

A review of oil-suspended particulate matter aggregation—a natural process of cleansing spilled oil in the aquatic environment

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It has been acknowledged that following an oil spill in coastal areas where suspended particulate matter (SPM) is rich, aggregation between oil and SPM can be naturally formed. This kind of aggregation product is termed as oil-SPM aggregates (OSAs). Because OSAs are not as sticky to the shorelines as crude oil and the oil–water contact area is greatly increased due to the formation of OSAs, both oil dispersion into the water body and oil biodegradation would be significantly enhanced. In this review article, the authors (1) describe in detail the mechanism of OSA formation and controlling parameters which can influence OSA formation (the parameters discussed include the oil nature and properties, sediment types and concentrations, and the environmental factors such as salinity, temperature and mixing energy); (2) briefly review qualitative and quantitative methods used for characterization of OSA formation (two main methods used for the OSA characterization are the UV epi-fluorescence microscopy and gas chromatography equipped with flame ionization detector (GC-FID)); (3) elucidate the applications of OSA formation in oil spill response strategies including natural attenuation, sediment relocation, and sediment mixing; and (4) discuss research needs in the future which would further improve our understanding of OSA formation and move towards the development of adequate oil behaviour models.

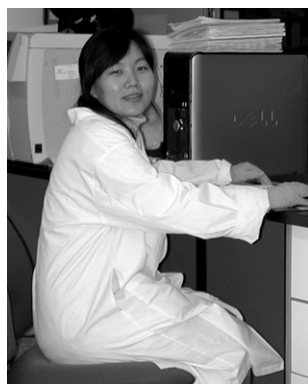
Introduction

The worldwide demand for petroleum and their refined products has grown significantly during the last decades. Unfortunately, more oil spills into the aquatic ecosystem as a consequence of the increasing demand of marine transportation of the crude oils from the remote locations of the crude oil production sites (many

in the Middle East countries). Because of toxic components (such as polycyclic aromatic hydrocarbons, PAHs) in the petroleum and their refined products, oil spills could be devastating to the aquatic environment, especially to the fragile shorelines. Fast and effective response measures to clean spilled oil should be taken once an oil spill accident occurs. Traditional cleanup methods (such as application of skimmers) are often confined to a large extent by weather conditions and are not able to clean the spilled oil effectively, thus they are more suitable just as the first recovery of oil spills. The usage of chemical dispersant itself may cause secondary pollution, and it may also accelerate the filtration of oil into the deeper beach aquifer, therefore there may be a risk of causing more persistent and toxic pollution. In facing these facts, the oil spill response community is seeking an

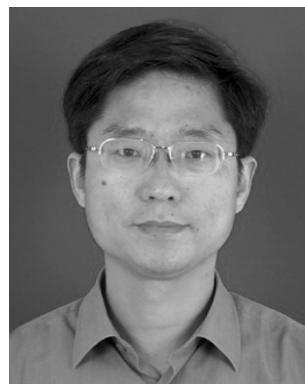
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economical and environmental friendly technology for spilled oil cleanup. Actually it was early in the 1970s that scientists had observed flocculation of clay and oil in saltwater, and stabilization of oil-in-water emulsion by solid particles.^{1–4} The significance of this process in natural cleansing of oiled shorelines was ignored for decades until the Exxon Valdez oil spill in 1989. A large portion of the oiled shorelines cleaned themselves naturally even in the sheltered coast by the production of a fluffy colloidal emulsion composed of oil droplets surrounded by micron-sized clays. This kind of emulsion did not adhere strongly to the sediment, thus largely increased oil dispersion into the water body; oil biodegradation was highly accelerated due to the increase of the oil–water contact area. This natural process has been demonstrated in other oil spill accidents and laboratory studies to have the ability to enhance cleaning of oiled shorelines greatly. In addition to the natural attenuation of spilled oil, other shoreline cleanup techniques, such as sediment relocation and sediment mixing can greatly accelerate this process.^{5–17} Various terminologies have been used to refer to this process, such as mineral-stabilized droplet, clay–oil flocculation,^{5,7,10} oil and fine-particle interaction,⁹ more frequently oil–mineral aggregation (OMA)¹² and oil-suspended particulate matter (SPM) aggregation (OSA).^{18,19} However, as the aggregation between oil droplets and non-mineral particles are widely observed, the term of oil-suspended particulate matter aggregates (OSAs) was introduced and used in this study.

