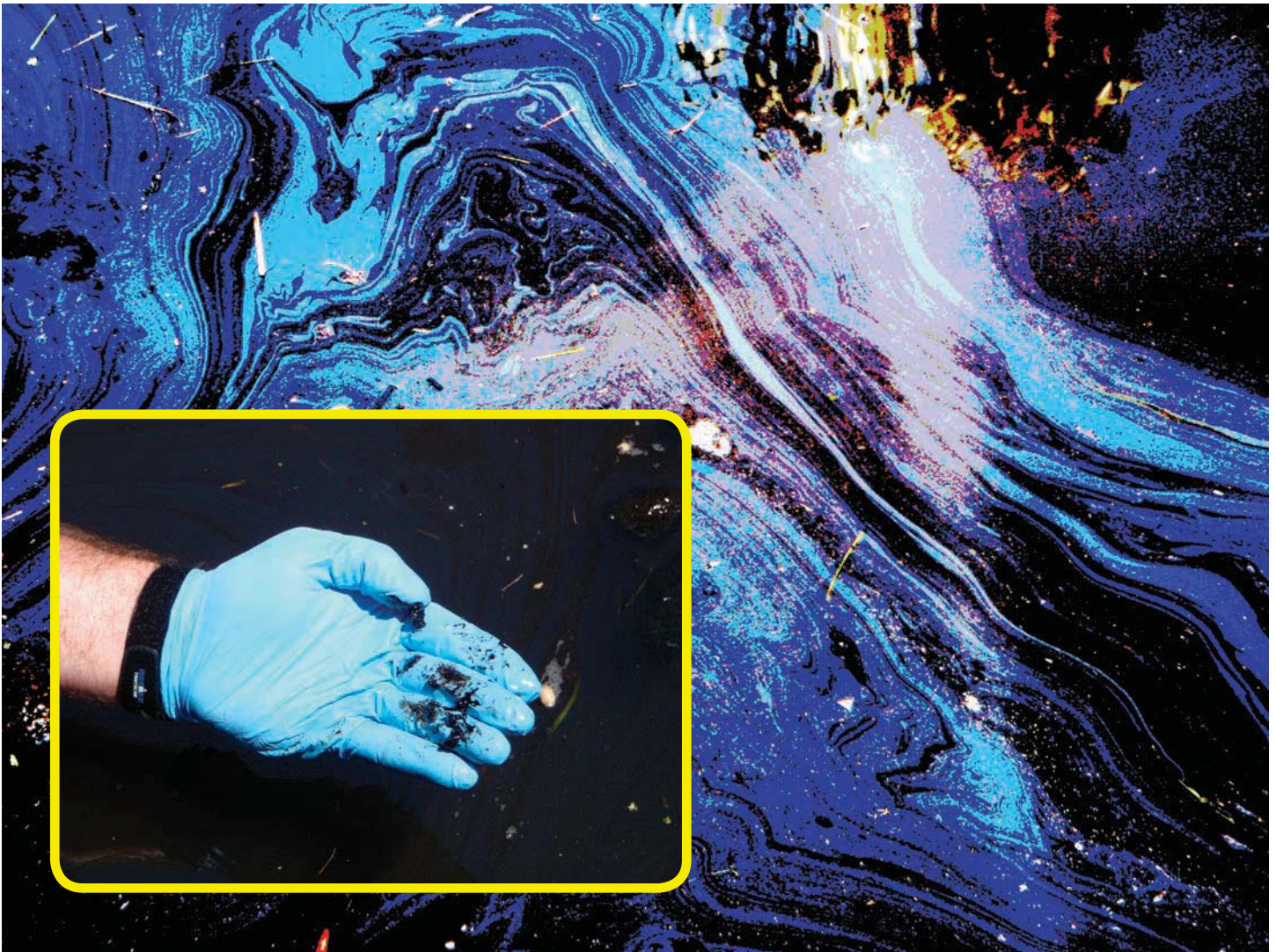**USGS**
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Oil-Particle Interactions and Submergence from Crude Oil Spills in Marine and Freshwater Environments—Review of the Science and Future Science Needs

Open-File Report 2015–1076

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U.S. Department of the Interior
SALLY JEWELL, Secretary

U.S. Geological Survey
Suzette M. Kimball, Acting Director

U.S. Geological Survey, Reston, Virginia: 2015

Acknowledgments

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Conversion Factors

SI to Inch/Pound

Multiply	By	To obtain
Length		
micrometer (µm)	0.000039	inch (in.)
centimeter (cm)	0.3937	inch (in.)
millimeter (mm)	0.03937	inch (in.)
meter (m)	3.281	foot (ft)
kilometer (km)	0.6214	mile (mi)
Area		
square meter (m^2)	0.0002471	acre
square kilometer (km^2)	247.1	acre
square centimeter (cm^2)	0.001076	square foot (ft^2)
square meter (m^2)	10.76	square foot (ft^2)
square kilometer (km^2)	0.3861	square mile (mi^2)
Volume		
liters (l)	0.0063	Barrel (petroleum, 1 barrel = 42 gal)
liters (l)	0.2642	gallon (gal)
cubic meter (m^3)	6.290	barrel (petroleum, 1 barrel = 42 gal)
cubic meter (m^3)	35.31	cubic foot (ft^3)
cubic meter (m^3)	1.308	cubic yard (yd^3)
Flow rate		
meter per second (m/s)	3.281	foot per second (ft/s)
cubic meter per second (m^3/s)	35.31	cubic feet per second (ft^3/s)
Density		
gram per cubic centimeter (g/cm^3)	62.4220	pound per cubic foot (lb/ft^3)
Stress		
pascal (Pa)	0.000145	pound per square inch (psi)
Dynamic viscosity		
centipoise (cP)	2.42	pound/foot-hour (lb/ft-hr)
Energy dissipation rate		
square meters per cubic second (m^2/s^3)	10.76	square feet per cubic second (ft^2/s^3)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows: °F=(1.8×°C)+32

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By Faith A. Fitzpatrick[1], Michel C. Boufadel[2], Rex Johnson[3], Kenneth Lee[4], Thomas P. Graan[5], Adriana C. Bejarano[6], Zhenduo Zhu[7], David Waterman[7], Daniel M. Capone[8], Earl Hayter[9], Stephen K. Hamilton[10], Timothy Dekker[11], Marcelo H. Garcia[7], Jacob S. Hassan[12]

Abstract

Oil-particle interactions and oil submergence are of much interest to oil spill responders and scientists, especially as transportation of light and heavy crude oils increases in North America's coastal marine and freshwater environments. This report contains an up-to-date review of the state of the science for oil-particle aggregates (OPAs), in terms of their formation and stability which may alter the transport, fate, and toxicity of the residual oil and, hence, its level of ecological risk. Operational considerations—detection, containment, and recovery—are discussed.

Although much is known about oil-particle interactions in coastal marine environments, there remains a need for additional science on methods to detect and quantify the presence of OPAs and to understand their effects on containment and recovery of oil spilled under various temperature regimes and in different aquatic habitats including freshwater environments.

Introduction

Suspended particles affect the fate and transport of spilled oil in aquatic environments (Muschenheim and Lee, 2002; Owens and Lee, 2003; Khelifa and others, 2005a, b, c; Sun and Zheng, 2009; Gong and others, 2013), such as rivers and floodplains, shorelines and beaches along lakes and oceans, coastal and riparian wetlands, and deeper waters of oceans and lakes. The manner in which oil interacts with particles and its eventual transport and fate depend on the physical properties of the oil and the particles, as well as environmental conditions including the geomorphic setting, weather, currents, and vertical mixing of the water column (Lee, and others, 2011a; Lee and others, 2002) (fig. 1).

Combinations of oil and particles have various names, including clay-oil flocculation (Bragg and Yang, 1995), oil-mineral aggregates (Lee and others, 1998) and oil-suspended sediment-aggregates (Khelifa and others, 2002) depending on the type of particle involved in the interaction. The term oil-particle aggregate (OPA) is used in this report because it is the more generic term that includes a wider range of particles containing both mineral sediment and organic matter in association with oil that may be retained in suspension and (or) settled out.

[1]U.S. Geological Survey Wisconsin Water Science Center, [2]New Jersey Institute of Technology, [3]Global Remediation Technologies, Inc., [4]Commonwealth Scientific Industrial Research Organization (CSIRO), [5]Weston Solutions, Inc., [6]Research Planning, Inc., [7]University of Illinois Ven Te Chow Hydrosystems Laboratory, [8]Mannik Smith Group, [9]U.S. Army Corps of Engineers, Engineer Research and Development Center, [10]Michigan State University, [11]LimnoTech, Inc. [12]U.S. Environmental Protection Agency
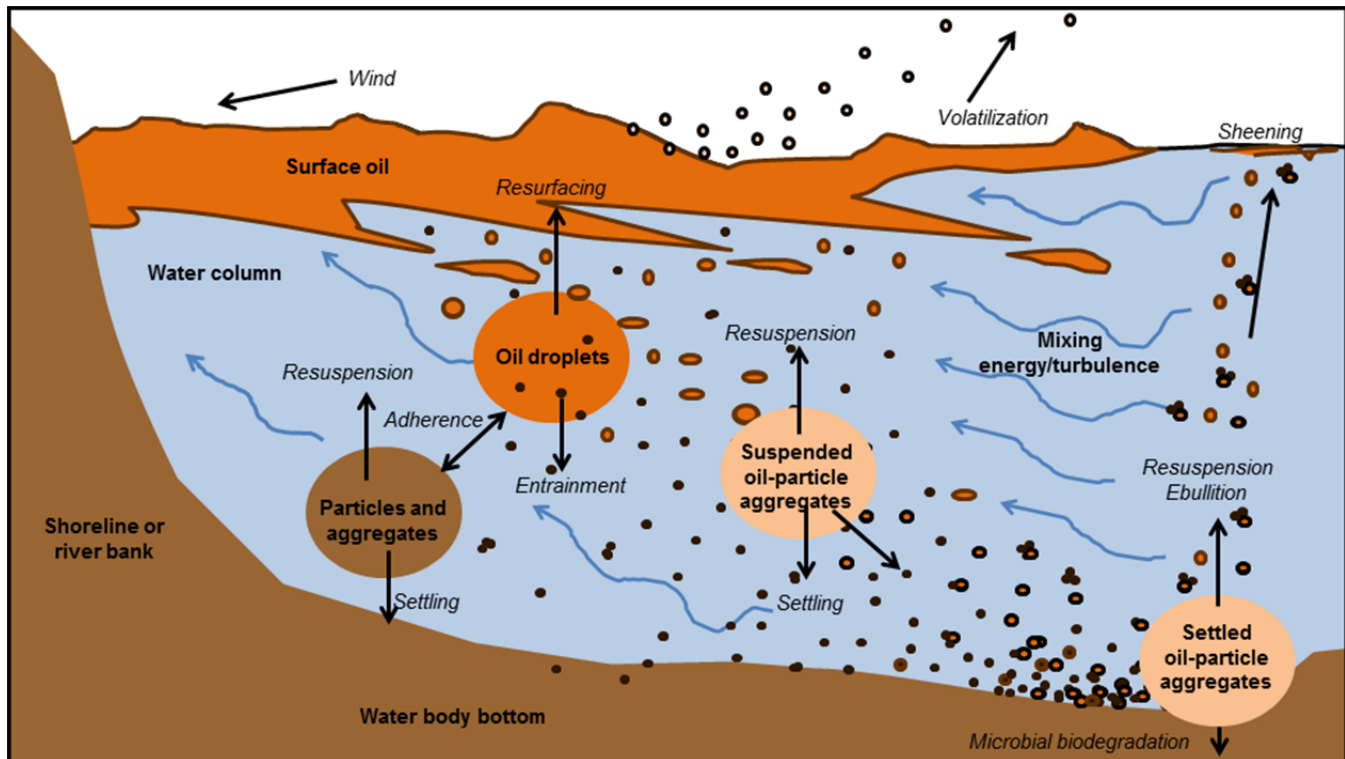
Figure 1. Simplified diagram of the processes and mechanisms leading to oil-particle aggregate formation and breakup in marine and freshwater environments. (modified from Environment Canada, 2013; OPA, oil-particle aggregate).

