Coastal Response Research Center

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State-of-Science for Dispersant Use in Arctic Waters

Physical Transport and Chemical Behavior

I. Arctic Physical Oceanography

A. General Statements

Knowns:

1. The “*western surface waters*” come from the North Pacific through the Bering Strait into the Chukchi and Beaufort Seas. The “*eastern surface waters*” come from the North Atlantic and the local river systems.
2. There are large river systems which introduce freshwater and suspended and dissolved materials to Arctic Ocean waters.
3. There is seasonal ice formation and melting.
4. Seasonal ice melting and large river systems contribute to low salinity surface waters and create a near-surface pycnocline, which inhibits mixing.
5. The deeper waters in the Arctic Oceans are formed deep in the Atlantic and enter through the Fram Strait.
6. The Beaufort Gyre circulates water and ice in a clockwise manner around the “*western*” Arctic Ocean. The coastal circulation can circulate in the opposite direction.
7. In an ice-covered ocean, direct wind-induced mixing is reduced.

B. Sea Ice and Mixing

Knowns:

1. For all sea ice types, relative motion between ice floes, due to wave penetration and ice floes moving on the water’s surface caused by the wind, can create mixing. The following need to be taken into consideration:
    - Land Fast Ice: Over winter in land fast, stable, or non-moving ice-covered areas, there is very little or no mixing unless there is a tide or current underneath.
    - Pack Ice: Friction of the ice on the water causes mixing.

- Marginal Ice Zone: The marginal ice zone is the transition area between the pack ice and the open water regimes.
- In regions of sea ice, the turbulence regime is very dynamic and transient from waves, wind, swell, and relative motion of ice.
- In regions of sea ice, there is significant wave dampening as ice transitions from frazil ice to grease and slush ice, and to small ice pancakes.
- Open Water: Surface turbulence is caused primarily by wind-generated waves.

2. During ice formation, the brine, that is exuded from the ice, is transported to the bottom waters and makes a stable and persistent boundary layer depending on environmental conditions (weeks to months to over winter). This movement of brine creates a transport mechanism for moving dissolved constituents (e.g., aromatic hydrocarbons, dispersant constituents) to the bottom (Payne et al., 1991a).
3. Dispersant use during ice formation may enhance the transport of the dissolved constituents to the bottom waters where elevated concentrations may persist throughout the winter period (particularly in near-shore lagoons along the Beaufort Sea coast) (Payne et al., 1991a).
4. There are a wide variety of mixing scales in the Arctic, both horizontal and vertical (e.g., McPhee and Stanton, 1996; Skyllingstad et al., 2003; McPhee et al., 2008; Marcinko et al., 2015). Ice formation, transport and melting result in additional types of mixing compared to open water.

C. Storms

Knowns:

1. There are frequent large storms in winter in the Bering-Aleutian system.

II. <u>Oil and Dispersed Oil Behavior</u>

A. Droplet Size/Formation

Knowns:

1. Dispersants reduce the interfacial tension between oil and seawater.
2. For a given level of turbulence, a reduction of interfacial tension will result in smaller droplet sizes. Therefore, given sufficient turbulence, dispersants decrease oil droplet size.
3. Increased turbulence leads to decreased droplet sizes.
4. The smaller the oil droplets, the slower their rise velocity. Therefore, the smaller oil droplets remain in the water column longer.

5. The greater the turbulence, the greater length of time the oil droplets will remain in the water column.
6. The greater the turbulence, the larger the oil droplet size that will remain in suspension in the water column.
7. As droplet size gets smaller, the surface area to volume ratio increases.
8. The dispersant does not change the oil chemically. Rather, a dispersant-mediated increase in oil droplet surface area to volume ratio facilitates hydrocarbon dissolution of water soluble constituents. This leads to a spiked increase in oil droplets and dissolved constituents in the water column that will decrease with time with sufficient dilution.
9. For a given oil and dispersant combination and set of environmental conditions, chemically-enhanced dispersion decreases with lower dispersant to oil ratio (DOR). Conversely, limits exist where dispersion effectiveness will not continue to increase indefinitely with increasing the DOR.
10. Formation of smaller, dispersed oil droplets rapidly leads to higher concentrations of soluble hydrocarbons in the water column.
11. Dissolution is not reversible; however, the dissolved-phase concentrations may decrease with time.