The significance of OSA formation in shoreline cleanup has motivated many studies on characteristics of OSAs under different conditions, especially studies on quantitative effects of SPM size and concentration, the oil type, and the water salinity on the OSA formation. This article aims to provide a brief review on OSA formation and its role in oiled shoreline cleansing. The effects of different controlling factors, such as oil and sediment type and concentration, salinity, temperature and mixing energy on OSA formation are discussed. Methods used for the OSA characterization studies are summarised. Related topics which are under investigation and research needs in the future to further improve our quantitative understanding of this natural process are also outlined.

Mechanism of OSA formation

OSA formation occurs when oil and suspended particulate matter are present in the same turbulent aqueous system. It is believed to be caused by interactions between the polar compounds of oil and the fine solid particles by the intermediary of a cation. Till now, there have been three types of OSAs observed by microscopical examination: droplet, solid and flake.^{12,20,21} Droplet OSA is the most common type, defined as individual oil droplets surrounded by micron sized solid particles, and sometimes more than one oil droplet is present to form multi-droplet OSA (see Fig. 1). Solid OSA has elongated forms, and sometimes curved or even branched, with size varying widely and even reaching 250 μm in length (see Fig. 2). It was proposed that this type of OSA forms when enough solid particles adhered to the oiled surface and an oil layer with particles mixed in detached. Flake OSA is usually several millimetres wide, floating or neutrally buoyant, and looks like membranes (see Fig. 2). This type of OSA was reported to be observed in the laboratory with

montmorillonite and with sediment rich in smectite.^{20,21} High shear strength (extended or faster agitation) tends to break or crumple flake aggregates.

It was believed that oil trapped in OSAs exists mainly in the form of oil droplets, with size distribution ranging from 1 μm to about 60 μm .^{10,22–25} In simple, there are two steps for OSAs to form: the first step is the break-up of oil film into oil droplets and the second step is the interaction between oil droplets and SPM. Oil droplets form by the interaction of two types of forces: one is the external disturbing force produced by the flow field to deform the oil, such as the inertia or viscous force; the other one is the internal restoring force of the oil, such as the interfacial tension to sustain the oil droplet shape.²⁶ When the deformation is big enough, the oil droplets will split into smaller ones. Therefore, the main controlling parameters for the first step are level and duration of the mixing energy, oil viscosity and interfacial tension between oil and water.^{22,27} The second step is actually the interaction between SPM and polar compounds in the oil droplets in the medium of anions in the water, so the factors controlling the second step are salinity, oil type and concentration, sediment type and concentration, level and duration of the mixing energy.

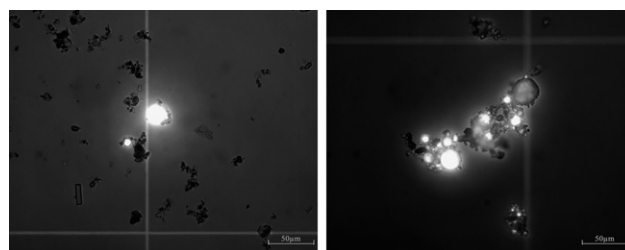


Fig. 1 Photomicrographs of negatively buoyant single-droplet OSAs (left side) and of negatively buoyant multi-droplets OSAs (right side) formed with Arabian medium crude oil and SRM-1941B sediment at 200 mg/L observed using an UV epifluorescence microscope: the oil appears bright (fluorescence) and the minerals are darker surrounding the droplets. Pictures were taken in the Oil Research Lab of ESTS, Environment Canada, under the supervision of Dr. Ali Khelifa with the assistance of Ms. L. C. So from the University of Waterloo.

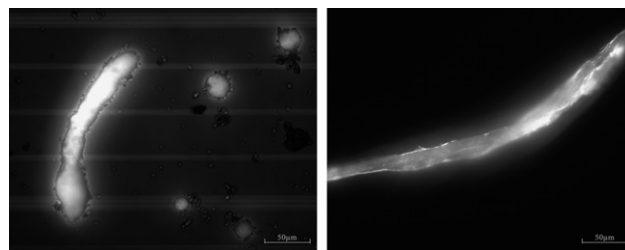


Fig. 2 Photomicrographs of negatively buoyant solid OSA (left side) with single-droplet OSAs on the right of this image and of a positively buoyant flake OSA (right side) formed with Arabian medium crude oil and SRM-1941B sediment at 200 mg/L (left) and 400 mg/L (right) observed using an UV epifluorescence microscope: the oil appears bright (fluorescence) and the minerals are darker surrounding the oil droplets or solid OSA or throughout the solid and flake OSAs. Pictures were taken in the Oil Research Lab of ESTS, Environment Canada, under the supervision of Dr. Ali Khelifa with the assistance of Ms. L. C. So from the University of Waterloo.