Traditional clean-up methods based on physical recovery of oil slicks on surface waters, such as booming and skimming, are ineffective for spilled oil once it submerges. Observations of OPA formation associated with the transfer of oil to the benthic environment (Lee, 2002; Payne and others, 2003; Sterling and others, 2005; Passow and others, 2012) have provided the justification for additional scientific studies to understand the processes and characteristics associated with OPA formation and their transport and fate. Results from additional studies will likely influence oil spill response contingency planning and spill response operations that include methodologies for detection, monitoring, recovery, and containment (Bandara and others, 2011; Environment Canada, 2013; Dollhopf and others, 2014; Hansen, 2014).

OPA formation has been correlated with the removal of oil stranded within sediments in freshwater and marine environments by both natural recovery (natural attenuation) and active remediation procedures (the addition of suspended particulate material in the presence of turbulent mixing energy) (Bragg and Yang, 1995; Lee and others, 1996; 1997; Wood and others, 1997; Lee, 2002; Lee and others, 2002; Owens and Lee, 2003). Lee and others (1997; 2003a) note that OPA formation accelerated the removal of stranded oil within the intertidal/surf zone by reducing the adhesive properties of the oil and the tendency of dispersed droplets stabilized by mineral fines to re-coalesce. Thus, either formed naturally or enhanced with addition of clay minerals, the relatively stable OPAs are dispersed more easily in the water column, potentially reducing the oil to concentrations below toxicity threshold limits (Lee and others, 2003a; Lee and others, 2003b) and making the oil more available for biodegradation (Weise and others, 1999; Lee and others, 1996; Lee and others, 1997; Lee and Merlin, 1999; Owen and Lee, 2003). Like chemical dispersants, the exposure pathway is altered

from water surfaces and shorelines to the water column, which transfers the toxicity risks from water fowl and shoreline organisms to planktonic, open water, and benthic species (Venosa and others, 2014).

Submergence can happen to light and heavy oils after they bind to relatively small amounts of particles (mineral sediment or organic matter). This can occur in suspension or while the oil moves along the bottom of a water body, bank, or coastline (Lee and others, 1985; Lee, 2002; Cloutier and others, 2003). The behavior of bitumen from the Canadian tar sands (usually more dense and viscous than traditional heavy oil), and particularly its interaction with particles leading to eventual submergence and accumulation of OPAs in sediments, has recently become a topic of much interest because of the 2010 Enbridge Line 6B pipeline release into the Kalamazoo River when more than 3.2 million liters of diluted bitumen were released into the Kalamazoo River in Michigan (Dollhopf and others, 2011). Response operations for that release began with conventional recovery techniques for floating oil and recovered about 2.9 million liters; however, submerged oil became the focus approximately 1 month into the cleanup and remained the focus through the summer of 2014 (Enbridge Energy, L.P., 2010; Dollhopf and others, 2014). Given the timely research efforts pertaining to the Canada Northern Gateway proposed pipeline, recent studies provided insights on the buoyancy (King and others, 2014), interaction with mineral fines (King and others, 2015), and the ultimate fate of OPAs formed from bitumen (Environment Canada, 2013).

Light crude oil can interact with particles along rivers, as indicated by the 2013 derailment, explosion, and spill of light crude oil in Lac-Mégantic, Quebec when an estimated 100,000 liters of oil spilled into the Chaudière River. A management plan by the Government of Quebec was developed that included recommendations for cleanup of river bottom sediment contaminated with hydrocarbons (Gouvernement du Quebec, Depot Legal, 2014). Laboratory tests at Louisiana State University using E2MS 303 oil from the February 2014 spill of Bakken crude from a barge collision into the lower Mississippi River indicate that the "oil will quickly adhere to suspended solids in the water column, forming unstable emulsions" (Doelling and others, 2014).

More than 15 years ago, before the emergence of concerns about increased pipeline transport of diluted bitumen, the National Coastal Research Council (on behalf of the U.S. Coast Guard) published "Spills of Nonfloating Oils: Risk and Response," a report that included specific recommendations for detection, monitoring, modeling, and recovery of submerged oil, mainly in marine environments (National Research Council, 1999). These recommendations were further tabulated into science needs for detection and monitoring, fate and transport, containment and recovery, and effects and restoration and included specific mention of OPAs (Coastal Response Research Center, 2007). Some areas of science support included developing better sensors to detect OPAs, mapping the extent of OPAs, and determining future resuspension and remobilization of OPAs in bottom sediment. The Coastal Response Research Center (2007) noted that improved characterization of the size, composition, and distribution of particles would enable better forecasting, observation, understanding, and hind casting of OPA behavior for a range of ecological and geomorphic settings.

Fisheries and Oceans Canada has been conducting oil-particle interactions studies with oil and chemically dispersed oils since the mid-1980s. An oil-particle interactions workshop was organized in 2000, and a compendium of papers appeared in the Spill Science and Technology Bulletin in 2003 and 2004 (Lee and Jarvis, 2004). These publications formed the basis for a quickly growing body of literature on the topic of OPAs in both marine and freshwater environments.

Because oil transportation in North America increased greatly on rails, through pipelines, and on barges and vessels as a result of the increased production of Bakken crude in the Williston Basin, North Dakota, and bitumen in the western provinces of Canada (Frittelli and others, 2014; Association of American Railroads, 2014; Committee for a Study of Pipeline Transportation of Diluted Bitumen,

2013), more attention is being given to submerged oil detection and response techniques in marine and freshwater environments (Coastal Response Research Center, 2007; Hansen, 2014). It is clear that more science is needed on the formation, settling, resuspension, and toxicity of OPAs, and the manner in which these properties vary depending on the nature of the oil and the characteristics of the aquatic environment it enters. Quantification of residual oil following spill response operations needs to account for the fraction of oil associated with suspended/settled particulate material.

Purpose and Scope

The purpose of this report is to describe the state of the science concerning OPAs—their formation, transport, settling, resuspension, and breakup in a variety of geomorphic environments including coastal marine, deep ocean, freshwater lacustrine (Great Lakes), and riverine, and brackish river mouths and harbors. The report contains a synthesis and review of available literature on OPAs from laboratory, experimental tank and flume studies, and some large-scale field experiments. Ongoing studies are described and needs for continuing investigation and new science on OPAs are listed.

Review of the Science

The U.S. Geological Survey (USGS) mission is to provide reliable scientific information to describe and understand the Earth; minimize loss of life and property from natural disasters; manage water, biological, energy, and mineral resources; and enhance and protect our quality of life. That mission has involved the USGS in providing science support for oil spill recovery. This review of the science on oil-particle interactions was motivated by questions that have arisen during oil spill response of the Enbridge Line 6B spill in Marshall, Michigan. However, the review is holistic in the sense that it incorporates spills of oils with various properties in freshwater and marine environments, as a result of concerns about spills from the rising quantities of crude oil produced and transported across the Nation. The following questions helped to form the major sections included in this review:

- What environmental conditions lead to the formation of OPAs?
- What is the effectiveness of adding particles to an oil spill for physical dispersion of oil as a spill countermeasure?
- What is the long-term fate and transport of OPAs?
- What are the ecological implications (fate and effects) of OPAs?
- Are there special circumstances for OPAs in cold climates for use as a spill countermeasure or for recovery in icy water?
- What are the operational considerations for recovery of OPAs?

Formation of Oil-Particle Aggregates

Formation of OPAs happens naturally when oil and suspended particles mix in turbulent water (Lee, 2002; Muschenheim and Lee, 2002; Owens and Lee, 2003; Khelifa and others, 2005a; Sun and Zheng, 2009; Gong and others, 2013). An understanding of the exact mechanisms of OPA formation comes mainly from the use of laboratory shaker and wave tanks, including those at the Bedford Institute of Oceanography, Dartmouth, Nova Scotia (Center of Offshore Oil and Gas Environmental Research, 2004), and flume experiments. Results from wave tank and laboratory shaker experiments provide empirical data for models of OPA formation and breakup (Stoffyn-Egli and Lee, 2002; Li and others, 2007; Ma and others, 2008; Wang and others, 2011). However, field observations and data from

assessment and monitoring activities at spill sites yield information on the timing and range of environmental conditions under which OPAs have formed (Niu and others, 2011).

Major factors affecting the formation of OPA are (1) quantity and viscosity of the oil, interfacial tension of oil-water, and chemical composition of the oil; (2) quantity, type, and surface properties of the particles; (3) magnitude and variability in physical energy of the aquatic environment; (4) temperature; and (5) salinity (Lee, 2002; Khelifa and others, 2002; Payne and others, 2003). Recent tests have focused on the highly viscous diluted bitumen (dilbit) product (Zhao and others, 2014a). In spills of heavy crude oil, particularly bitumen, freshwater environments with fine-grained sediment in the water column and bottom, abundant sunlight, warm temperatures, and strong currents and turbulence create a high potential for oil submerging and ultimately being deposited in the sediments (Silliman, 2014).

The first step to forming OPAs lies with the initial breakup of a slick of oil into oil droplets. Once spilled into a water body with turbulence created by waves or currents, floating oil can break up into droplets and reach a stable droplet size distribution (DSD) relatively quickly, perhaps in minutes to tens of minutes (Zhao and others, 2014b). Smaller droplets are generated when the interfacial tension of oil-water is small and (or) the oil viscosity is small. The interfacial tension of oil-water is more or less constant in the absence of surfactants. However, oil viscosity can increase by orders of magnitude among different types and temperatures of oils (fig. 2). For example, the viscosity of a heavy crude oil or bitumen is at least 1,000 times that of light crude such as a product from the Alaska North Slope or Bakken Formation oil (http://www.etc-cte.ec.gc.ca/databases/oilproperties/Default.aspx). Figure 2 contains a summary of American Petroleum Institute (API) gravity and viscosity for the major categories of crude oil (American Petroleum Institute, 2011). Crude oil densities are usually measured in terms of degrees API gravity. A higher API gravity corresponds with lighter density, with freshwater at 10 degrees API. Crude oils are generally further categorized by their type of hydrocarbon base (paraffinic or naphthenic) and sulfur content (high–sour, low–sweet).