Uncertainties:

1. Models do not yet exist to predict the droplet size distribution of naturally or chemically dispersed oil in ice-infested waters. Confounding factors include ice concentration and type, limited mixing energy due to wave damping caused by ice, temperature, and DOR.
2. Studies aimed at understanding the relationship between mixing energy and droplet size distribution may not use conditions that represent those that exist under field conditions. In one example, the Aman et al., (2015) test system allows the droplet size distribution to come to or approach equilibrium because of the constant level of shear used by the high energy mixing system for each experiment. This does not simulate the rapidly decreasing mixing energy oil experiences in a jet released from a point source (i.e., from a release at the sea floor). The continuing equilibration of the droplet size distribution would lead to smaller droplet sizes without dispersant injection and more of the oil-remaining subsurface in model predictions. Droplet size distributions are not expected to equilibrate in a jet, especially in those cases when dispersants are not used. Systems that use a different approach to form and measure dispersed and undispersed droplets (e.g., Brandvik et al., 2014; Merlin 2014), do show significant differences in average droplet size distributions with and without the use of dispersant. In addition, laboratory studies have been done at higher temperatures (e.g., 25°C), which are not representative of Arctic or deep ocean conditions.

B. Coalescence and Slick Reformation

Knowns:

1. In typical open ocean near-surface turbulence, dispersed oil droplets below a certain size (approximately 50 microns in diameter) do not rise to form slicks to any appreciable degree.
2. An increase in droplet concentration increases the coalescence of droplets.
3. A particular droplet population is formed under a certain level of mixing energy.
4. If the mixing energy weakens, it is possible for droplets to coalesce, but in the case of sufficient dilution, we do not expect concentrations of larger droplets to be large enough to reform slicks.

Uncertainties:

1. It is uncertain how to apply existing under-ice turbulence models to predict droplet rise under pack ice.
2. It is uncertain if resurfaced chemically-treated oil will be readily amenable to dispersion if mixing energy is reintroduced. Dispersants remain with the oil for an extended amount of time (SL Ross, 2006) – upon reintroduction of energy, dispersion will reoccur. Recent CEDRE study indicates surfaced subsurface dispersed oil will disperse effectively (Merlin, 2014).

C. Transport

Knowns:

1. In subsurface releases, differences in rise velocity can cause horizontal separation in droplet size in the presence of a cross current.
2. Dissolved oil and the smallest droplets will move with the water. They will remain in their initial water density layer, which may not stay at a constant depth.
3. Dilution of contaminant concentrations is driven by mixing. In most cases, vertical mixing is of lower magnitude than horizontal mixing in ocean waters.
4. In general, concentrations of oil droplets and dissolved components in the water column decrease over time as the spill expands away from the source in 3-dimensional space.
5. With a continuous or intermittent subsurface release, it is possible that a previously contaminated water mass passing through the rising plume (e.g., through a current reversal) can have an increase in dissolved and particulate hydrocarbon concentrations.

Uncertainties:

1. Pooling capacity and transport of oil trapped under ice is not easy to predict.
2. Waterborne transport of surface oil in regions with intermediate ice coverage is uncertain (Deslauriers et al., 1977; Deslauriers and Martin, 1978).
3. It is difficult to predict oil transport and mixing in frazil, grease and slush ice.
4. Though we know that oil droplets can rise to the surface during early ice formation stages, we do not know how much these ice forms (frazil, grease, slush) control the horizontal movement of the oil (Wilkinson et al., 2007a; Wilkinson et al., 2013; Wilkinson et al., 2014).