Controlling factors

There are four necessities for OSA formation: (1) a low viscous oil with a certain content of polar compounds, (2) a certain concentration of fine particles, (3) water with a certain salinity, (4) a certain level of mixing energy. Previous studies on these factors are summarised in Table 1, and are discussed in the following sections.

(1) Salinity. Salinity is a prerequisite for flocculation between oil and SPM. It affects the flocculation of solid particles and modifies surface properties of oil droplets, thus affecting aggregation rate between SPM and oil droplets. Early studies found that oil and SPM flocculate spontaneously when mixed in seawater, but none was found in freshwater.^{2,10} Recent studies on North Slope Rivers in Alaska^{28,29} and on OSSA II oil spill in Bolivia River^{13,14} showed OSAs form also in river water. However, it has been found that there is a minimum salinity below which OSAs will not form, and this minimum salinity value was reported to be different in different experiments. There is also a critical aggregation salinity at which the rapid increase of OSA formation ends and the concentration of OSA-stabilized oil droplets reaches its maximum value. The knowledge about this critical salinity is that it was controlled mainly by sediment type and, to a lesser extent, by oil type. Some recent studies indicate that the critical salinity varies between 1.2 and 3.5 ppt, but might be as large as 35 ppt and as small as 0.2 ppt.^{30–34} The effect of salinity on OSA formation is closely related to mineral type, as the chemistry of the high-ionic-strength seawater dominates the surface properties of the minerals. However, in fresh water with ionic strength 100 times lower than seawater, the surface charge on minerals plays an important role in OSA formation. The effect of salinity on OSA-stabilized oil concentration can be predicted by the following equation:³²

$$N_* = \frac{S_*^{1.97} + 0.01}{S_*^{1.97} + 0.12} \quad (1)$$

where $N_* = N/N_{\max}$ represents the normalized number concentration of OSA-stabilized oil droplets and $S_* = S/Sc$ is the normalised salinity in which S is the salinity and Sc is the critical

aggregation salinity at which the concentration of stabilized droplets N reaches its maximum value N_{\max} . The formation of OSAs increases rapidly when S_* varies between 0.1 and 1. The salinity of water can also influence size and shape of OSAs. As the attraction energy of OSAs decreased with increasing salinity, the mean diameter of OSAs was significantly larger at 15 ppt than that at 30 ppt.³⁵ It was also found that oil droplets were more elongated in saltwater than in freshwater, but the effect of salinity on size distribution of oil droplets is negligible when the sediment contains high content of organic matter.³²

(2) Sediment type and concentration. In the process of OSA formation, SPM acts to prevent re-coalescence of dispersed oil droplets. Fine sediments readily form OSAs, as usually smaller particles have a larger specific surface area, thus with stronger forces between oil and sediment.^{1,3,5,10,31,36–42} OSAs formed when the sediment size was smaller than 5 μm , and OSAs were more ready to form when the sediment size was $<2 \mu\text{m}$, but negligible OSAs formed when the sediment size was $>10 \mu\text{m}$ or 6 μm . The smaller the solid particles, the smaller the minimum particle concentration to form OSAs, and the OSAs concentration increased slowly; whereas the larger the solid particles, the larger the minimum particle concentration to initiate OSA formation and the OSAs concentration reached the equilibrium within a shorter time.

In early studies, it was believed that sediment type has negligible influence on OSA formation as long as sediment size reaches the clay size range. However, Stoffyn-Egli *et al.* found a clear relationship between types of OSA structure and the particular mineral.²¹ For example, kaolinite and quartz formed only droplet aggregates and montmorillonite formed only flake aggregates, which were also found to mainly form solid OSAs before.¹² Additionally, it was found that chalk formed OSAs easier than bentonite.⁴³ However, it is still necessary to consider the structure and surface chemistry of minerals to understand the process controlling the apparent affinity of oil for fine particles in seawater. There is also some controversy on the relationship between concentrations of oil trapped in OSAs and mineral exchange capacity.^{12,31,37} The surface chemistry of minerals demonstrates some relationship of OSA formation with oil

