Distribution of Polycyclic Aromatic Hydrocarbons in Sunken Oils in the Presence of Chemical Dispersant and Sediment

Yali Gao 1, Deqi Xiong 1*, Zhixin Qi 1, Xishan Li 1, Zhonglei Ju 1 and Xueqiang Zhuang 2,*

1 College of Environmental Sciences and Engineering, Dalian Maritime University, Dalian 116026, China
2 School of Marine Engineering, Jimei University, Xiamen 361021, China
* Correspondence: xiongdq@dlmu.edu.cn (D.X.); xqz@jmu.edu.cn (X.Z.); Tel.: +86-0411-8472-9615 (D.X.)

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Abstract: The formation of sunken oils is mainly dominated by the interaction between spilled oils and sediments. Due to their patchiness and invisibility, cleaning operations become difficult. As a result, sunken oils may cause long-term and significant damage to marine benthonic organisms. In the present study, a bench experiment was designed and conducted to investigate the quantitative distribution of polycyclic aromatic hydrocarbons (PAHs) in sunken oils in the presence of chemical dispersant and sediment. The oil sinking efficiency (OSE) of 16 priority total PAHs in the sediment phase was analyzed with different dosages of dispersant. The results showed that the synergistic effect of chemical dispersant and sediment promoted the formation of sunken oils, and the content of PAHs partitioned in the sunken oils increased with the increase of dispersant-to-oil ratios (DORs). Furthermore, with the addition of chemical dispersant, due to the solubility and hydrophobicity of individual PAHs, the high molecular weight (HMW) PAHs with 4–6 rings tended to partition to sediment compared with low molecular weight (LMW) PAHs with 2–3 rings. The synergistic effect of chemical dispersant and sediment could enhance the OSE of HMW PAHs in sunken oils, which might subsequently cause certain risks for marine benthonic organisms.

Keywords: sunken oils; polycyclic aromatic hydrocarbons; chemical dispersant; suspended sediment

1. Introduction

The consecutive increase of oil production and marine transportation pose an ever-increasing risk of accidental release of oils during the last decades [1–5]. About 3000 oil spill accidents occurred in the period 1973–2011 according to reports in China (Ministry of Transport, 1974–2012). Once oil spills occur at sea, the spilled oils normally float on the surface of the water column and then are spread over a wide area by currents, wind, and waves. However, some oils, especially heavy oils, occasionally sink to the seabed [6,7]. Several studies have indicated that the amount of sunken oils ranged from 2% to 11% of the total spilled oil [8,9]. Although the sinking oil has historically accounted for a small percentage of oil spill accidents [10], its environmental impacts on the benthos are of concern [11–14]. Field and laboratory exposures have demonstrated that the accumulation of sunken oils on the seafloor has far-reaching ecological implications adversely impacting benthic organisms, including corals, fish, and sea urchin [15–18]. Generally, it has already been considered that the main toxic components of the oil are polycyclic aromatic hydrocarbons (PAHs), a group of ubiquitous persistent organic pollutants, which are composed of two or more fused aromatic rings in linear, angular, or cluster arrangement [19]. PAHs pollutions have been a topic of concern for years because of their mutagenic and carcinogenic effects [17]. Moreover, PAHs could cause adverse effects not only in aquatic ecosystems but also for human health via food chain transmission.
In the case of marine oil spills, common oil spill responses (OSRs), such as mechanical containment and recovery and the application of chemical dispersants, are based on the simple principle that oil floats [6]. However, for sunken and suspended oils (SSO), these physical and chemical OSRs are not applicable [20]. It is worth noting that the SSO cannot be easily monitored by the typical techniques of visual observation or remote sensing [21,22], leading to the cleaning operations being difficult [23]. The SSO may occur in many forms depending upon the oil density, degree of weathering, addition of dispersants, and participation of sediments. As summarized in Figure 1, SSO can form mainly following accidental spills of (1) heavier oils that are denser than the receiving water; (2) lighter oils that lose their light constituents in the short-term weathering process and become heavier than water, and (3) oils that interact with sediments through direct aggregation to form oil-suspended sediment aggregates (OSAs), adsorption on the sediment phase, or incorporation in the sediment phase [24]. SSO is divided into suspended oils and sunken oils based on their buoyancy. Suspended oils are defined as oils that have neutral buoyancy and are below the water surface, which include dissolved hydrocarbons, dispersed oil droplets, suspended oil-contaminated sediments, and neutral OSAs; whereas sunken oils are defined as oils that have negative buoyancy and have been deposited on the seabed, which mainly consist of negative OSAs and sunken oil-contaminated sediments. Compared with suspended oils, the sunken oils may be settled at the seabed, or be buried by sediments, which are difficult to be biodegraded by microorganisms. As a result, sunken oils may cause long-term and more significant damage to benthonic organisms that have limited or null motility [25–28].