For the common numerical models for the evolution of the DSD, it has been assumed that the interfacial tension is the only force resisting the breakup of droplets (Prince and Blanch, 1990; Tsouris and Tavlarides, 1994), which is not the case for high viscosity oils or for situations when surfactants (in the form of chemical dispersants) are used (Wang and Calabrese, 1986). Alternatively, Delvigne and Sweeney (1988) developed an expression that predicts dispersion, which is based on oil viscosity without any information on the oil-water interfacial tension. Thus, the Delvigne and Sweeney (1988) formula cannot be relied upon to account for the reduction in the interfacial tension when dispersants are used. Recently, Zhao and others (2014b) developed a comprehensive model that accounts for resistance to breakup from both interfacial tension and viscosity of the oil. This model is called VDROP to stress the important role of viscosity. The DSD depends also on the mixing energy, namely the dissipation rate of kinetic energy (National Research Council, 2005; Kaku and others, 2006). Thus, high mixing energy promotes the breakup of droplets (fig. 1). In addition, dilution (as oil mixes with a larger volume of water away from the source) increases the distance between oil droplets and thus minimizes the probability of collision and subsequently the coalescence of oil droplets into larger droplets.
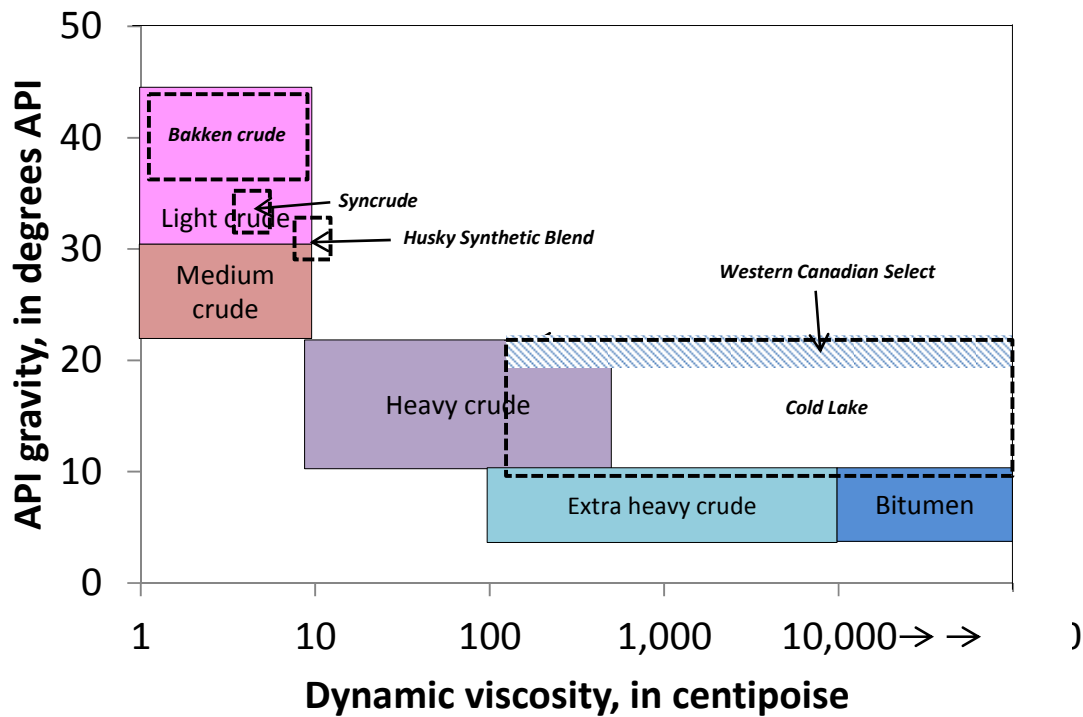
Figure 2.   Summary of American Petroleum Institute (API) gravities and dynamic viscosities (at approximately 10-20 degrees Celsius) for major categories of crude oil types and bitumen/oil sands. Overlays are of example crude oils commonly transported in North America. Data summarized from Attanasi and Meyer (2007), American Petroleum Institute (2011), Sia Partners Energy Outlook (2011), Environment Canada's Oil Properties Web Site http://www.etc-cte.ec.gc.ca/databases/oilproperties/Default.aspx, Andrews (2014), Doelling and others (2014), Crude Quality, Inc. (2014); and Enbridge Energy Partners, L.P. (2013).

The size of the oil droplet is a very important factor in the transport and fate of the oil and its interaction with particles. Because large droplets have higher buoyancy than smaller droplets, they tend to float to the water surface, whereas smaller droplets could be driven more easily in the water column as a result of mixing energy (Boufadel and others, 2007). Smaller droplets also have a larger specific area than large droplets, which would enhance dissolution and microbial biodegradation (Lee and others, 1997; Lee and Merlin, 1999; Reddy and others, 2012; Geng and others, 2013).

When particles are attached to oil droplets, they form a type of barrier around the droplet that keeps it from coalescing with other oil droplets (Khelifa and others, 2005a). Droplets with particles result in three main features that contribute to the eventual fate and submergence of droplets: (1) OPA-enhanced stability of the oil droplets that limits coalescence; (2) increased specific density of coated droplets which causes dispersion into a water body and possible settling; and, (3) enhanced microbial degradation.

The actual attachment of oil droplets to particles depends on the viscosity and adhesion properties of the oil droplet and the surface area of the particles, as well as salinity of the water body (Lee, 2002; Khelifa and others, 2005a). There is evidence that salinity increases the formation of OPAs as a result of the reduction of the thickness of the double layer with increased ionic strength of water (Clark, 2009). However, OPA was also observed to form in freshwater (Lee, 2002; Lee and others, 2002). If the droplet size distribution of oil has not reached a steady state prior to interaction with the

particles, the interaction would affect the breakage mechanism of oil droplets. The reduction in the net interfacial tension resulting from attachment of particles would make the oil viscosity the main force resisting oil breakup. In such a case, a model that accounts for oil viscosity in resisting breakup is needed, such as VDROP (Zhao and others, 2014b).

Particle size, amount, and type are important to the formation of OPAs. Clay-sized mineral particles are effective at forming OPAs, especially if the particles are present in large concentrations (Lee and others, 1998; Lee, 2002). However, most natural waters have a range of particle sizes or at least bimodal distributions, and natural particle-size distributions also may vary with the amount of mixing resulting from waves or currents (Boufadel and others, 2007). The particles may be smaller than the oil droplet and form a coating, or they may be larger or the same size for an aggregate. In either droplet type (fig. 3A), the attachment of the oil droplet and particle reduces the interfacial tension of the OPA with the water, and thus the particles have an overall effect similar to surfactants (Lee, 2002). Oil also may attach to mineral or organic matter (Lee, 2002). Phytoplankton can readily form oil-organic aggregates in laboratory tests (Lee and others, 1985). Particle concentrations can be relatively low and still form OPAs (Lee and Stoffyn-Egli, 2001; Rymell, 2009); Khelifa and others (2002) note that, in laboratory shaker experiments with seawater, mineral concentrations as low as 100 milligrams per liter (mg/L) and moderate shaking resulted in OPA formation with various types of oil.

The shape and makeup of OPAs can take multiple forms. Methods used to study the shape and makeup of OPAs, which are generally less than 1 millimeter (mm), involve instrumentation such as combined transmitted light/ultraviolet (UV) light epi-fluorescence microscopy, confocal scanning laser microscopy, and environmental scanning electron microscopy (Stoffy-Egli and Lee, 2002; Lee and others, 2012). The most common forms of OPAs involve a spherical oil droplet surrounded by particles or multiple spherical droplets in a particle aggregate (Bragg and Owens, 1994; Stoffyn-Egli and Lee, 2002; Khelifa and others, 2005a; Zhang and others, 2010; Lee and others, 2012) (fig. 3A). Spherical shaped OPA indicate that the spilled oil formed droplets before forming aggregates, as described in the previous paragraphs. Stoffyn-Egli and Lee (2002) also found two other types of aggregates in laboratory experiments—solid and flake types (figs. 3B and 3C)—that do not necessarily form from dispersed droplets. These additional types are distinguished in that the oil takes on more of the form of the particle or mineral, and the flake type is distinguished by having folds or rolls in a dendritic or feather shape. For all types, the combination of oil and particles can result in a range of specific gravities that are usually similar to, or heavier than, water; thus OPAs can be floating, neutrally buoyant (in suspension), or negatively buoyant (submerging or settling) (Stoffyn-Egli and Lee, 2002). Sometimes the mineral makeup of particles determines their buoyancy, and Omotoso and others (2002) found that low-viscosity oils formed negatively buoyant OPAs with hydrophilic minerals (having a strong affinity for water) but formed positively buoyant OPAs with calcite minerals. Lastly oil-particle interactions can be enhanced by colloidal mechanisms of coagulation of ions (Lee and Stoffy-Egli, 2001), as well as biological activity associated with bacteria and phytoplankton (Passow and others, 2012).

Laboratory simulations of the formation of OPAs in a brackish (salinity of 1.5 parts per thousand) high-energy riverine environment (Rio Desaguadero) were done by mixing sediment-laden water and heavy crude oil from the 2000 OSSA II pipeline spill into the Rio Desaguadero in the Bolivian Altiplano (Lee and others, 2001; 2002). In this spill, a missing oil fraction of 27–37 percent was not recovered; presumably it succumbed to from oil dispersion and enhanced biodegradation caused by the formation of OPAs. The river sediment was rich in smectite clay minerals, which have an affinity for attracting or adsorbing water molecules. Also, the river was in flood stage, with velocities of 2.5 meters per second (m/s) and depths of less than 3 meters (m). Both of these factors may have enhanced OPA formation. The laboratory experiments, which were run at water temperatures of 20–22 degrees Celsius

(^{o}C), showed that the amount of OPA formation increased with increasing salinity, which is known to cause flocculation of clays. With a combination of fresh OSSA II oil (diluted with a kerosene-range petroleum product), Rio Desaguadero sediment, and solutions using natural seawater and dilution to obtain salinities of 0.35, 0.7, 1.2, 3.5, and 35 parts per thousand (ppt), OPA formation increased with increasing salinity, and at 35 ppt almost all of the oil was taken up in OPA formation (fig. 4). In contrast, a minimal amount of oil was present as OPAs with fresh oil, distilled water, and river sediment, but when the brackish river water was used (1.5 ppt salinity), about 25 percent of the fresh oil formed OPAs.
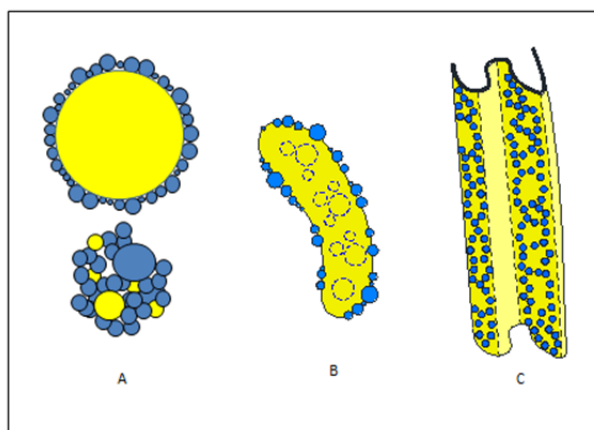
Figure 3.   Types of oil-particle aggregates: A, single and multiple droplet aggregate, B, solid aggregate of large, usually elongated mass of oil with interior particles (dashed blue circles), and C, flake aggregate of thin membranes of clay aggregates that incorporate oil and fold up (modified from Stoffyn-Egli and Lee, 2002). Blue color represents particles and yellow represents oil.
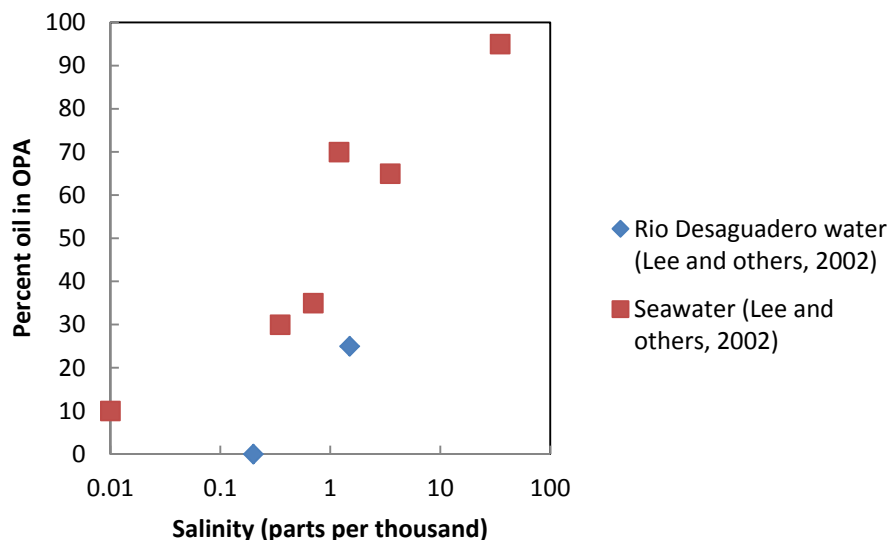
Figure 4.   Salinity in relation to the percent of oil in oil-particle aggregates (OPAs) from laboratory shaker tests of diluted heavy crude oil form the 2000 OSSA II spill into the Rio Desaguadero in Bolivia and its smectite-rich sediment. (Graph replotted from Lee and others, 2002).