Table 1 Factors influencing OSA formation

Factors	Main findings about OSA formation	References
Salinity	OSA formation was enhanced by increasing salinities up to a certain value, the effect above that was negligible.	2,10,14,24,28,30–32
Sediment type and concentration	Smaller size was more effective in OSA formation, OSA formation increased with increasing sediment concentration and a critical sediment concentration exists.	5,24,31–33,37–41,46,47
Oil type	OSA formation increased with oil polar component content; decreased with oil viscosity.	3,10,12,14,31,37,48,50
Temperature	Fewer OSAs formed at lower temperature; more elongated oil droplets formed at higher temperature.	1,10,28,50
Mixing energy	High mixing energy enhanced OSA formation, and there was a minimum mixing energy needed for OSA formation.	10,27,28,31,35,51–54

properties, for example, hydrophilic quartz and kaolinite interact more strongly with low-viscosity oils than with high-viscosity oils, whereas oleophilic calcite interacts strongly with crude oils irrespective of their viscosities.³⁶

The fraction of the initially added oil trapped in OSAs is called trapping efficiency (E), which is roughly proportional to the sediment mass concentration (C_S), till E asymptotes at the maximum possible trapping efficiency (E_{\max}), the relationship is represented in the following equation:^{39–41}

$$E = \frac{E_{\max} \left(\frac{C_S}{C_{S50}} \right)}{\left[1 + \left(\frac{C_S}{C_{S50}} \right)^n \right]} \quad (2)$$

where C_{S50} is the sediment concentration at a trapping efficiency of 0.5; n is the shape of the trapping efficiency *versus* sediment concentration curve. Here C_{S50} represents the critical sediment concentration, which is the concentration required to form a monolayer of sediment grains around all droplets in suspension, and below this concentration, OSAs will not form.^{39–42,44,45} The critical concentration is a function of the size ratio (ratio between sediment diameter and oil droplet diameter) and oil concentration. The value of this critical concentration was reported to be 0.5–200 mg/L,^{29,46,47} and occasionally there were values beyond that, such as 700 mg/L³¹ and 490 mg/L (for 16 μm sediment size).^{40,41}

For medium sediment concentration (180 mg/L), more multi-droplet OSAs with up to 15 droplets in a single OSA were observed, and the trapping efficiency of negatively buoyant OSAs was high.^{24,39} The clay concentration resulting in the largest average aggregate size can be determined by fitting the experimental data with a Gaussian curve. The average aggregate size was positively related to the oil–mineral ratio of the settled phase: the size was 800 μm with the oil–mineral ratio of 5 and 100 μm with the oil–mineral ratio of 1, and it was also related to the environmental parameters and oil properties. Both droplet and solid OSAs formed with oil concentrations in 80–520 mg/L and oil/mineral ratios in 0.2–6.2, and more solid OSAs formed with oil concentrations above 200 mg/L. However, at low oil/mineral ratios, and oil concentrations above 200 mg/L, greater abundance of flake OSAs was observed. Although approximately equal at an oil/mineral ratio of 3, the quantity of floating *versus* sinking OSAs generally increased with higher oil/mineral ratio.²¹

(3) Oil type and temperature. Oil with high viscosity is difficult to disperse and only forms the large droplet size.^{3,27} Therefore, oil with low viscosity is favourable for OSA formation.^{5,10,11,14,37,48–50} The viscosity threshold, above which no OSAs will form, was indicated to be 9500 mPa·s.¹²

There was no flocculation observed in experiments with either hexadecane or recombination of the saturate and aromatic fractions from the weathered Exxon Valdez oil and suspended mineral fines from Smith Glacier and various Arrow spill locations. It was demonstrated that polar hydrocarbons were needed for OSA formation because polar hydrocarbons can enhance adhesion between oil droplets and sediment particles.⁵ Furthermore, there was an inverse correlation between the polar content

of oil and the clay concentration needed for aggregation, confirming OSA formation is the result of interactions between the polar compounds of the oil and the solid particles by the intermediary of a cation. However, almost any natural crude oil or residual refined fuel has sufficient polar content to produce flocculation with mineral fines. The following equation was developed to predict the effects of oil type on the interactions between oil and sediment:⁵⁰

$$\frac{W_o}{W_{ar}} = 0.3e^{3.23(\mu_d/\mu_c)^{-0.22}} \quad (3)$$

where W_o is a ratio between the mass of oil stabilized by OSA and the initial mass of oil introduced in the system, W_{ar} is the asphaltenes-resins content of the oil, μ_d and μ_c represent viscosities of the oil and the water, respectively. For a given viscosity ratio, oils with high W_{ar} are trapped more efficiently in OSAs than those with low W_{ar} . However, oils with high W_{ar} also have high viscosities.