D. Oil in Ice

Knowns:

1. Oil spills in heavy sea ice have occurred:

Spill Name	Location	Year	Reference
T/V Kurdistan	Nova Scotia	1979	Reimer 1980
Godafoss	Norway	2011	Broström et al., 2011
Runner 4	Gulf of Finland	2006	Wang et al., 2008

2. Spreading and transport of oil in ice are two different processes; transport involves the relocation of the oil and ice, while spreading involves the movement of the oil within the ice field.
3. Spreading of oil can be constrained by the presence of ice.
4. Oil in close pack ice will move or be transported with the pack ice.
5. At low concentrations of pack ice, oil will move the same as it would in open water, which may be at a different speed than the pack ice.
6. Movement of ice containing fresh or weathered oil can result in a secondary release upon melting at distances far from, and long after, the initial spill.
7. In leads, during early ice formation or refreezing conditions, fresh oil may emulsify due to wave action without appreciable evaporation (Payne et al., 1991b). Depending on the type and percentage of ice coverage and the crude oil involved, emulsions can form to different degrees and display different responses to treatment with dispersants, ranging from partial to complete dispersion (Brandvik et al., 2010).
8. The window of opportunity for dispersant use increases in the presence of high ice coverage and at low air and sea temperatures due to reduction in oil weathering.

Uncertainties:

1. A general algorithm for transitioning between ice regimes has been discussed since the late 1970s, however there is not agreement on the transport of oil within ice between

about 3/10th and 8/10th ice cover. It is assumed that at about 3/10th ice coverage, the oil moves as though it was in open water, and is controlled by the ice at about 8/10ths ice coverage (El-Tahan et al., 1988). However, there is no specific field calibration for this guidance, though theoretical arguments have been made (Venkatesh et al., 1990; El-Tahan et al., 1988). The presence of frazil or brash ice between larger floes would increase control of the oil as compared to open water.

E. Temperature Effects on Oil Weathering

Knowns:

1. Aqueous solubility and vapor pressure decrease with decreasing temperature.
2. During warming temperatures in the spring, oil encapsulated in first-year ice can migrate to the ice surface through brine channels. The surface oil warms due to solar radiation, promoting formation of melt pools. The bulk properties of the oil are essentially the same as when first encapsulated and will be subject to evaporation.
3. Water-soluble constituents in the oil can be released to the brine and be transported to the water underneath the ice during melting.

F. Weathering

Knowns:

1. Evaporative weathering increases the oil's viscosity and may decrease dispersibility.
2. Water-in-oil emulsification significantly increases viscosity and may decrease dispersibility.
3. Oil can be found in between ice floes, under the ice, encapsulated in ice as pools, in ice brine channels, and on top of the ice. Each of these has specific implications for weathering.
4. Oil-ice-weather interaction is controlled by ice specific physiochemical processes not observed under ice-free conditions.

Uncertainties:

1. The variation in weathering of dispersant-treated oil with ice concentration and type is uncertain. For example:
    - The degree of water-in-oil emulsification, as a function of ice concentration and type, is difficult to predict.
    - Spreading of dispersant-treated oil in ice-infested water is difficult to predict.

- It is difficult to predict the dissolution of dispersant-treated oil in ice-infested waters (e.g., droplet size influence, role of diffusion within droplets, effects of emulsification).
- There are limited field data on oil weathering in ice-infested waters to improve the prediction of oil evaporation (Sørstrøm et al., 2010; Daae et al., 2011; Brandvik et al., 2013).

G. Testing/Monitoring

Knowns:

1. Standardized measurement methods are crucial to acceptable data generation.
2. Testing conditions should mimic field conditions to the best of their ability (e.g., various forms of sea ice).

Uncertainties:

1. It is difficult to extrapolate lab and tank test results on physical transport and chemical behavior to field conditions.
2. The lack of standardized methods for mesoscale tests (e.g., wave tanks) makes comparison of results difficult.
3. Because there is such a wide range of ice conditions in the Arctic and it is so time consuming and expensive to run mesoscale tests with oil and ice, it is uncertain which field conditions are most important to simulate. Field tests can help to resolve uncertainties, but are difficult to conduct (e.g., permits, controls, safety).