Natural formation and submergence of OPAs occurred in the freshwater, low-gradient environment of the Kalamazoo River after the 2010 Enbridge Line 6B pipeline spill of diluted bitumen into Talmadge Creek, a tributary of the Kalamazoo River near Marshall, Michigan (Dollhopf and others, 2014). The diluent of natural gas condensate (which is used as a solvent in the mixture) volatilized and submergence of the bitumen occurred within a few weeks following the spill (Dollhopf and Durno, 2011; Lee and others, 2012). On the basis of laboratory tests of Cold Lake Blend by Belore (2010) and in an outdoor flume by King and others (2014), the density of the spilled bitumen (mainly Cold Lake Blend) was likely between 0.93 and 0.936 grams per cubic centimeter (g/cm^3) with diluent and 0.981 g/cm^3 after the diluent evaporated. The dynamic viscosity of the Cold Lake Blend in the Belore (2010) laboratory tests ranged from approximately 400 centipoise (cP) with diluent to more than 14,500 cP after evaporation of the diluent. Both the works of Belore (2010) and King and others (2014) were conducted at approximately 15^oC.

Some features of the Kalamazoo River likely enhanced the formation, resuspension, and deposition of OPAs. The Enbridge Line 6B pipeline release happened during a flood on the Kalamazoo River with an exceedance probability of 4 percent (for example, a 25-year event) (Hoard and others, 2010) and with a mean velocity of about 1.1 m/s and a mean depth of 1.2 m near the USGS streamgage at Marshall, Michigan (04103500). On the basis of later measurements of suspended sediment at the Marshall streamgage, it can be inferred that, at the time of the spill, the river had relatively low suspended sediment concentrations (less than 100 mg/L) (fig. 5) with suspended particle sizes mainly in the silt-sized range (65–75 percent) (fig. 6). Water temperatures were warm, in the range of 23–25 ^{o} C (Stephen Hamilton, Michigan State University, written commun., 2014). Floodwater increased turbulence in river flows and increased the presence of suspended particulate matter. Additional mixing from flows over two dams may also have played a role, although OPAs and submerged oil accumulated in the first 5 kilometers (km) of river length, between the spill source and the first dam. Aggressive sediment agitation techniques (raking, flushing, aeration, and skimming the river bottom physically or with water jets) were conducted in 2011 to liberate submerged oil as recoverable sheen in 2011 (Enbridge Energy L.P., 2011b; Dollhopf and others, 2014), potentially contributing to further OPA formation and transport of OPAs to downstream reaches (Lee and others, 2012). Lee and others (2012) found that oil from the pipeline spill readily formed OPAs when mixed with Kalamazoo River sediment in laboratory tests (fig. 7).

Assuming that the fraction of spilled oil not recovered by conventional techniques was lost to submergence, the bitumen that submerged in the Kalamazoo River was greater than 300,000 liters, which is around 10 percent of the spilled oil. This is based on the Enbridge Energy, L.P., reported spilled amount of 3.2 million liters and recovered amount of 2.9 million liters after the first year (U.S. Environmental Protection Agency, 2011). Although the volume of oil released and remaining in the river are not finalized at the time of this writing (January 2015), the estimated percentage is similar to that found by Lee and others (2002) for distilled water and brackish water of the Rio Desaguadero (fig. 4). Even though OPA formation in freshwater may be less than that in seawater, the persistent residual submerged oil and oiled sediment in the Kalamazoo River resulted in a protracted cleanup that ultimately required dredging and has accounted for a major share of the cleanup costs, which have surpassed $1.2 billion (Dollhopf and others, 2014).
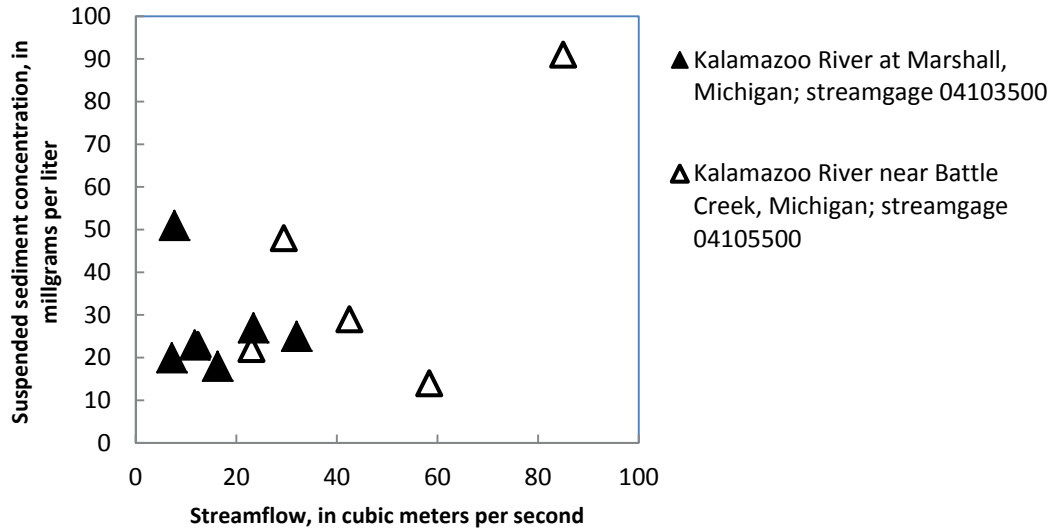
Figure 5.   Streamflow in relation to suspended sediment concentration in the Kalamazoo River, Michigan, August 2012-March 2014. Streamflow during the pipeline release on July 28, 2010, during a receding flood event with a 4-percent exceedance probability, was about 34 cubic meters per second (m³/s) at Marshall, Michigan and 85 m³/s near Battle Creek, Michigan. The Kalamazoo River is generally a suspended sediment supply -limited system, shown by the overall low concentrations over the entire flow range at both streamgages.
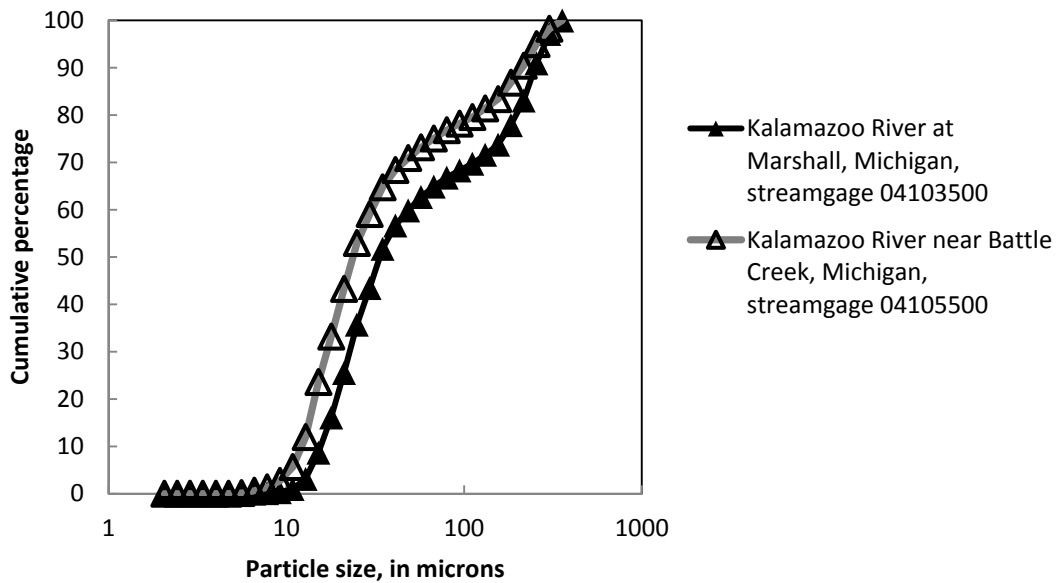
Figure 6.   Cumulative particle-size distribution for suspended sediment collected April 22, 2013, during flows of 32 cubic meters per second (m³/s) at Marshall, Michigan, and 85 m³/s near Battle Creek, Michigan. Most of the suspended sediment was in the silt-size class—about 65 percent at Marshall and 75 percent near Battle Creek. Samples analyzed with portable laser in-situ scattering and transmissiometry.
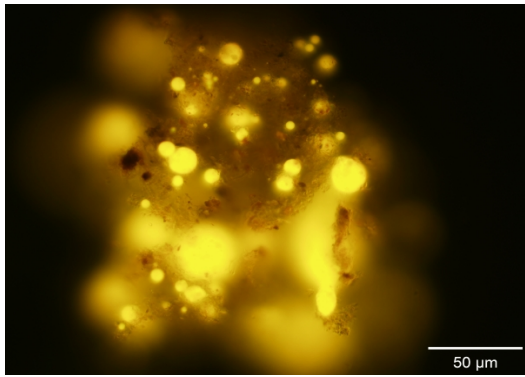
Figure 7.   Kalamazoo River sediment spiked with weathered source oil after 48 hours, under ultraviolet-epifluorescence microscopy at 320 times magnification. (from Lee and others, 2012).

Some additional features of the Kalamazoo River may have been important factors in OPA formation, transport, and deposition. The floodplain of the Kalamazoo River has abundant wetlands, thus suspended and bottom sediments have relatively high organic matter content, on the order of 20 percent or more. The river is wide (width/depth ratios of 40) and has an average gradient of 0.06 percent in the spill-affected reach. Deposition of OPAs occurred along channel margins, backwaters, side channels, and oxbows, and in impoundments throughout the entire 61- km stretch of the river affected by the oil spill. Surveys over time provided evidence for resuspension and resettling of OPAs in downstream areas, presumably during post spill floods (Dollhopf and others, 2014).

Oil-Particle Aggregates as a Natural Physical Dispersant

Enhancing physical dispersion of spilled oil through the addition of particulate matter is one of several techniques that have been used for spill cleanup and to prevent oiling of marine coastal areas (Zhang and others, 2010). The oil would be dispersed into small droplets by turbulent mixing from waves or currents and subsequently mixed with mineral and organic particles in the water column. The aggregation of the oil with particles to form OPAs and their subsequent physical dispersion by natural processes would reduce the bioavailability and toxicity of the residual oil to aquatic organisms in the vicinity of the spill. Furthermore, as the activity of oil degrading bacteria is focused at the oil water interface, the formation of small oil droplets enhances microbial biodegradation (Lee and others, 2002; 2009). Petroleum hydrocarbons are not new to the environment because of natural sources such as seepage from oil bearing rocks and biological production by plants and animals. Thus, indigenous oil degrading bacteria are readily available in many aquatic ecosystems (Atlas and Hazen, 2011).

OPA formation has been reported to be a significant contributor to the natural cleansing mechanisms observed during the Baffin Island Oil Spill (BIOS) project and recovery following the Exxon Valdez oil spill incident in 1989 (Bragg and Owens, 1994; Bragg and Yang, 1995). Studies have shown that microorganisms (namely bacteria and archea) within ocean floor sediments in the proximity of natural oil seep sites, such as Scott Inlet, Baffin Island, and the Gulf of Mexico have adapted to utilize oil droplets as a carbon and energy source (Grant and others, 1986; Atlas and Hazen, 2011). The current scientific consensus is that a considerable portion of the oil spilled in the Gulf of Mexico from the Deepwater Horizon incident has been degraded by indigenous bacteria (Atlas and Hazen, 2011; National Research Council, 2013). Considering the magnitude of the spill, Edward Owens (Polaris Applied Science, Inc., oral commun., 2014) has hypothesized that the volume of oil affecting the Gulf of Mexico shoreline was much less than expected, because of the interaction of dispersed oil and surface oil slicks with the naturally high concentration of particulate suspended material near the coast.