The effect of temperature on OSA formation is essentially the resulting modification of oil viscosity.^{28,50} Low temperature reduces OSA formation, as viscosity increases with decreasing temperature. Temperature also affects the shape of oil droplets, for example the elongated and non-spherical oil droplets are more common at higher temperature. Khelifa *et al.*⁴³ found that OSAs form readily in cold (−0.5 °C) brackish and seawater.

(4) Mixing energy. The role of mixing energy in OSA formation is its positive role in helping oil droplet formation, suspension of SPM and oil droplets, collision between oil and SPM, thus increasing the oil concentration trapped in OSAs,^{27,28,51–53} and also its negative role by breaking sediment flocs and OSAs.^{10,53} Recently, Sun *et al.* found from their experimental study that the maximum trapping efficiency of oil in negatively buoyant OSAs, the oil-to-sediment ratio in settled OSAs, and the maximum OSA formation rate increased with the increasing mixing energy.⁵³ The interaction between oil and sediment was insignificant at the beginning of the shaking. This insignificant interaction shortened from 1 hour to less than 2 min when the shaking rate of the reciprocating shaker increased from 2.0 Hz to 2.3 Hz. As was observed in the field that even only the flushing of tide could accelerate the OSA formation, a minimum mixing energy, which was needed for OSA formation, was observed in the laboratory.⁵⁴

Time scale for OSA formation

The time scale for OSA formation is the time necessary for all the suspended oil droplets to be coated with a layer of sediment grains. Both field and laboratory observations suggested OSAs formed rapidly.^{24,27–29,31,53–56} The experimental results of Delvigne *et al.* and Payne *et al.* indicated that most of the OSAs formed during the first 10–20 min of the reaction.^{27,55} The aggregation time scale strongly depends on the sediment concentration. The time scale is long at low sediment concentration, while it is short at high sediment concentration, and it is intermediate at median sediment concentration.⁵⁷ Equation (4) can be used to calculate the time scale for OSA formation, assuming the collision between sediment and oil droplets is controlled mainly by turbulent fluctuations,⁴⁵ with β given by equation (5):

$$t_c = - \frac{\ln \left(1 - \frac{2\pi \left(\frac{D_o}{D_s} \right)^2 \left(\frac{N_o}{N_s(0)} \right)}{\beta} \right)}{\beta} \quad (4)$$

$$\beta = 0.16\alpha_{os}(D_s + D_o)^3(\varepsilon/\nu)^{1/2}N_o \quad (5)$$

In these equations, D_o and D_s are the diameters of oil droplets and sediment grains, respectively, N_o is the oil droplet number concentration, $N_s(0)$ is the sediment number concentration at time zero, ε is the turbulent-kinetic-energy dissipation rate, ν is the kinematic viscosity of water, and α_{os} is the oil–sediment coalescence efficiency which was estimated to be about 0.0016 from laboratory data of Payne *et al.*⁵⁵

Khelifa *et al.* developed a Monte Carlo model,⁴² assuming the collision was due to turbulence, differential settling and Brownian diffusion. Simulations showed that the time scale of OSA formation varies linearly (in logarithmic scale) with percentage of OSA-stabilized oil if the sediment concentration is sufficient. However, the time scale increases dramatically when the sediment concentration becomes critical to stabilize a given percentage of the reacting oil. The increase is higher with finer sediment. The minimum time was obtained with the size ratios of sediment to oil droplet larger than or equal to 1, and the minimum time to stabilize 100% of the initial oil was about 3 minutes accordingly. For a given concentration ratio, there exists a maximum percentage of stabilized oil, at which the formation time increases rapidly when the size ratio decreases below 1. It can take several hours and possibly a day for size ratios less than 0.2.

Recently, Sun *et al.* demonstrated from their experimental study that the time scale for OSA formation depends on the mixing energy. The critical time for OSA formation decreased from 2.2 hrs to 0.4 hr when the shaking rate of the reciprocating shaker increased from 2.0 Hz to 2.3Hz. Experiments were conducted with SRM 1941B and Arabian Medium crude oil.⁵³

Very little is known about the stability of OSAs after their formation. From theoretical considerations, an isolated solid sphere, partially wettable by both oil and water, is trapped at the oil/water interface in a very deep energy well. McCourt and Shier²⁸ found from most of the samples that increase in the settling time had no effect on the oil loading, indicating the fairly stable oil–mineral aggregates. However, Ajijolaiya *et al.*^{40,41} observed a more distinct trend from the trapping efficiency obtained immediately after the overnight period than that obtained days or weeks afterwards. Therefore, they concluded OSAs may not be stable over extended periods as days to weeks, which is consistent with observations of other researchers that the quantity of OSAs can change during storage.^{10,12,21}

