory of the oil is modeled. With ice concentrations ranging from 30 to 80%, there is a reduction in the advection, evaporation, entrainment, and spreading of the oil. In ice waters with greater than 80% coverage, oil moves completely with the ice and there is no evaporation and entrainment modeled by OILMAP.

OILMAP Deep is a near-field model used to simulate subsurface releases of oil and gas. The outputs of OILMAP Deep can integrate with OILMAP for farfield simulation of the oil release. OILMAP Deep models oil and gas plumes and droplet size for a specified scenario. A subsurface dispersant treatment module that incorporates the effects of time varying subsurface dispersant treatment is also available. OILMAP Deep has been used for contingency planning and Environmental Impact Assessments for oil and gas development off Nova Scotia (Horn and French-McCay, 2014). Additional details on the theory behind OILMAP Deep are available in Crowley et al., 2014; Spaulding et al., 2015, 2017.

RPS developed a more advanced version of OILMAP called the Integrated Oil Spill Impact Model System (SIMAP). Similar to OILMAP, SIMAP is a three-dimensional physical fates model that calculates the distribution of whole oil and oil components on the water surface, shorelines, water column and sediments (Creber et al., 2017). It uses the same oil fate and trajectory

algorithms as OILMAP but has the ability to integrate different environmental and biological databases into the model to determine the impact the spill could have on habitats and biological life. Detailed descriptions of the SIMAP model including the underlying assumptions and algorithms can be found in the following papers: French McCay, 2002; 2003; 2004. The SIMAP model has been validated with more than 20 case histories on several large spills (French and Rines, 1997; French McCay, 2003; 2004; French McCay and Rowe, 2004) as well as test spills designed to verify the model (French and Rines, 1997).

A summary of fates and effects incorporated in OILMAP/SIMAP is detailed in Tables 5.1a and 5.1b of the National Academies of Sciences, Engineering, and Medicine report "The Use of Dispersants in Marine Oil Spill Response" (2020).

SPILLCALC

SPILLCALC is the commercial oil spill fate and trajectory model developed by Tetra Tech. It is a time step model that computes the motion and weathering of petroleum hydrocarbons spills. SPILLCALC gets its current inputs from Tetra Tech's proprietary three-dimensional hydrodynamic model, H3D, which provides time and space varying currents across the entire water column. SPILLCALC can use other sources of hydrodynamic data from other models besides H3D. SPILLCALC obtains wave conditions using SWAN. SPILLCALC simulates oil released on the surface of the water using lagrangian elements (called Slicklets). SPILLCALC can be run in deterministic or stochastic modes. SPILLCALC includes algorithms for spreading, evaporation, emulsification, vertical dispersion and resurfacing, sinking and submergence, biodegradation, oil-sediment interaction, oiled shoreline, and oil-ice interaction (Stronach and Hospital, 2014). Environmental and biological effects are not considered in the SPILLCALC model.

SPILLCALC includes ice in the model by extracting daily ice information from various sources, including data from the Canadian Ice Service. The ice is then incorporated into the hydrodynamic model to model its movement (Dillon, 2019). Recovery of spilled oil can be modelled in SPILLCALC and includes booming, mechanical recovery, dispersant application and in-situ burning. SPILLCALC does not have a module that can simulate subsea well releases. Additional details on SPILLCALC can be found in Hospital et al., 2015; Dillon, 2019.

COSMoS

COSMoS (Canadian Oil Spill Modelling Suite) is a software suite currently being developed at Environment and Climate Change Canada for future operational use to model oil slick trajectory and basic fate and behavior, such as oil spreading, evaporation, entrainment, emulsification, mass loss to shores from stranded oil, and density, viscosity, and composition change (Barker et al., 2020; Chang et al., 2020; Marcotte et al., 2016). Developed under the Canadian Centre for Meteorological and Environmental Prediction (CCMEP), COSMoS has direct access to the best forecast data from ice, ocean, wave, and atmospheric models available at any given moment for regions of Canadian interest. Similar to other operational oil spill models, COSMoS features two modes by default for oil spill discharge: instantaneous discharge (i.e., all Lagrangian elements released at one time-step) and continuous discharge (i.e., constant release rate over a finite number of time).

SUMMARY

Dispersants are one response option to mitigate the effects of oil spills on the marine environment whether the oil is released at the surface or subsurface. Dispersants can be used in cold climates and ice-infested waters, particularly when other response options are limited.

When oil is released into the water, it naturally disperses. Dispersants enhance this process by increasing the formation of smaller oil droplets which allows the oil to spread vertically and horizontally in the water column. Dissolution, dilution, and biodegradation is then promoted over a larger volume of water as compared to natural attenuation. Effective use of dispersants reduces the potential for oil droplet collisions, and thus reduces the potential for coalescence and reformation of surface slicks.

The use of dispersants reduces the exposure to oil for organisms at the water surface and on shorelines and intertidal areas. Initially, following dispersant application subsurface organisms may be temporarily exposed to increased concentrations of chemically dispersed-oil. The chemically dispersed-oil has been found to have a similar aquatic toxicity as oil alone but the duration and intensity of exposure to an organism is mitigated by the rapid dilution of the chemically-dispersed oil. Cold water species present in Canadian waters have been shown to have similar sensitivities as temperate species to the acute toxicity of chemically dispersed-oil and untreated oil.

Marine organisms can be affected by untreated and chemically dispersed-oil through the toxic components of the oil but also through physical, chemical, and biological interactions. Laboratory-based toxicity tests provide critical information on the impacts of oil and chemically dispersed-oil but are limited in replicating the complexity of open water conditions. Results from laboratory-based experiments can be input into models to enable the prediction of potential effects to individuals, populations, and ecosystems when all parameters are considered.

During and following dispersant application, monitoring of the spill and environment should be conducted. Specific requirements for monitoring are dependent on the site, incident, and context of the oil spill. Operational monitoring, to assess the effectiveness of dispersant application during response operations, is required to determine when application operations should stop. Incident specific environmental monitoring, to assess the impacts and recovery of the environment to the spill, is conducted during and following response operations.

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