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Boufadel et al. (2014) conducted a comparison between the DWH and the Exxon Valdez spills, and based on calibrated modeling, they estimated that around the same mass of oil reached the shorelines from the two spills (around 20,000 tons). But the percentages to the total mass of oil were around 5 percent and 50 percent for the DWH and Exxon Valdez, respectively. For the 1989 Exxon Valdez oil spill, much of the oil along shorelines was depleted (Atlas and Hazen, 2011), except in some beaches with anoxic conditions (Boufadel and others, 2010; Li and Boufadel, 2010).

With natural particulate matter readily available in a coastal marine or lacustrine environment, and especially along river systems, OPA formation must be considered a natural process that enhances the physical dispersion of oil. Indeed, expanding on this hypothesis, Lee and others (2009) suggested that active enhancement of OPA production as a "physical" means to promote oil dispersion, could be an alternative to the use of chemical dispersants that may be potentially toxic in their own right. However, prescribed sinking of spilled oil, or the use of sinking agents, is currently prohibited by U.S. Environmental Protection Agency (EPA) because of the potential risks of acute and chronic toxic effects on benthic organisms and possibly less biodegradation once the oil is deposited (U.S. Environmental Protection Agency, 1993; also 40 C.F.R. §§ 300.310(b), 300.910(e)).

Laboratory experiments have expanded on the knowledge base of the manner in which OPAs facilitate physical dispersion in both seawater and freshwater. For seawater, simulations of coastal environments by Li and others (2007) in wave tank experiments found that chemical dispersants and the addition of fine mineral particles, alone and in combination, enhanced the dispersion of light crude oil in the water column and increased the number of OPAs formed. Similarly, results from wave tank studies of light crude oil with seawater (Lee and others, 2008) indicate that chemical dispersants enhanced OPA formation by transferring oil from a slick floating on the water surface into oil droplets in the water column that more easily interacted with suspended particles. Zhang and others (2010) considered three crude oils (Mesa, Alaska North Slope, and Heidrun) with specific gravities from 0.8746 to 0.9058 g/cm^3 (at 22°C). They conducted laboratory experiments in seawater to evaluate the combined effects of three factors—chemical dispersants, mixing energy, and mineral types—on OPA formation. They also discussed the usage of OPA as a response technique. They found that hydrophobicity (aversion toward water), particle size, and specific surface area of minerals are key factors, which is consistent with other findings in the literature. Slightly hydrophobic particles enhanced formation of OPAs by promoting the attachment of mineral particles to oil. However, highly hydrophobic particles clumped together and did not interact with the oil. Therefore, there was an optimum range of hydrophobicity for maximum OPA formation. If minerals were hydrophilic, the OPAs were generally spherical. Hydrophobic minerals formed irregularly shaped OPAs. The OPAs were larger for hydrophobic particles than for hydrophilic minerals. Chemical dispersants when added became the overriding factor affecting OPA formation because of their stabilizing effect on oil droplets. High mixing energy enhanced dispersion of oil into the water column to form droplets and small-sized OPAs. The Zhang and others (2010) study concluded that in areas of low mixing energy, a chemical dispersant might be needed with a co-application of fine mineral particles to form OPAs.

Laboratory studies in freshwater using automated shaker tests of mixtures of kaolinite clay-sized particles and heavy and intermediate fuel oils (viscosities of 3,900 and 1,350 cP, respectively) were conducted by Perez and others (2014) to simulate of the interaction of oil slicks and suspended sediment in steep, turbulent rivers. Using a spectrophotometer for oil measurement, the amount of oil entrained by sediment was observed to be moderate for heavy fuel oils at wave heights of 2.5 and 7 cm and kaolinite concentrations of up to 16,000 parts per million (ppm). They predicted that a surface slick of 1,000 kg of IFO across a river width of 10 m would result in about 8 percent of the oil entrained in OPA over a 1 km length. However, there was a large variability in the data, and thus these results still need

confirmation of scaling factors using either large scale experiments or with computational fluid dynamics models.

Khelifa and others (2005b) and Niu and others (2010, 2011) developed predictive models to estimate the contribution of OPAs to the dispersal of spilled oil and their potential to cause secondary detrimental effects associated with physical inhibition (that is smothering of benthic organisms) or toxicity. Factors considered in these models include the calculation of the maximum size of droplets, prediction of oil droplet formation from a slick, prediction of sediment aggregate formation, and the calculation of the density of the resultant oil-sediment aggregate. Inputs to the models include environmental conditions, oil properties, and concentration and particle-size distribution of suspended sediment. In a model sensitivity analysis of five crude oils (Hibernia, Louisiana, Prudhoe Bay, Arabian Light, and Alaska North Slope), with a range of densities from 25 to 37 degrees API and dynamic viscosities from 8 to 68 cP, the kinetic energy dissipation rate was varied from 10^{-3} to 10^2 square meters per cubic second (m^2/s^3) with a sediment particle size of 3 micrometers (μm) and concentration of 250 mg/L; the study showed that OPA formation is strongly dependent on the oil-water interfacial tension and kinetic energy dissipation rate. The OPA contribution to oil dispersion increased when energy dissipation rates were about 1 watt/kg or higher. High turbulence in surf zones or in rivers should therefore be conducive to higher rates of OPA formation.

Transport and Fate of Oil-Particle Aggregates

As described in the section "Oil-Particle Aggregates as a Natural Physical Dispersant", formation of OPAs changes the fate and transport of oil by potentially changing its rate of horizontal and vertical transport, and biodegradation and levels of bioavailability, which ultimately influence the ecological effects of OPAs. Because of the range of variance in physical, chemical, and biological conditions between sites (for example, types of suspended particulate organic/inorganic material, type of oil, mixing energy) differences in the transport and fate have been observed between marine and freshwater environments. In the coastal marine environment, the formation of OPAs has been found to improve removal of stranded oil from low-energy intertidal environments and is considered to be a natural self-cleansing process that enhances recovery rates following a spill (Lee, 2002). In contrast, in lowland rivers with gentle gradients, naturally formed OPAs can lengthen oil spill cleanup times and require deployment of less conventional and more costly sediment remedial measures (Dollhopf and others, 2014; Gouvernement du Quebec, Depot Legal, 2014). For example, in the 2010 Enbridge Line 6B spill of diluted bitumen into the Kalamazoo River, approximately 100 hectares (250 acres) of oiled sediment remaining in impounded sections of the river was removed by dredging and excavation during 2013–14, in response to persistent sheening problems (Dollhopf and Durno, 2011; Dollhopf and others, 2014). Oil globules and OPAs of various sizes, up to a few mm in size, were resuspended during floods, released upon mechanical agitation or physical disturbance of the sediment, and liberated by gas bubbles rising to the surface in a process called ebullition (as happens naturally when methane is produced in freshwater sediments) (fig. 1). Similarly, following the Lac-Mégantic light crude train spill in the Chaudière River, Quebec, Canada, oiled sediments created a challenge to clean-up operations downstream from the spill site over a 30 km reach of the Chaudière River (Gouvernement du Quebec, Depot Legal, 2014).

Modeling the transport and fate of OPAs in riverine systems requires integration of hydrodynamic, sediment transport, and contaminant fate and transport models (Dollhopf and others, 2014; Niu and others, 2010, 2011), while employing some of the same guidelines used for developing conceptual and mathematical models of fate and transport of contaminated sediment at hazardous waste sites (U.S. Environmental Protection Agency, 2005). Simplified fate and transport studies were done for

the 2010 Kalamazoo River spill by considering OPAs in a steady state of physical properties, including size, concentration, specific gravity, erosion rates, and settling velocities, as well as hydrocarbon content (Dollhopf and others, 2014). More complex models, accounting for advection/diffusion, settling, resuspension, and breakup characteristics, are being considered for freshwater (riverine and deep-water settings) and marine environments (Lee and others, 2011a; Niu and others, 2011, 2014) and can be built from simpler models that simulate oil slicks (Weaver, 2004).

For the Enbridge Line 6B diluted bitumen spill into the Kalamazoo River, a 2-dimensional (2-D) Environmental Fluid Dynamics Code (EFDC) model was constructed to determine areas of the river prone to resuspension and deposition of submerged oil and oiled sediment under different flow conditions (Hamrick, 1992; Enbridge Energy L.P., 2012a; Dollhopf and others, 2014). Initially, OPAs were assumed to behave similarly to silt-sized particles because the OPAs accumulated in depositional areas and impounded sections of the river with organic- and silt-rich soft sediment. To account for differences in behavior, the model was updated with a new algorithm for OPAs that was incorporated into the sediment transport code of the SNL-EFDC model—a modified version of the original EFDC code developed and maintained by Sandia National Laboratory (James and others, 2005; Thanh and others, 2008). This version of the EFDC model incorporates a custom sediment transport sub-model that is based on the SEDZLJ model algorithms developed by Craig Jones and Wilbert Lick at the University of California – Santa Barbara (Jones and Lick, 2001). The OPA algorithm includes particle classes for representing two types of OPA—a sediment coating on an oil droplet and oil droplets in a particle-dominated aggregate. This algorithm and its application to EFDC and SEDZLJ are under development by the U.S. Army Corps of Engineers Engineering Research and Development Center at the time of this writing (January 2015). Hydrodynamic model results of velocity and horizontal bed shear stress from 2-D and 3-dimensional (3-D) EFDC model simulations of various flows and containment situations on the Kalamazoo River helped to target areas of the 61 km of oil-affected Kalamazoo River where submerged oil and OPAs were subject to resuspension and downriver migration during high flows (Dollhopf and others, 2014; Enbridge Energy L.P., 2012a).

Erosion rates of soft sediment became an important parameter in the modeling because these areas tended to have moderate/heavy oiling, and some of the areas in impoundments switched from depositional to erosional during high flows. The soft sediment was cohesive, and onsite sedflume tests were performed by the U.S. Army Corps of Engineers to parameterize the sediment transport and OPA algorithms in the EFDC models (Perkey and others, 2014). Critical shear stresses of soft sediment with moderate/heavy oiling ranged from 0.1 Pascals (Pa) at the surface to 1.0 Pa at 20 cm beneath the surface (Perkey and others, 2014).

Another approach for fate and transport modeling in rivers is a Lagrangian approach, also known as particle tracking. This approach has been used by the Ven Te Chow Hydrosystems Laboratory at the University of Illinois for the Kalamazoo River and builds on the existing EFDC-based hydrodynamic model.

For impoundments with accumulations of thick fine-grained sediment, the process of bubble formation and release from sediments (ebullition) is likely to be an important mechanism for resuspending OPAs in the water column and releasing oil as sheen on the water surface. Spontaneous releases of oil globules and floating OPAs have been observed regularly in the impounded sections of the Kalamazoo River during 2011–14, resulting in oil sheens at the water surface (Dollhopf and others, 2014). The impoundments had generally 0.5 to 4-m thick accumulations of fine-grained organic-rich sediment which, under anaerobic conditions, allows for bacterial generation of methane (McLinn and Stolzenburg, 2009). These bubbles could rise based on their size and buoyancy, and their release from the sediments could be enhanced by disturbances such as fish and boats movement, falling water levels,

and dropping barometric pressures. Methane production and ebullition are enhanced by warm summer water temperatures (as high as 28°C) that promote bacterial activity and reduce the solubility of methane in sediment porewaters.