H. OMA/OSA

(OMA (oil-mineral-aggregates) or OSA (Oil-Suspended Particulate Matter Aggregation)

Knowns:

1. There are several general reviews of this topic: (Sun and Zheng, 2009; Khelifa et al., 2005a, 2008a; Lee, 2002; Gong et al., 2014).
2. OMA/OSA production is a natural process that occurs when oil comes in contact with organic and inorganic material.
3. OMA/OSA formation depends on the concentration of and type of suspended particulate matter and the type of oil spilled (Khelifa et al., 2008a).

4. In the Deepwater Horizon Oil Spill, deep water OMA/OSA production and sedimentation near the well was affected by varying uses of drilling mud injection in well control efforts (OSAT, 2010).
5. In the Arctic, river outputs and glacial till could be significant. OMA/OSA is known to occur in cold waters and in the presence of ice (Lee et al., 2009; Khelifa et al., 2005b).
6. The effect of adding dispersants to oil in the presence of suspended particulate material and mixing energy will increase the rate of formation of OMA/OSA (Khelifa et al., 2008a; Khelifa et al., 2008b; Zhang et al., 2010; Fu et. al., 2014).
    - Temperatures in some of the studies ranged from 0°C to 25°C.
7. The buoyancy of OMAs/OSAs depend on the oil to mineral ratio ((Stoffyn-Egli and Lee, 2002).
    - Once formed OMAs/OSAs are very stable structures.
    - Individual OMAs/OSAs can sink, float, or be neutrally buoyant.
    - Mixing energy is a major factor in controlling sedimentation of OMAs/OSAs.
    - Coagulation and flocculation can cause individual OMAs/OSAs to aggregate, causing them to sink.
8. In general, oil sedimentation in offshore areas is less likely to occur because sediment/particulate matter concentrations are typically low in that environment (Brandvik et al., 2010).
9. Field and laboratory observations have shown:
    - Particle fines less than ~10 microns are likely to promote OMA/OSA formation (Khelifa et. al., 2008a).
    - OMA/OSA formation has been observed at sediment concentrations as low as 50 – 100 mg/L (Khelifa et al., 2007; Khelifa et al., 2008a).
    - Dispersed oil has a high surface area making it more likely to aggregate with fine particles, possibly promoting sinking of this oil.
    - For a given mixing energy, OMA/OSA formation increases with lower viscosity oils (Khelifa et al., 2002).
    - OMA/OSA formation decreases with decreasing temperature (Khelifa et al., 2002).
    - OMA/OSA buoyancy depends on the oil-sediment-dispersant mixture, oil and sediment size distribution and density, and the mixing energy. OMAs/OSAs can be negatively, neutrally or positively buoyant (Stoffyn-Egli and Lee, 2002; Khelifa et al., 2008a; Khelifa et al., 2008b; Khelifa et al., 2008c).
    - OMA/OSA formation increases with water salinity (Khelifa et al., 2005c).

Uncertainties:

1. There are uncertainties about the formation, behavior and fate of OMAs/OSAs in ice-infested water (e.g., possibilities of sinking, effects on microbial degradation, in-ice and under-ice turbulence regimes).