Coastal sediment has been regarded as an important transport medium and repository for environmental pollutants [29–31]. After many major oil spills, such as Tsesis, Ixtoc-I, Vista Bella, and others, the formation of sunken oils was mainly dominated by the interaction between spilled oils and sediments [6,9,32,33]. Several studies have been conducted to understand the formation and characteristics of sunken oils in the presence of sediment [34–37]. However, the synergistic effect of sediments and chemical dispersants on the formation of sunken oils is still unclear. Generally, the use of chemical dispersants is restricted in shallow waters. However, due to perceptions of dispersants being of net environmental benefit, chemical dispersants were applied as the optimum OSR in some oil spills that occurred near the shoreline, such as the “7–16” oil spill in Dalian, China, in which more than 1500 tons oils were spilled into the Yellow Sea, and approximately 200 tons of dispersants were sprayed into the seawater in Dalian Bay [38]. Because of the amphiphilic nature of surfactants, the application of chemical dispersant can accelerate the dispersion and dissolution of oil and enhance the break-up of oil into small droplets by reducing the oil–water interfacial tension [39]. The resulting dispersed oil droplets and dissolved hydrocarbons may aggregate with or adsorb the sediment, which facilitates the formation of sunken oils [40,41]. On the other hand, chemical dispersant reduces the stickiness of the oil. As a result, chemically dispersed oil droplets become less likely to adhere to sediment, which prevents the formation of sunken oils [42].

**Figure 1.** Formation and fate of sunken and suspended oils (SSO) in the marine environment.
Decisions on whether or not to use dispersants need to consider the net environmental benefits, and exposure of the benthos is also a concern. At present, there is still a significant knowledge gap concerning the synergistic effect of chemical dispersants and sediments on the formation and characteristics of the sunken oils. Most of the previous bench-scale studies have focused on the oil sinking efficiency (OSE) in the presence of dispersants and sediments [3,32,34–36,43]. Few studies were conducted on the quantitative distribution of polycyclic aromatic hydrocarbons (PAHs) in the sunken oils. Furthermore, dispersants may affect exposure to these oil constituents by altering their fate, transport, and biodegradation [9]. The effects of the dispersant on the OSE of PAHs with different molecular weight were not well understood. The present study investigated the synergistic effects of chemical dispersants and sediment on the distribution of total 16 PAHs partitioned in sunken oils, which have been identified as priority control pollutants by the US Environmental Protection Agency (EPA) [44]. The present study aimed to elucidate the underlying mechanisms of different dosages of chemical dispersant on the partitioning of PAHs in the sediment. The OSE of total PAHs and different rings PAHs were also quantitatively analyzed.

2. Materials and Methods

2.1. Experimental Materials

Heavy fuel oil 380 (HFO 380), as the main fuel oil for large ships, was employed in this study. As the most common constituent of sand, quartz sand was chosen as the test sediment. The natural seawater was collected from the Bohai Sea and was pre-filtered through 0.45 \( \mu \)m pore-size filters. The properties of HFO 380, sediment, and seawater were summarized in Table 1. The size distribution of the quartz sand was measured and shown in Figure 2.

| Properties of Oil at 25 °C | HFO 380 |
|---------------------------|---------|
| Density (g/mL)            | 0.9821  |
| Asphaltenes (wt %)        | 11.35   |
| IFT \(^1\) (N/m)          | 0.034   |
| Viscosity (mm\(^2\)/s)    | 15,529.70|

| Properties of Sediment |
|------------------------|
| Quartz sand            |
| Density (g/mL)         | 2.08    |
| Contact angle <10 °C   |         |
| Volume median diameter (\(\mu\)m) | 6.38 |

| Properties of Seawater |
|------------------------|
| Seawater               |
| pH                     | 7.60 ± 0.30 |
| Salinity (%w)          | 35.00 ± 1.00|
| Conductivity (ms/cm)   | 41.70 ± 1.20|

\(^1\) IFT is the abbreviation of interfacial tension.