Ecological Risk and Toxicity of OPAs and Oiled Sediment

The aquatic toxicity of OPAs is of interest, whether the OPAs formed through addition of minerals as a dispersant or from association of oil droplets with suspended inorganic and organic particles naturally present in a water body after the spill. Once oil droplets are aggregated with particles and submerge, associated contaminants, especially polycyclic aromatic hydrocarbons (PAHs), become a potential problem to suspended and benthic aquatic organisms, including plankton, zooplankton, invertebrates, mussels, and clams, and any higher level organisms that consume them (Long and others, 1998; MacDonald and others, 2000; Passow and others, 2012; Almeda and others, 2013). On the other hand, as illustrated during field studies, oil bound up in OPAs may be diluted to below toxicity threshold limits (Lee and others, 2003b) and may become more available for biodegradation (Lee and others, 1997; Lee and Merlin, 1999). An important ecological consideration is closely linked to the turbulent energy of the environment with more risk associated with submerged OPAs in depositional or low energy environments. Freshwater depositional environments are common in low-gradient rivers, river mouths and harbors, impoundments, ponds, lakes, and wetlands. Low-energy marine environments are likely similar (Niu and others, 2011). Thus, a major factor in ecological risk is whether the OPAs are physically diluted in suspension or concentrated in deposition. The added context of water depth and the geographic extent are also important. However, oil droplets and OPAs have a size range similar to that of planktonic food sources for zooplankton, and biogeochemical processing by organisms could increase or decrease toxicity within different components of the aquatic food web (Passow and others, 2012; Almeda and others, 2013).

Data are sparse on the specific toxicity of OPAs in marine and freshwater environments but there are a few studies to draw upon. Qualitative analysis indicated that residual oil was in a highly biodegraded (that is, less toxic) state in suspended particulate material associated with OPA formation from surf washing operations during the Sea Empress Spill in the United Kingdom (Lee and others, 1997). In terms of the application of bioassays, samples recovered from sediment traps deployed in the immediate area off an experimentally oiled beach site in Svalbard, Norway, remediated by the enhancement of OPA formation by surf-washing, were found to be within Environment Canada's acceptable regulatory limits for the disposal of dredge spoils (Lee and others, 2003a; Lee and others, 2003b).

For freshwater riverine environments, limited acute toxicity testing was done for oiled sediment in the Kalamazoo River after the Line 6B oil release (Bejarano and others, 2012). As part of a Net Environmental Benefits Analysis, effects on aquatic organisms from weathered oil were assessed in laboratory acute toxicity studies of seven sediment samples collected from oil-affected backwater habitats along the Kalamazoo River in February 2012, about 19 months post-spill (Bejarano and others, 2012). Ten-day whole sediment toxicity tests using *Chironomus dilutus* (a species of midge) and *Hyalella azteca* (an amphipod crustacean) were performed by the Great Lakes Environmental Center, Inc., and included survival, growth and biomass as the toxicity endpoints (Great Lakes Environmental Center, 2012). Results from the toxicity tests indicated that *Chironomus dilutus* were more sensitive to oiled sediment (and presumably OPAs) than *Hyalella azteca* but that all samples exceeded the minimum survival (70 percent) and growth (0.48 mg ash-free dry weight at test termination) criteria for acceptable controls for the *C. dilutus* tests (Great Lakes Environmental Center, 2012).

Chemical analyses (PAHs, total extractable hydrocarbons) and sediment characterization (total organic carbon and sediment composition) were performed on a subset of the above described Kalamazoo River sediment toxicity samples (Bejarano and others, 2012; Great Lakes Environmental Center, 2012). Potential adverse acute and chronic effects on benthic organisms were evaluated using the Equilibrium Sediment Benchmark Toxic Unit Approach (U.S. Environmental Protection Agency, 2003) for sediment PAH data from the same samples used for the bioassays. The results from these analyses indicate that sediment from two heavily oiled sites and one lightly oiled site may pose acute and chronic risks to benthic fauna (*Chironomus dilutus* and *Hyalella azteca*). However, further analyses of the toxicity results in the context of several other sediment characteristics (chemical and physical) showed that unrelated variables, such as percentage of silt in the sediment sample, may have affected survival (table 1). On the basis of the weight of evidence approach and additional risk metrics, it is possible that residual oil from the Enbridge Line 6B oil spill at two heavily and one lightly oiled area may pose some risks to benthic receptors. Chronic toxicity effects from the Enbridge Line 6B residual oil remain unknown at the time of this writing (January 2015).

Table 1.   Nonparametric Spearman's Rho correlation coefficients between acute sediment toxicity test results and analytical variables using *Chironomus dilutus* and *Hyalella azteca*. Highlighted cells indicate a statistically significant correlation at α=0.05. Negative correlation coefficients indicate that survival, growth, and biomass were reduced in sediment with higher concentrations of low molecular weight polyaromatic hydrocarbons (PAHs) and total extractable hydrocarbons (TEHs) (from Bejarano and others, 2012).
[LMW, low molecular weight; HMW, high molecular weight; µg/kg, micrograms per kilogram; mg/kg, milligrams per kilogram; TPAH, total polyaromatic hydrocarbons; TOC, total organic carbon; %, percent]

Variables	*Chironomus dilutus*			*Hyalella azteca*		
	Survival	Growth	Biomass	Survival	Growth	Biomass
Sum LMW-PAH (µg/kg)*	-0.53	-0.47	-0.51	-0.44	-0.18	-0.17
Sum HMW-PAH (µg/kg)*	-0.45	-0.36	-0.40	-0.36	-0.20	-0.17
TPAH (µg/kg)	-0.49	-0.43	-0.47	-0.39	-0.22	-0.21
TEH (mg/kg)**	-0.52	-0.53	-0.54	-0.47	-0.29	-0.39
%TOC	-0.67	-0.35	-0.42	0.04	-0.65	-0.65
% Gravel	-0.08	0.02	0.03	0.01	0.07	0.18
% Sand	0.56	0.40	0.41	0.23	0.41	0.54
% Silt	-0.54	-0.52	-0.52	-0.36	-0.44	-0.55
% Clay	-0.53	-0.21	-0.25	-0.13	-0.41	-0.53

*Low molecular weight (LMW) PAHs include Naphthalene to Benzo(b)fluorine (38 analytes), whereas high molecular weight (HMW) PAHs include Fluoranthene to Benzo[g,h,i]perylene (26 analytes).

** Total Extractable Hydrocarbons (C9-C44; TEH).

Summaries of the physical effects from burial of benthic organisms by deposited OPAs can be found in available literature on burial effects from agitation dredging (Chapman, 2012) and on sediment deposition in streams (Waters, 1995). Aquatic organisms most likely affected by burial are fish eggs, larvae, and fry; sessile filter feeders such as mussels; and macrophytes (Chapman, 2012; Morton, 1977; and studies cited in Kaplan and others, 1974; Erftemeijer and Lewis, 2006). For marine benthic organisms, recommendations have been made to limit disposed sediment to 15 cm, but species survival is highly variable, with some species destroyed by as little as 5 cm (OSPAR, 2008) and fish eggs by as little as a few mm (Berry and others 2003; see other citations in Chapman, 2012). Deposition effects vary by species requirements, extent and spatial connection of habitat types, and size of the waterbody.

Effects of Ice in Northern Climates on OPA Formation and Spill Response

Most of the cold-condition studies that have been conducted have looked at the behavior of spilled oil and not how the oil interacted with particles to form OPAs (Fingas and Hollebone, 2003; Lee and others, 2011b; Wang and others, 2013) under controlled laboratory and pilot-scale tank studies. Lee and others (2011b) summarize findings from laboratory studies funded by the Canadian Coast Guard to elucidate the potential significance of OPA formation under cold climatic conditions that included ice (Cloutier and others, 2005; Khelifa and others, 2005c). These studies showed that OPAs can form quickly with strong turbulence, within the first 10 minutes of a spill. Within 40 minutes, most of the oil was converted to OPAs. Brackish water (18 ppt) with slush and broken ice had similar results with strong turbulence. Most particles were less than 1 mm in diameter and about 50 percent of the oil was physically dispersed within 30 minutes (Blouin and Lee, 2007; Cloutier and Doyan, 2008).

Field trials in the St. Lawrence River estuary near Matane, Quebec were conducted during the winter to further evaluate the feasibility of enhanced OPA formation as a spill response countermeasure in ice-infested waters (Lee, Li and others, 2011b). An icebreaker's propeller was used to generate strong turbulence during this exercise to facilitate the formation of OPAs with experimentally released fuel oil sprayed with slurry of fine-grained chalk using the fire hose system on board the ship. Visual observations and results of laser particle size analysis (LISST) indicate that fuel oil physically dispersed as OPA into the water column by this experiment did not readily reform a surface slick. Without the addition of mineral fines and consequential OPA formation, the fuel oil resurfaced within minutes and was difficult to recover because of interference by large ice blocks. Half of the total petroleum hydrocarbons in recovered samples biodegraded after 56 days incubation at a temperature of 0.5 $^{\circ}$C, which is most likely because of microbes in the water that were well adapted to their surrounding environment, despite the low temperatures.

Although not specific to OPAs, Belore (2010) provided a detailed description of simulations of oil and condensate spills over a range of expected temperatures at the marine trans-shipment terminal and confined channel assessment area (CCAA) of concern for syncrude synthetic light oil, Condensate Blend (CRW), Cold Lake bitumen diluted with condensate, and MacKay River heavy bitumen diluted with Suncor synthetic light oil (MKH). The simulations included a hypothetical marine terminal spill and three hypothetical tanker spills for Emilia Island, Principe Channel, and Wright Sounds for spring, summer, fall, and winter conditions. The tests did not consider interactions between oil and particulate matter, but they provided a thorough set of physical properties and behaviors for these oils including density, viscosity, interfacial tension, pour point, flash point, evaporation, emulsion formation, and oil adhesion.

The formation of OPAs and its effect on promoting dispersion of spilled residual oil may vary because of changes in the properties of the oil, water, particle type, temperature, and extent of ice cover. For example, the viscosity of diluted Cold Lake Blend ranges over an order of magnitude from summer water temperatures (for example, 393.2 square millimeters per second (mm^2/s) at 15 $^{\circ}$C) to winter water temperatures (1437.8 mm^2/s at 1 $^{\circ}$C) (Belore, 2010).

Biodegradation and toxicity need more research because potential exposure and biological activity are affected by temperature. Recent results by McFarlin and others (2014) found that oil degrading microorganisms were present in surface, middle, and deep water samples from the Arctic Ocean and that oil biodegradation potential exists for offshore Arctic environments; however, this study did not specifically look at biodegradation of OPAs.

Researchers from the Institute of Northern Engineering–University of Alaska Fairbanks and NewFields LLC have conducted several studies of the toxicity of physically and chemically dispersed

oil in arctic environments (McFarlin and others, 2011) that provide some insights into OPA toxicity. In one study, the toxicity of physically versus chemically dispersed oil to selected arctic species representative of the Beaufort and Chukchi Seas was examined at typical arctic water temperatures of 2 $^{\circ}$C (McFarlin and others, 2011). Using fresh Alaska North Slope oil, physically dispersed under increased mixing energy in a laboratory, spiked exposure toxicity testing was performed for three arctic species: *Calanus glacialis* (copepod), *Boreogadus saida* (arctic cod), and *Myoxocephalus sp.* (sculpin). When subjected to physically dispersed oil, mean lethal concentration (LC_{50}) values were lower by 3.3 and 3.7 mg/L total petroleum hydrocarbons (TPH) for arctic cod and early season copepods, than the corresponding values in the presence of chemically dispersed oil of 55 mg/L and 22 mg/L, respectively. With the exception of this case, toxicity effects for arctic species from physically dispersed oil were found to be generally no better or worse than for temperate species and warm water temperatures.