Research methods for studying OSA formation

OSAs are usually less than 100 μm in size, therefore, specific laboratory or simple on-site demonstration tests are needed to illustrate this OSA formation process. Methods have been developed for the identification and characterisation of OSAs. In

the laboratory, OSAs similar to those observed in actual oil spills were generated by mixing oil, water and sediment particulates by hand shaker, orbital shaker, or oscillating shaker. The oscillating shaker was proven to be effective in OSA formation studies.⁵⁸

UV-epifluorescence microscopy is particularly sensitive for detection of crude oil because aromatic hydrocarbons can generate strong fluorescence under the UV light. Therefore, traditional OSA characterization and its routine identification almost inevitably rely on UV epi-fluorescence microscopy, especially the UV epi-fluorescence microscopy combined with bright field transmitted light to visualize both the oil droplet and the surrounding SPM.^{5,10–15,21,30–32,36,37,39–41,43,48,50} However, recent studies showed that this method is not appropriate when used to measure the amount of oil trapped in OSAs. This is because the volume of oil calculated is based on using two-dimensional images of oil droplets and on assumption of the oil droplets to be spherical or cylindrical in shape, which may produce large, even 100% error when OSAs are big in size and with complex shapes.¹⁸ Although ultraviolet fluorescence spectroscopy (UVFS) and ultraviolet absorption method are relatively simple and economic to quantify oil trapped in OSAs, they are unable to accurately measure oil with low concentrations or individual hydrocarbon components. Comparing between these two methods, UV fluorescence spectrophotometer exhibits more advantages as a rapid analytical method, because it does not need the extraction nor the concentration procedures.^{49,59–61}

Another important method to quantify concentrations and composition of oil trapped in OSAs is application of GC-FID and GC-MS after dichloromethane (DCM) extraction.^{5,10–12,15,38,59,62} GC/MS is effective and sensitive to measure small variances of the total and individual petroleum hydrocarbon concentrations. Khelifa *et al.* developed a GC-FID procedure to measure the variance of oil trapped in negatively buoyant OSAs, including the procedure to separate and extract the settled OSAs on the bottom of the reaction chamber.¹⁸ The biodegradation rates of oil trapped in OSAs can also be calculated by determination of ratios of concentrations of target hydrocarbons to the concentrations of highly degradation-resistant oil biomarker compounds at different times.^{63,64}

The HPLC methods have also been developed and used by some scientists to measure concentrations of polar compounds, in addition to the saturate and aromatic fractions.^{5,10} Recently, Lee *et al.* used thin layer chromatography coupled with flame ionized detection (TLC-FID) to analyze the major hydrocarbon fractions of crude oil (including alkanes, aromatics, resins, and asphaltenes).⁶¹

Scanning confocal laser and scanning electron microscopy have been used to characterize the three-dimensional geometry of OSAs.^{13,40} X-ray diffraction and laser scattering particle size analyzer have also been reported to be used for characterization of the mineralogy and size of sediment particulates.

Applications of OSAs in oiled shoreline clean-up

It has been understood that the process of OSA formation helps natural cleansing of oiled shorelines because of the following three reasons: first, OSAs appear to be more readily removed from the shorelines as they do not stick to the shorelines as the

original oil does; second, OSAs have higher density than the original oil, and this may cause more oil dispersed in the water column; third, biodegradation of oil trapped in OSAs can be significantly accelerated by increase of the oil–water contact area. This OSA formation process has been demonstrated at several spill sites such as the Exxon Valdez, Arrow, Metula, Nosac Forest, Tampa Bay, and BIOS (Baffin Island Oil Spill). Subsequent studies after the Sea Empress oil spill and during the Svalbard Shoreline Field Trials^{5–8,10,15,16} clearly documented the OSA formation.

It has been proved that a large portion of stranded oil in shorelines could be removed by OSA formation. In the experiments on the six Alaska Rivers, oil removed by the OSA formation was between 0.03 and 0.24 g oil/g solid with the average being 0.13 g oil/g solid.²⁹ In the most recent experiments with SRM 1941B and Arabian Medium crude oil, the maximum oil–sediment ratio in the settled OSAs could be as high as 0.29–0.38 g oil/g sediment.⁵³ OSAs may be suspended in the water column or either positively or negatively buoyant, depending on the OSAs' size, the ratio of oil to mineral in each individual aggregate and the hydrodynamic conditions.¹³ In the previous studies, most of the aggregates were found to be positively buoyant because of the large hydrodynamic cross section of the flocculated particles, which would favour dispersion and transportation and minimize the accumulation of hydrocarbons in subtidal sediments.^{10,31,65} Although the particles tended to sink, there was sufficient wave energy to keep them in suspension, which would also enhance oil dispersion, and this may well explain the observations why a low concentration of aggregates was produced in river water (there was no evidence of accumulation of oil in the near shore bottom sediments) but an abundance of OSAs can be formed in the laboratory with the same river water and the same oil.¹³