![Figure 2](attachment://Figure_2.png) *Figure 2.* Size distribution of quartz sand, measured by laser in situ scattering and transmissometry (LISST-100X, Type C, Sequoia Scientific, Seattle, WA, USA).
2.2. Experimental Conditions and Procedure

Two sets of experiments were performed in this study. In the first set, a blank experiment was carried out without dispersant. In the second set, GM-2 conventional chemical dispersant (purchased from Qingdao Guangming Environmental Technology Co., Ltd., Qingdao, China), as one of the most common dispersants used in an oil spill, was tested. Three dispersant-to-oil ratios (DORs) were selected based on the manufacturer’s instructions. The experimental conditions and factorial levels were listed in Table 2. At least triplicate runs were conducted for each experimental condition following the procedure described below.

| Experimental conditions | Experiment 1 | Experiment 2 |
|-------------------------|--------------|--------------|
| Volume of flask         | 500 (mL)     |              |
| Seawater volume         | 400 (mL)     |              |
| Initial oil mass        | 100 (mg)     |              |
| Reciprocating shaker speed | 180 (cycles/min) |             |
| Sediment concentration  | 200 (mg/L)   |              |
| Temperature             | 25 (°C)      |              |
| Shaking time            | 240 (min)    |              |

| Factorial levels         | Experiment 1 | Experiment 2 |
|--------------------------|--------------|--------------|
| Sediment type            | quartz sand  | quartz sand  |
| Dispersant type          | -            | GM-2         |
| DOR                      | -            | 1:10; 1:5; 1:3 |

Experiments were conducted following a modified EPA baffled flask test (BFT) [45,46]. The improved BFT method could provide sufficient mixing energy for dispersion, akin to that observed in the field and better reproducibility [47]. The procedure used to prepare sunken oils was performed as previously described [32]. Briefly, sunken oils were prepared using 400 mL natural seawater, 100 mg HFO 380, and predefined amounts of quartz sand in 500 mL Erlenmeyer flasks closed by silicone stoppers wrapped with aluminum foil to avoid the evaporation of light compounds. The simulated formation of sunken oils was achieved using a temperature-controlled reciprocating shake at a stroke frequency of 180 cycles/min, corresponding to the energy dissipation rate of 2600 W/m³ with water splash of 66 mm height [48]. This value falls within the range of breaking waves (10³–10⁴ W/m³) [49]. The mixing system may represent the breaker zone in the nearshore region with low depth and intense turbulence. Dry sediment was added to seawater and shaken for 30 min. Using a pre-calibrated hypodermic syringe, 100 mg test oil was then dispensed to the surface of the sediment/seawater suspension. The flasks were shaken for another 240 min to generate sunken oils. In the second experiment, a predetermined amount of GM-2 was added rapidly on the oil film after dispensing oil before the flasks were shaken. The amount of GM-2 was calculated using the mass of oil initially added and the different DORs. After the shaking time, the mixtures were placed to settle for 18 h in a refrigerator. Negatively buoyant sunken oils were separated from the suspensions for oil extraction, and then total petroleum hydrocarbons (TPH) analysis was performed using the analytical procedure as previously described [32].