In conclusion, the toxicity of suspended and deposited OPAs requires further investigation. OPAs that submerge and accumulate in depositional areas have chemical and physical ecological risks associated with them, either because of toxicity from high concentrations of hydrocarbons, or physical damage, which can result from the smothering and burial of benthic organisms. The appropriate application of laboratory tests to different geographic areas with a range of water depths and water currents needs further consideration.

Operational Considerations

As described in preceding sections, oil can submerge, and OPAs can form rapidly after a spill of light and heavy crude oils, given the right environmental conditions. Key environmental factors that increase the probability of submergence for bitumen spills include (Silliman, 2014):

- Low salinity resulting in relatively low water density,

- Particles that have relatively high roughness in their surface area or are porous,

- High turbidity or high suspended sediment concentrations,

- Exposure to sunlight (UV radiation),

- Strong currents and mixing energy, and

- High temperatures.

Silliman (2014) concludes that if one of these factors is present, then emergency response personnel should equip themselves with response tactics for submerged oil. The following sections describe the state of the science for detection, containment, and recovery of submerged oil, especially submerged OPAs.

Detection

OPAs can be detected by direct observation using specialized microscopy techniques that enable the visualization of oil. On the basis of the strong natural fluorescence of aromatic hydrocarbons and chlorophyll when excited by UV light, Lee and others (1985) devised a bright field transmitted light/UV epi-fluorescence illumination technique that enabled the observation of interaction between chemically dispersed oil droplets and phytoplankton. This technique was subsequently refined and used in a routine manner to characterize and quantify OPAs (Stoffyn-Egli and Lee, 2002; Lee and others, 2003a; Ma and others, 2008). Detailed investigations of the surface and internal structure of OPAs have been conducted by the application of confocal laser scanning microscopy (Stoffyn-Egli and Lee, 2002; Zhang and others, 2010; Wang and others, 2011). Environmental scanning electron microscopy (ESEM) was used to produce high resolution 3-D topographical images of OPA surfaces in their natural state to

confirm the existence of "droplet" OPA composed of oil droplets that were stabilized by mineral fines on their surface (Stoffyn-Egli and Lee, 2002). The U.S. Coast Guard's Research and Development Center recently specified requirements for submerged oil detection systems that included 80 percent detection probability, 1-m radius of detection, real-time results, reasonable setup time, accommodation of 1.5-m (5-ft) seas and 0.8 m/s (1.5 knot) currents, and coverage of 1.6 km^2 (1 mi^2) in a 12-hour shift (Hansen, 2014). Established on-site mass spectrometer systems to monitor oil in the water column may not be effective if the oil occurs as OPAs or has already settled out. This was the case in the oil-affected reach of the Kalamazoo River.

Laser fluorometers offer the potential for detection of oil in oil-sediment mixtures and were successful in detecting residual oil in pore water in beach deposits along the coast of Taean, South Korea, following the *Hebei Spirit* oil spill (Kim and others, 2010). In addition, trials with submersible fluorometers with an excitation wavelength of 120-325 nanometers (nm) and emission wavelengths of 410-600 nm met with some success for the Kalamazoo River when the OPAs were in suspension during in situ tests of erosion characteristics of deposited oiled sediment from the 2010 Enbridge Line 6B oil release. A limited number of samples collected at the time the OPAs were in suspension were analyzed at the USGS Wisconsin Water Science Center for both absorbance and fluorescence excitation-emission matrices using an Aqualog instrument (Peter Lenaker, U.S. Geological Survey, written commun., 2013). However, once the OPAs are submerged and mixed with bottom sediment the fluorescent properties of the oil are masked by other particles (Lee and others, 2012). As a result of these short-falls identified with current methodologies for oil spill detection in aquatic environments, Hansen (2014) stressed the importance of simultaneous use of multiple systems.

Detection of OPAs by sonar can be difficult because the detectable sonar signature associated with pure oil is diminished when it is mixed with suspended and bottom sediments. Furthermore, particle size is a factor; oil associated with fine-grained (silt and clay-sized) organic-rich particles is difficult to detect by sonar (Hansen, 2014; authors' experience on the Kalamazoo River cleanup).

A novel sediment poling technique was developed for detecting and assessing the spatial distribution of submerged oil and oiled sediment in the Kalamazoo River; it was adapted from studies of contaminated sediment (David Richardson, Tetra Tech, Inc., oral commun., 2011). This became the primary submerged oil assessment tool used in the Kalamazoo River cleanup (Enbridge Energy, L.P., 2013a; Dollhopf and others, 2014). The sediment was agitated using a graduated aluminum pole with a 20-cm-diameter metal disc on the submerged end. If submerged oil was present in the sediment, the agitation action liberated oil from the sediment, allowing it to float to the water surface. The percent coverage of oil sheen and number of globules at the water's surface within 1 m^2 were observed and categorized as none, light, moderate, or heavy according to the field observation submerged oil flowchart (fig. 8). Thickness of soft sediment in depositional areas could be estimated by quantifying the difference between a 1- and 2-hand push of the graduated pole into the sediment. This procedure was used to map the relative concentration and extent of oiled areas to depositional areas of the river with soft sediment (silt and organic matter) accumulations. From 2010 to 2014, over 20,000 poling points were assessed throughout the affected river system. Global positioning system (GPS) coordinates and field observations were recorded upon poling and managed in a geographic information system, which allowed for detailed mapping of sheening as well as bathymetry, substrate, and flow velocity. Some limitations of the method include the need for water temperatures generally greater than 15°C for consistent categorization, velocities less than about 0.3 m/s (otherwise the sheen and globs are swept too quickly downstream), and water depths of generally less than 3 m. At greater water depths, it is unknown whether the liberated oil can rise the full distance to the water surface, resettles, or is transported downstream.

For the Kalamazoo River spill, multiple rounds of sediment cores were collected, and two types of in situ suspended sediment samplers were deployed for monitoring and assessment (Enbridge Energy, L.P., 2011a). About 25 in situ suspended sediment samplers (Phillips and others, 2000) were placed along the 61-km stretch of the affected river to collect any submerged oil and oiled sediment in suspension in the water column that was being transported over a range of flows including during cleanup activities. In addition, about 70 suspended sediment settling jars, also known as sediment traps (Thomas and others, 2007), were placed in depositional areas of the Kalamazoo River with little to no flow to collect particles that were recently in suspension and settled to the river bottom. These jars were similar to column sampling devices used in lacustrine environments for particulate resuspension and chemical fluxes with ponded water or multiple flow directions, such as wave action and longshore currents (Eadie and others, 1984; Murdoch and MacKnight, 1994).

Initially in the cores, globs of submerged oil from the Kalamazoo River Line 6B spill fluoresced under UV light, making it possible to identify the presence and depth of oil in the cores. In 2012, 2 years after the spill, it became necessary to positively identify that the oil in river sediment originated from the spilled oil and not from a previous spill or other background hydrocarbons (Dollhopf and others, 2014). It was at this time that the oil in the sediment cores was becoming more difficult to visually quantify using UV-fluorescence because of dilution, dispersion, and quenching of oil droplets within the sediment matrix (Lee and others, 2012). It then became necessary to identify a chemical fingerprint of the Line 6B oil using forensic oil chemistry techniques that distinguished a signature of triaromatic stearene biomarkers in Line 6B oil that was unique from other oil contaminants present in Kalamazoo River sediment before the spill (G. Douglas, NewFields, written commun., 2014; Dollhopf and others, 2014). This technique was used to quantify the remaining Line 6B oil concentrations in all three types of sediment samples collected in the Kalamazoo River—sediment cores, in situ suspended sediment samples, and recently deposited samples.

Containment

Conventional containment strategies for floating oil do not address the submergence, potential resuspension, and subsurface transport and redistribution of OPAs. OPAs will easily pass underneath a surface boom. Subsurface booms and silt curtains are more effective. An example of the equipment used to keep submerged oil and oiled sediment from the 2010 Line 6B spill from migrating farther downstream in the Kalamazoo River and into Morrow Lake is shown in figure 9A. The top curtain contains a boom similar to conventional setups to trap floating oil. The bottom curtain is meant to cut off bottom currents and promote deposition. This type of containment curtain is oriented at an angle to river currents to maximize settling of OPAs while limiting the chance for new areas of scour (fig. 9B) (Enbridge Energy, L.P., 2012b, 2013b).
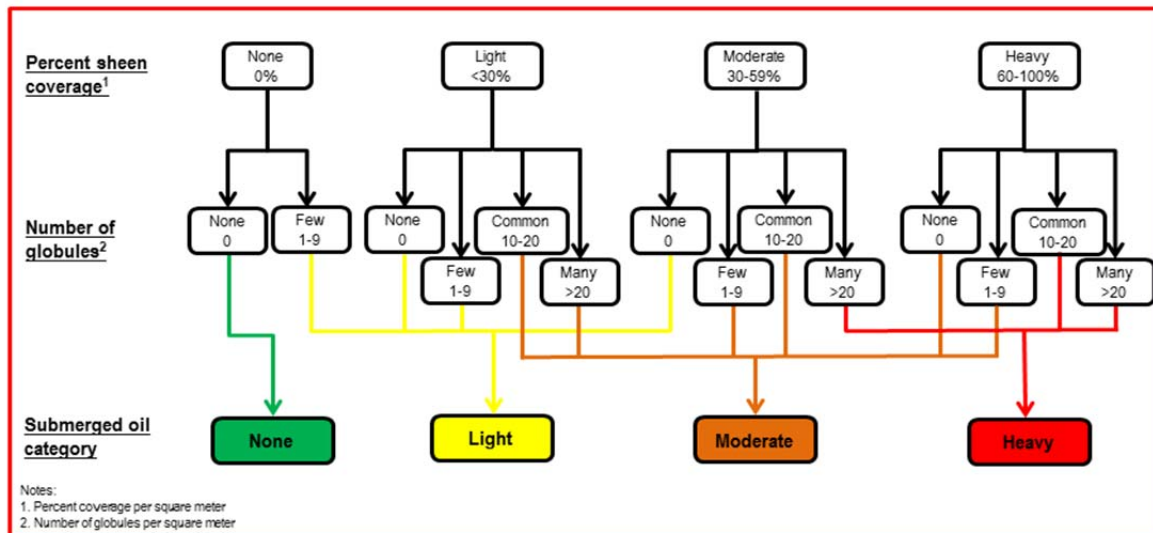
Figure 8. Flowchart used for field observations of submerged oil during poling assessments. (from Enbridge, 2013a; %, percent; <, less than; >, greater than).

Recovery

Recovery techniques for submerged oil and OPAs in freshwater and marine environments are still in the development phase. In a recent document on the fate and transport of potentially spilled oil associated with the proposed Energy East Pipeline Project from Alberta to New Brunswick the following recovery equipment and techniques were recommended by Energy East Pipeline Ltd. (2014): specialized nets, bottom booms, dams and underflow weir dams, dredging, manual recovery, and air injection. Challenges of oil recovery in cold climates, whether in marine or freshwater environments, involve accounting for the following variables: presence of ice, air and water temperatures, remote locations, and low solar radiation (Lee, Li and others, 2011a, b).

Early on in spills, weighted sorbent materials can be dragged along the sea floor or draped along a river bottom to capture submerged oil and OPAs (Hansen, 2014; Enbridge Energy, L.P., 2010). Subsurface sorbent pom-poms (Pister and others, 2009) have been used for oil in suspension. Where oil in deposited OPAs remains at concentrations that cause concerns for benthic organisms or excessive sheening problems, dredging may be necessary (Dollhopf and others, 2014; Gouvernement du Quebec, Depot Legal, 2014).