However, the OSA formation does not merely help to move oil from one location to another environment compartment, but accelerates oil biodegradation rates. The association of suspended particles and bacteria may be more sufficient to biodegrade dispersed oil droplets than bacteria alone. In the presence of suspended minerals the influence of nutrients to biodegradation is less important than the level of dispersion, as the increased oil dispersion resulting from the SPM appears to be sufficient to encourage the growth of bacteria without the need for additional nutrients.³⁷ Recent studies have demonstrated that oil dispersed into nearshore waters and sediments by interaction with SPM was biodegraded more rapidly than residual oil in the beach. Addition of SPM can advance the onset of biodegradation and increase significantly total n-alkane loss rates over a period of a couple of months.⁶⁶ So SPM can promote both oil dispersion into the water column and microbial interactions with oil. This may well explain part of the unaccountable fraction of the oil mass balance in the previous studies.¹³

Enhanced oil dispersion and micro-biodegradation due to OSA formation may help the oiled shorelines to clean up in several days. However, oils that penetrate into the deep layer of the beach may combine with the fine particles stuck in the pores for tens of years. Meanwhile, oil stranded in the upper part of the beach may be there for years, as it is above the effect of wave action and only has the chance to be removed from the sediment by occasional storms years after the spill to make them in the

effect of wave action. According to those conditions, there are some oil spill clean-up technologies developed subsequently based on acceleration of OSA formation to clean-up oiled shorelines. These shoreline treatment technologies include sediment relocation (surf washing, berm relocation) and sediment mixing (sediment tilling).^{8,15,16}

Sediment relocation is the treatment to move oiled sediments into the zone of wave action to promote the interaction between oil and mineral fines. It harnesses the hydraulic action of waves, and the processes of OSA formation and physical abrasion usually occur in tandem on open coasts. It is not simply pushing the oil into water, but is a valuable method to remove oil from shorelines by OSA formation to accelerate oil dispersion into the sea and micro-biodegradation in the continuous action of tides and waves. Some time later, the sediment removed to the lower part of the beach can return to the upper part of the beach naturally. Additionally, this technology is particularly well suited to remote locations, as there is no need to find space to place the oiled sediments and it does not need extra treatment for the oiled sediments, therefore the cost of applying this technology is much less than the traditional treatments. This new type of technology is based on acceleration of natural processes, and there are no chemicals added to the environment, so it is also more environmentally friendly than the traditional ones. The effect of this new technology can be present after the next high tide following the treatment, so it is fast and effective. In all, it is a promising technology.

Sediment mixing is the treatment to simply expose subsurface oil that penetrates into the deeper layer of the aquifer or is buried by the re-deposition of beach sediment, accelerating the interaction between oil and sediment in the condition of coastal hydrodynamics. This treatment does not involve movement of the sediment from one part of a beach to another, and actually there is no big difference between the two techniques and sediment relocation involves mixing. Both actions promote physical abrasion and OSA formation.

Sediment relocation was first used intentionally to promote OSA formation as a final cleaning step on tourist beaches during the Fred Bouchard oil spill in Tampa Bay, Florida, USA in 1993. The orange-colored, stained sands remained on the intertidal zone after manual and mechanical removal turned to white, oil-free sediments after the next high tide following movement of the oiled sediments down to the water line at low tide. And then it was successfully used in the Sea Empress response in 1996 on Amroth Beach, and Marros Beach. It provides a valuable opportunity to show the significance of OSA formation in shoreline cleanup during the 1997 Svalbard Shoreline Field Trials. In those shoreline trials, treatments based on OSA formation were natural attenuation, sediment relocation and sediment mixing. Although there was only limited content of fine particles in the experimental beach sediment, OSAs can form naturally. During the first tide following the treatment of sediment relocation, the release of fine oiled sediments was largely enhanced and there were significant amounts of OSAs observed in the near-shore water. There were no significant detrimental side-effects of residual oil in pelagic or benthic environments associated with the use of these treatment options. These treatments were also compared with the strategy of bioremediation during this trial.^{8,16}