2.3. Analytical Procedure of PAHs

The n-hexane extracts of sunken oils were taken for PAHs analysis. First, the extracts were concentrated to 1 mL by rotary evaporation and then transferred to a silica gel column for two separate elution with 12 mL n-hexane and 15 mL dichloromethane/n-hexane (1:1, v/v). The latter purified elution solution was collected, concentrated, and then spiked with an internal standard mixture of PAHs. All samples were analyzed using an Agilent 6890 Series GC with a 5975 MS (Agilent Technologies Inc.,
Santa Clara, CA, USA) operated in the SIM mode. Purified sample extracts were spiked with internal standards. A 30 m × 0.32 mm ID DB-5MSUI capillary column with a 0.25 μm film thickness was used. The carrier gas was helium at 1 mL/min. The column temperature was programmed at 50 °C for 2 min, then increased to 150 °C at 8 °C/min, held for 3 min, then increased to 300 °C at 3 °C/min, and kept constant for 15 min. In this study, 16 priority PAHs listed by the EPA were analyzed, and their basic information was listed in Table 3.

| Compound           | Abbreviation | Water Solubility at 25 °C (mg/L) | logK_{ow} |
|--------------------|--------------|----------------------------------|-----------|
| Naphthalene        | Nap          | 31.00                            | 3.30      |
| Acenaphthylene     | Acy          | 16.10                            | 3.90      |
| Acenaphtene        | Ace          | 3.80                             | 3.97      |
| Fluorene           | Fl           | 1.90                             | 4.18      |
| Phenanthrene       | Phe          | 1.10                             | 4.57      |
| Anthracene         | Ant          | 0.045                            | 4.54      |
| Fluoranthene       | Flu          | 0.26                             | 5.22      |
| Pyrene             | Pyr          | 0.13                             | 5.18      |
| Benz[a]anthracene  | BaA          | 0.011                            | 5.91      |
| Chrysene           | Chr          | 0.0015                           | 5.79      |
| Benzo[b]fluoranthe | BbFlu        | 0.0015                           | 6.44      |
| Benzo[k]fluoranthe | BkFlu        | 0.00080                          | 6.44      |
| Benzo[a]pyrene     | BaP          | 0.0038                           | 6.44      |
| Dibenzo[ah]anthracene | DBahA   | 0.00050                          | 7.19      |
| Indeno[1,2,3-cd]pyrene | IcdP | 0.062                            | 7.04      |
| Benzo[ghi]peryene  | BghiP        | 0.00026                          | 7.10      |

2.4. Data Analysis

The ratio of the PAHs content between sunken oils and initial addition of HFO 380 is a measurement of the extent of oil partitioning in the sediment. The oil sinking efficiency (OSE) was calculated using the following equation:

\[ OSE = \frac{m}{M} \times 100\% \]  

where \( m \) is the mass of PAHs or total petroleum hydrocarbon in the sunken oils, and \( M \) is the mass of PAHs or total petroleum hydrocarbon of HFO 380 initially added in total.

3. Results

3.1. Effect of Sediment Alone

The effect of sediment on sunken oils was explored by GM/MS analysis of the distribution of PAHs. Without the addition of sediment, there was no sedimentation because of very low dispersion with positive buoyancy caused by the high viscosity of HFO 380 with the density less than the receiving seawater. The addition of sediment slightly enhanced the formation of sunken oils. The mass of total PAHs in the sunken oils only accounted for 1.47% of total PAHs in the pure HFO 380 initially added. Figure 3 summarizes the distribution of PAHs in the sunken oils in the presence of quartz sand. The results showed that the main components of sunken oils were lower molecular weight (LMW) PAHs (2–3 rings) comprised 79.83% of total PAHs. The relative proportion of higher molecular weight (HMW) PAHs from 4- to 6-rings accounted for 15.61%, 3.19%, and 1.37%, respectively. The content of naphthalene (Nap) was the highest in the sunken oils with sediment, accounting for 37.74%, followed by phenanthrene (Phe) (22.54%), and fluorene (Fl) (10.29%). However, compared with the content of PAHs of pure HFO 380, the relative proportion of Nap in the sunken oils was remarkably reduced, whilst that of Fl, Phe, anthracene (Ant), benzo[a]anthracene (BaA), chrysene (Chr), benzo[k]fluoranthe (BkFlu), and benzo[a]pyrene (BaP) increased.
3.2. Combined Effect of Dispersant and Sediment