Enbridge used a combination of agitation toolbox techniques and sheen sweeps in contained areas of the Kalamazoo River, but sheening problems continued in depositional areas after these techniques were used, leading to the adoption of dredging as the final solution (Enbridge Energy, L.P., 2010; Dollhopf and others, 2014). Agitation toolbox techniques used on Kalamazoo River bottom sediment included mechanical agitation through raking, hand-held tillers, and chain drags, along with hydraulic agitation using hand-held water jets arranged as a single wand or on a rotating head (known as stingers) and vessel-mounted or dragged spreader bars with multiple water jets (Enbridge Energy L.P., 2011b). Conventional oil skimming techniques and sheen sweeps were used in response operations in the Kalamazoo River cleanup during periods of spontaneous release of oil globules from depositional areas of the river.

A
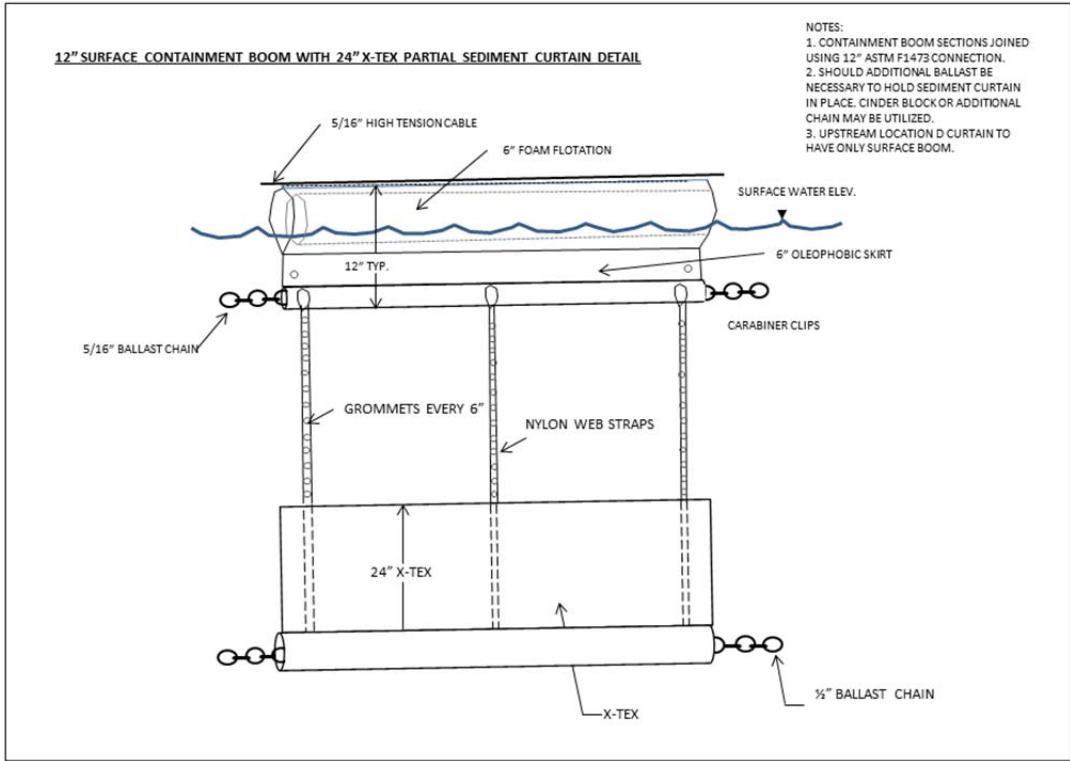
B

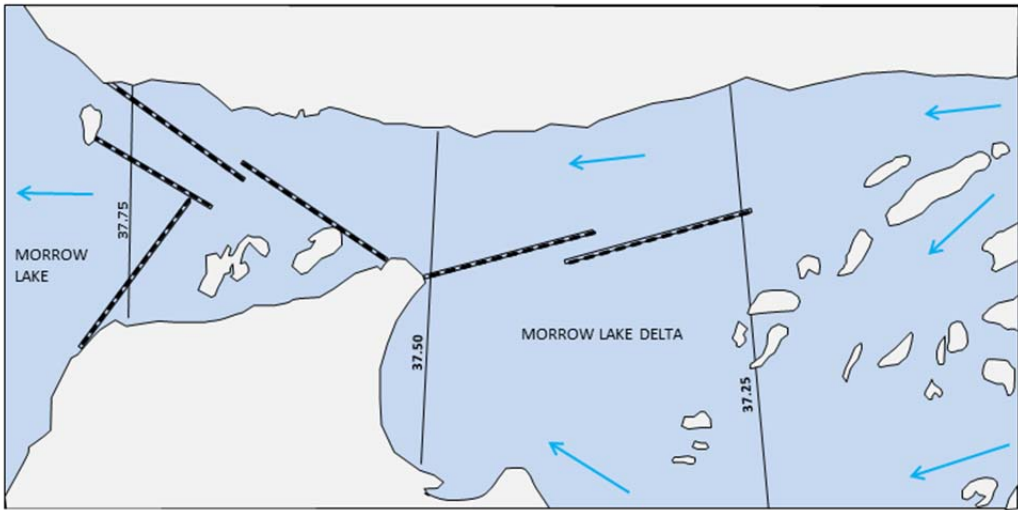Figure 9.   A, Diagram of subsurface curtain boom, and B, map of containment boom locations for submerged oil in Morrow Lake Delta from river miles 37.25 to 37.75, Kalamazoo River, Michigan related to the Enbridge Line 6B oil release. Blue arrows on map show general flow direction from right to left. Bold dashed lines are containment boom locations. Redrawn diagrams from Enbridge Energy, L.P. (2013b) containment permits.

Some of the methods that have been used for OPAs in suspension and on the bottom along shorelines include (Pister and others, 2009)

- Weighted sorbent materials (for example, plastic pom-poms),
- Dredging,
- Natural attenuation,
- Vacuum truck (limited by access),
- Small portable submersible pumps,
- Debris removal and wrack cleaning,
- Sediment reworking,
- Flooding, and
- Low and high pressure flushing (ambient water) (may leave a significant quantity of oil that requires additional effort).

Techniques that were generally not recommended for marine shorelines and beaches include (Pister and others, 2009)

- Offshore barriers and berms,
- Mechanical oil removal,
- Vegetation removal,
- Low and high pressure flushing (hot water),
- Steam cleaning,
- Sand blasting,
- Solidifiers,
- Shoreline cleaning agents, and
- Natural microbe seeding.

Unfortunately, there is not a simple operational endpoint for spill clean-up operations when it comes to residual OPAs. Remediation for each spill, whether in marine or freshwater environments, can benefit by the development of a Net Environmental Benefit Analysis, which weighs the benefits and drawbacks of leaving oil in place rather than causing further physical damage to aquatic habitats by aggressive removal techniques such as dredging or agitation (Efroymson and others, 2003; Rayburn and others, 2004; Bejarano and others, 2012). It cannot be automatically assumed that in all situations the oil concentrations in deposited OPAs will fall below toxic concentrations during a short period of time as a result of natural attenuation (dilution and biodegradation). Furthermore, it is important to note that the biodegradation of residual oil associated OPA is disadvantaged under anaerobic conditions that form after burial (Lee, 2000). However, depending on the spatial extent of the OPAs, the environmental setting, or presence of sensitive habitat, oil concentrations in OPAs may be adequately diluted to warrant no recovery and allow natural attenuation to happen (Lee and others, 2011a; Bejarano and others, 2012; Fitzpatrick and others, 2013).

Future Science Needs

This report has summarized the state of knowledge regarding the formation of OPAs in natural waters, their eventual transport and fate, and considerations for cleanup of oil spills. The existing knowledge base is insufficient but rapidly growing with recent observations from large spills in freshwater and brackish riverine environments, additional laboratory tests and modeling, and studies of environmental effects of proposed new and expanding pipeline systems in North America carrying bitumen products (http://nas-sites.org/dilbit/). Specific science needs for submerged oil and OPAs are listed below.

- Laboratory experiments of resuspension and breakup of OPAs.

- Updated and new models and simulations of fate and transport of oil and OPAs in freshwater and cold climate environments with a range of oil and sediment types.

- Quantitative monitoring and mapping of large areas of OPAs in water depths greater than 3 m.

- Refinement of the Kalamazoo River poling technique with deployment of a fluorometer in the plume of sediment OPAs resuspended by the poling agitation.

- Monitoring and assessment of transport and fate of spreading oil in ice and below ice.

- Field trials in cold climates. More study is needed using realistic field trials or field observations of OPA formation during oil spills. Especially needed are studies of freshwater environments in and around the Great Lakes coastal environments and river mouths.

- Investigation of potential effects on benthic invertebrate communities from residual oil and OPAs in depositional environments including burial and smothering as well as hydrocarbon toxicity in marine, freshwater, and cold-climate environments.

- Investigation of OPA toxicity and physical effects on habitat. Not enough is known yet about the toxicity of OPAs, especially chronic toxicity and routes of exposure, and application of laboratory results to specific aquatic habitats. Data on the potential negative effects of augmented natural dispersion on burial and smothering of benthic organisms is needed, especially for freshwater environments.

- Vulnerability analyses of critical habitats.

- Incorporation of OPA properties into hydrodynamic and sediment transport models.

- Post-spill monitoring and assessment techniques.

- Operation endpoints—monitoring protocols to determine how much cleanup is enough and the manner in which natural attenuation may ameliorate effects in the future.

Summary and Conclusions

Studies of the formation of oil-particle aggregates (OPAs), and related behavior, fate, and toxicity in a wide variety of environments, including freshwater rivers, are of continued interest to researchers as transportation of light and heavy crude oils continues to increase across North America. This report contains an up-to-date review of the state of the science for OPAs from available literature, in terms of formation and stability, use as a physical dispersant, transport and fate, toxicity, behavior in cold climates, operational considerations, and future science needs. Although much is known about OPAs, there remains a good deal of science to be learned, especially in terms of laboratory experiments,

flume studies, toxicity and habitat effects, field exercises, and modeling at a range of spatial and temporal scales.

Questions that were investigated for this report, along with brief answers developed from the available literature are listed here.

- What is the effectiveness of adding particles to an oil spill for physical dispersion of oil as a spill countermeasure? The effectiveness varies with oil and particle properties and the salinity of water, but in general the addition of particles will almost always result in some OPA formation. The particles act to stabilize oil droplets and prevent them from re-coalescing at the water surface into an oil slick. Some potentially negative consequences occur when OPAs settle to the bottom possibly causing issues with protracted and increased cleanup costs, and loss of habitat to benthic organisms from smothering and burial. The toxicity of OPAs compared to oil droplets in the water column varies or is not known. Because of these negative effects, prescribed sinking of spilled oil, or the use of sinking agents, is prohibited by U.S. Environmental Protection Agency.

- What is the long-term fate and transport of OPAs? Particle interactions tend to stabilize the oil droplets. OPAs can be resuspended when currents or mixing energy increases. OPAs can also be released to the water surface through the process of bubble formation and release from sediments (ebullition) for years following a spill.

- What are the ecological implications of OPAs? Ecological implications have to do with whether the OPAs stay in suspension or settle out and the geographic extent and water depth of the aquatic habitat. If OPAs stay in suspension, then microbial degradation would be likely increased. If OPAs settle out, ecological effects would be likely from toxicity and physical smothering.

- What are the operational considerations for recovery of OPAs? Containment and recovery of submerged OPAs or OPAs in riverine and marine environments require different techniques than those used for floating oil, and a familiarity with hydraulics of sediment transport is helpful.

- Are there special circumstances for OPAs in cold climates? OPAs form readily in cold climates and the addition of particles likely acts as a physical dispersant similar to warm climates. The additional difficulty of using conventional skimming techniques for floating oil where there is broken ice makes physical dispersion a more attractive option. However, habitat loss, burial, smothering, and toxicity effects from submerged OPAs need to be considered, especially for shallow freshwater environments.

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