2. There are limited data on the effects of ice on OMA/OSA formation. (Lee et al., 2011).

I. Mathematical Modeling

Knowns:

1. Mathematical models may aid in the determination of the fate and transport of oil spilled in the environment.
2. Recent mathematical models of deep water well blowouts and their response options have become more sophisticated but still have limitations.
3. Mathematical models are only as good as the assumptions upon which they are founded.
4. Laboratory studies and field measurements were used to develop a weathering model that predicts mixing within the marginal ice zone in Arctic waters which affects the resurfacing of physically- or chemically-enhanced entrained oil droplets in the water column (Downing et al., 1997).
5. Models have been proposed to predict oil transport and spreading of oil under ice and in ice-infested waters (these are reviewed in Drozdowski et al., 2011; Khelifa, 2010; NAS, 2014; Reed et al., 1999).
6. For spreading (see uncertainties section on oil in ice), most existing models were developed using limited sets of data and are not applicable to all possible ice regimes (some examples are: Fingas and Hollebone, 2013; Gjøsteen, 2004; Gjøsteen and Løset, 2004; Wilkinson et al., 2007a, b; Yapa and Belaskas, 1993; Yapa and Weerasuriya, 1997; Yapa et al., 2006; Gearon et al., 2014).
7. State-of-the-art oil in ice models use coupled atmosphere-ice-ocean models for ice concentration and ice flux between grid cells. This allows calculation of flux of oil and ice between grid cells. These models continue to use the general algorithm described above in the uncertainty section on oil in ice.
8. Present day coupled atmosphere-ice-ocean models provide dynamically consistent fields as opposed to using disparate sources of winds, ice fields and currents (Gearon et al., 2014).
9. Very few validation studies of present day models to predict transport of oil spills in ice-infested waters exist (some examples are: Reed and Aamo, 1994; Daae et al., 2011).
10. Existing oil spill models do not include algorithms to model all of the effects of processes that control oil-ice interaction at small scales ranging from less than a meter to tens of meters (e.g., oil encapsulation in growing sea ice, oil migration in brine channels affecting pooling and ice melting, water-in-oil emulsification in frazil ice, mixing by ice-ice interaction, mixing caused by the movement of floes).

Uncertainties:

1. There are no peer-reviewed numerical models for turbulence in the Marginal Ice Zone (MIZ). We have good models for wave-generated turbulence and for turbulence under pack ice. The MIZ is a transition zone, where the water column is likely transitioning between wave-dominated turbulence and under-ice turbulence regimes. This is important for predicting whether or not dispersed oil will remain subsurface.
2. Modeling of how oil moves under and through ice is not mature (e.g., limited knowledge of critical shear stress).
3. Interfacial tension reduction with DOR in cold conditions is not well known, limiting our ability to model droplet size distribution.
4. Data access and visualization and analysis tools are usually on a projection that is not suitable for the Arctic.
5. Several oil spill models have implemented algorithms with higher concentrations of ice increasingly controlling oil movement, but there is not community consensus on how this should be done.

Areas of Non-agreement:

1. Overall, there is limited quantitative knowledge to develop improved predictive models for processes such as dispersed oil droplet sizes, dissolution, OMA/OSA formation, and water-in-oil emulsification during oil spills in ice.
2. The oil spill models can use output from Hibler formulation ice ocean models, but not from discrete element ice ocean models.
3. Discrete element models address individual pieces of ice and can be used at a much finer scale than Hibber formulated models and include processes such as ridging, rafting and fast ice which are important in oil transport in ice-covered waters (Khelifa, 2010; Hopkins, 1998; Hopkins and Thorndike, 2006).

J. Subsea Release

Knowns:

1. In shallower waters, the force from the rising gas of a blowout could break the ice. (Dickins et al., 1981, Brandvik et al., 2013; Johansen et al., 2013).

Uncertainties:

1. In a subsea release, the degree to which the presence of gas bubbles (including gas-to-oil (GOR) ratio), high pressure, and hydrate formation alters the droplet size distribution is uncertain.
2. Laboratory studies have been done on the change in droplet size distribution simulating a small subsurface release (Johansen et al., 2013; Brandvik et al., 2013). There is uncertainty about the droplet size distribution in a plume of oil from a subsea release with dispersant application in the field.
3. Although this is an area of active research, there is uncertainty about droplet and dissolved constituent intrusion in the water column associated with a subsea release (e.g., where it happens, droplet size, extent of down-current advection).
4. The extent to which the heat of the oil-water plume will melt ice is uncertain.

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