3.2.1. Distribution of PAHs in the Sunken Oils

The synergistic effect of GM-2 and quartz sand on the formation of sunken oils was investigated. Figure 4 shows the distribution of PAHs in the sunken oils in the presence of GM-2 with different DORs and quartz sand. The presence of GM-2 significantly increased the amount of PAHs in the sunken oils compared with sediment alone, and the content of PAHs increased with the increase in DOR. The nominal concentration of total PAHs in sediment was 36.44 µg/g without the dispersant. After adding GM-2, the nominal concentration increased to 382.90 µg/g at a given DOR of 1:10, and then gradually increased with the increase in DOR. The peak concentration 483.06 µg/g at the highest DOR (1:3) was about 1.26-fold and 13.26-fold higher than that at the lowest DOR (1:10) and without dispersant, respectively (Figure S1). Moreover, considering the relative proportions of PAHs, with the addition of GM-2, the composition of PAHs in sunken oils was still dominated by Nap and Phe. However, compared to the sediment alone, the relative proportions of Nap and Phe decreased to 29.17–32.23% and 19.21–19.46% at different DORs, respectively; while relative proportions of pyrene (Pyr) and Chr increased to 9.66–9.91% and 7.05–8.78%, respectively. In the presence of GM-2 and quartz sand, HMW PAHs (4–6 rings) comprised higher proportions of 31.66–33.85% with the increase in DORs than that in sand alone (20.17%). The combination of GM-2 with different DORs and sediment most significantly promoted the relative proportion of PAHs with four rings. However, there was no significant difference in the relative distribution of PAHs with different dosages of dispersant.

![Figure 3. The distribution of PAHs in the sunken oils in the presence of quartz sand.](image)

![Figure 4. The distribution of PAHs in the sunken oils in the presence of GM-2 and quartz sand.](image)
3.2.2. The OSE of PAHs in the Presence of GM-2 and Quartz Sand

The OSE of total PAHs in the sunken oil was further analyzed. As Figure 5 shows, without the addition of GM-2, only 1.47% of PAHs was enriched in the sediment. The addition of chemical dispersant noticeably enhanced the PAHs sedimentation, and the improvements in OSE ranged from 13.98 to 18.02% for different DORs. The OSE of total PAHs increased with the increase in DORs.

![Figure 5. The OSE of PAHs in the sunken oils in the presence of GM-2 and quartz sand.](image)

The OSE of individual PAHs exhibited similar trends to total PAHs with the increase in DOR. The findings of the present study were consistent with results from previous studies [42,50], which demonstrated the HMW PAHs with 4–6 rings prefer to partition to sediment compared with LMW PAHs with 2–3 rings in the presence of dispersant. The OSE of PAHs with different rings showed no significant difference with the sediment alone. In the presence of GM-2 and quartz sand, the OSE of PAHs for 2- and 3-rings was 11.18–13.46% and 20.48–25.67% with different DORs, whereas that for 4-, 5-, and 6-rings was 23.72–31.94%, 25.19–30.86%, and 15.69–26.56%, respectively. The OSE of 4-ring PAHs showed the highest improvements after adding the dispersant, and, at the highest DOR of 1:3, the OSE of that was 23.58-fold higher than that without dispersant.

3.2.3. The OSE of TPH in the Presence of GM-2 and Quartz Sand

The OSE of TPH in the sunken oil was also investigated. As seen in Figure 6a, the OSE of TPH exhibited similar trends to that of PAHs with or without dispersant. Without the addition of dispersant, only 0.38% of TPH was enriched in the sediment, and the improvements in OSE ranged from 23.99% to 30.75% for different DORs with the addition of dispersant.

![Figure 6. (a) The OSE of total petroleum hydrocarbons (TPH) in the sunken oils in the presence of GM-2 and quartz sand; (b) The Pearson’s correlation of OSE between total PAHs and TPH.](image)
Pearson’s correlation of OSE between total PAHs and TPH was calculated in Figure 6b, which showed a strong positive correlation ($R^2 = 0.9786$).