After years of laboratory work to investigate the effects of different controlling parameters on the OSA formation, scientists of Canadian Coast Guard evaluated this new technology in the Gulf of St. Lawrence during January 28th to February 1st, 2008.⁶⁷ They poured 200 L of crude oil onto the broken ice of Gulf of St. Lawrence, Quebec. Under those cold and icy conditions, traditional methods such as using skimmers and burning are quite limited and ineffective. They mixed bags of calcite with seawater and sprayed through fire hoses on an oiled surface. The mixing energy was provided by the ship propeller to shear the oil slick into small oil droplets. OSAs were formed just as anticipated to lower oil concentrations in the water column at the spill site and adjacent areas well below toxicity limits. Hydrocarbon concentrations in the sediments adjacent to the experimental area were never above the established regulatory values for ocean disposal. This was a great field experiment to fill the gap between lab and real-world application. Research on further control and applications of this technology is needed.

Future research needs

Understanding of the factors that control the OSA formation is crucial to evaluate the efficacy of this process for natural remediation of oiled shorelines. Significant insights have been gained, especially in recent years about the effects of sediment size and concentration, oil properties and salinity on the characteristics of OSA formation. However, there are still some crucial factors not clear to us. In order to improve our understanding on OSA formation and get a better picture of the oil behaviours after oil spills in the marine environment, the following research aspects are needed:

(1) Oil droplet formation as the first step and a key process in OSA formation needs to be studied under different conditions, like different mixing energy types and levels, different temperatures, various oil types and weathering states for validation of the existing theories and development of the new ones. The effect of chemical dispersants is important to oil droplet formation and needs to be investigated further.

(2) In previous studies, OSAs were generated by mixing at a fixed high energy for hours in almost all of the laboratory experiments. Although it has been known that mixing energy is a key parameter for OSA formation, it is difficult to find systematic studies on the effects of mixing energy on the OSA formation. Additionally, as mixing energy varies in time and space in the environment, it is difficult to simulate the field conditions in laboratories. Therefore, future studies are needed to correlate the OSA formation under different energy levels generated in lab with those in field.

(3) Although there are few studies on the time scale of OSA formation, the present understanding of OSA formation is still suffering from a lack of good understanding of the kinetics of OSA formation. Proper studies on kinematics of OSA formation under different conditions may be valuable to help the integration of OSA formation into the present oil spill models, thus provide quantitative guidance for spill risk assessment and proper decision making during the selection and application of oil spill response strategies. It may even help the generation of new countermeasure strategies for the spill response community.

(4) As the use of chemical dispersants is still an important oil spill response strategy when oil spill happens in coastal area, endeavouring at minimizing the transport of oil to shoreline environments. Its utilization may alter the rate and extent of OSA formation by modification of surface physicochemical properties of oil droplets.⁶⁸ Guyomarch *et al.* found multiple-droplet aggregates more common with the presence of chemical dispersant than without dispersant.^{24,31} Li and Lee *et al.* showed the synergistic effects of chemical dispersants and mineral fines enhancing oil transfer to the water column and the formation of smaller and denser OSAs.^{58,69,70} However, the application of chemical dispersant has to be approached with great caution due to its possibility to enhance the oil sedimentation, which may result in more persistent toxicity effects to the benthic organisms. Khelifa *et al.* validated recently the increased oil sedimentation with chemical dispersant than with physically dispersed oil at low sediment concentration of 25 to 50 mg/L.⁶² Meanwhile, another research group lead by Lee found that the oil sedimentation may not necessarily increase in particle-rich water when dispersants were applied.⁶¹ Further study needs to be conducted on the effect of chemical dispersant on oil droplet properties, oil–sediment interaction and the fate of oil after being spilled in the marine environment, thus provide proper understanding to the oil remediation community.

Conclusions

OSA formation has potential significance in shoreline cleanup after oil spills by largely acceleration of oil dispersion and degradation. Quantitative methods have been established in the laboratory for OSA characterization, including UV-epifluorescence microscopy and GC-FID procedures. Till now the quantitative understandings on OSA formation are about sediment size and concentration, oil properties, water salinity, and mixing energy. In addition to the laboratory studies, there are also some field applications, like natural attenuation, sediment relocation, sediment mixing, and addition of sediment in the absence of enough sediment particulates. All of those clean-up strategies based on OSA formation have been proved to be of promising future. More studies need to be conducted on oil droplet properties and oil–sediment interactions under more complex conditions, like under different energy levels and time space, and in conjunction with other spill remediation strategies like dispersant application, aiming at providing better knowledge for more efficient and effective oil spill response strategies in the near future.

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