4. Discussion

The stabilization of oil by suspended sediment to form OSAs has been well described in previous studies [24,51]. However, there is no consensus on the distribution of PAHs in the sunken oils under the combination of dispersant and sediment. In the present study, the content of PAHs partitioned to sediment was almost negligible without the addition of dispersant. Studies have indicated that the viscosity of oils is an important parameter in affecting the formation of sunken oils [52]. High viscosity oils are difficult to disperse, and less likely to form aggregates with sediments [53]. A previous study on the formation and structure of oil-mineral fine aggregates determined that OSAs could not form when the viscosity of oils reached or exceeded a threshold of 9500 mPa·s [54]. HFO 380 could hardly generate any dispersed oil droplets because of the high viscosity, which has exceeded the threshold [24]. The infrequent collision of oil droplets and sediment particles prevented the formation of sunken oil, and thus extremely few PAHs were detected without dispersant. With the addition of dispersant at different DORs, the content of total PAHs in the sunken oils was apparently promoted. This was attributed to the application of GM-2, which enhanced the oil dispersion, especially small dispersed droplets, by lowering oil-water interfacial tension [24]. Oil dispersion is positively correlated to the formation of sunken oils, as smaller oil droplets require fewer suspended particles to form OSAs [55]. The abundant chemically dispersed oil droplets, with a smaller size and larger surface area, might sufficiently interact with quartz sand of several micron scales. Considering the hydrophobicity of sediment particles, the addition of a chemical dispersant could enhance the surface hydrophobicity of quartz sand, leading to the improvement in the formation of OSAs [56,57].

In the pure HFO 380, the relative Nap content was enriched, but, in the sunken oils, it was significantly reduced as Nap dissolved. With the addition of a dispersant, the HMW PAHs also tended to partition to sediment compared with LMW PAHs. This was consistent with the results in Table 3 that demonstrates that the solubility of individual PAHs in seawater would decrease with the increasing number of aromatic rings [42], whereas the log$K_{ow}$ would increase. The findings of the current study demonstrated that the LMW PAHs with log$K_{ow}$ values between 3.30 and 4.54 would preferentially partition to the water column rather than associate with sediment particles, which was consistent with the results from previous studies [42,58,59]. Moreover, the application of dispersant could enhance the OSE of HMW PAHs in the sunken oils, especially 4-ring PAHs, which might subsequently cause more severe consequences for marine benthonic organisms [13,18,60]. Therefore, the present study could improve the understanding of the impacts of HFO 380 spillage on aquatic organisms and be complementary to field studies on sunken oils. Furthermore, the net environmental benefits of the dispersant between shoreline oil clean-up and benthos damage need to be evaluated.

Above all, the size ratio of sediment particles and oil droplets and the hydrophobicity of PAHs synergistically affected the formation of sunken oils in the presence of dispersant. The potential mechanism of the interaction between oil and sediment in the presence of chemical dispersant was illustrated in Figure 7. Because of the complexity of the nearshore environment, many factors may affect the formation rate of sunken oils in the real world resulting in the deviation, such as water depth and dilution effect [61]. While results from laboratory experiments cannot be directly extrapolated to in situ conditions, they supply insights that improve our predictive capability. The results presented in this study may provide some fundamental understanding and knowledge of the formation mechanism of sunken oils in the presence of dispersant in the nearshore region.
5. Conclusions

Unsourced oil contamination in coastal waters has recently attracted the attention of scholars to study the formation and characteristics of sunken oils due to concerns over their toxic effects on marine organisms, especially benthonic organism with limited or null motility. This study has provided quantitative data of PAHs partitioned in the sediment phase in the presence of chemical dispersant. Results indicated that the OSE of HMW PAHs with higher toxicity in the sunken oils increased gradually with the increase in DORs. At present, the invisible sunken oils have not been well considered in oil spill risk assessment. The synergistic effect of chemical dispersant and sediment on the overall fate and toxicity of sunken oils needs to be evaluated further to better improve the predictions of consequences of oil spill accidents. Furthermore, chemical dispersant should be restricted for use, especially in nearshore waters with abundant suspended sediments. In the present study, the chemical analysis of sunken oils covered only 16 EPA priority PAHs. Future research should work on analyzing more compounds in the sunken oils to reveal the toxic effects on the benthos, such as alkyl-substituted PAHs.

Supplementary Materials: The following are available online at http://www.mdpi.com/2077-1312/7/9/282/s1, Figure S1: Nominal concentration of PAHs partitioned in quartz sand in the presence of GM-2.

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