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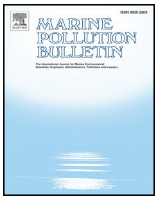

Simulated oil release from oil-contaminated marine sediment in the Bohai Sea, China

Lingling Yuan [a,b], Longxi Han [a,d,*], Wenjie Bo [c], Hua Chen [b], Wenshen Gao [c], Bo Chen [a]

[a] College of Environment, Hohai University, Nanjing 210098, China
[b] National Center of Oceanographic Standards and Metrology, Tianjin 300112, China
[c] Marine Environmental monitoring and Forecasting Center, Tianjin 300450, China
[d] Key Laboratory of Shallow Lakes of Ministry of Education, Hohai University, Nanjing 210098, China

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ABSTRACT

There is a high degree of heavy oil partitioning into marine sediments when an oil spill occurs. Contaminated sediment, as an endogenous pollution source, can re-pollute overlying water slowly. In this study, a static oil release process and its effects in marine sediment was investigated through a series of experiments with reproductive heavy oil-contaminated marine sediment. The oil release process was accurately simulated with a Lagergren first-order equation and reached equilibration after 48 h. The fitted curve for equilibrium concentration (C_0) and first-order rate constant (k_1) for sediment pollution levels exhibited a first-order log relationship. The instantaneous release rate ($\frac{dC_t}{dt}$) was also calculated. The C_0 increased with increases in temperature and dissolved organic matter (DOM), and decreasing salinity. The k_1 increased with temperature, but was not affected by DOM and salinity. These results can be used to better understand the fate of heavy oil in contaminated sediments of the Bohai Sea.

1. Introduction

Oil spills usually occur in the oceans during recovery, storage, transportation, and as a result of maritime accidents (Gong et al., 2014a). Petroleum is a complex compound composed of alkanes, cyclanes, and aromatics, which can potentially cause cancer, deformities, and mutations in humans (Pan et al., 2013). It can be a major environmental and financial threat to local communities, particularly if large volumes of unrefined hydrocarbons or crude oil are spilled into the sea (Graham et al., 2010a, 2010b; Li et al., 2015a). Dissolved oil components are more easily incorporated into bottom sediments and can persist for a long time (Yamada et al., 2003). Studies on the West Falmouth oil spill showed that a substantial amount of moderately degraded petroleum still existed 8–20 cm below the sediment surface almost 40 years after the spill (Culbertson et al., 2007; (Dincer Kirman et al., 2016). Conversely, partitioned oil present in sediments may be released into the water column (Chao et al., 2002; Zhao et al., 1997). In marine systems, the fate and transport of oil components are associated with solubilization, biodegradation, adsorption/desorption from sediment and suspended particle matter, and dilution in the water column (Gong et al., 2014a). A previous study showed that about 50% of the insoluble hydrocarbon fraction dispersed into the water column was removed by suspended sediments (Bandara et al., 2011). Thus, the fate and transport of oil can be significantly changed by the suspended sediment load (Bandara et al., 2011; Vorobiev et al., 2014). This is concerning because oil-contaminated sediments posed serious environmental hazards for both aquatic and terrestrial ecosystems (Agarwal and Liu, 2015).

The shallow Bohai Sea, located in northern China, is surrounded by Liaodong and Shandong peninsulas, and is connected to the northern Yellow Sea by the Bohai Strait. It is the second largest crude oil production base in China with >50 offshore platforms that discharged approximately 9.9 million tons of petroleum-contaminated water in 2006. This caused 30% of the Bohai Sea water to fail quality standards. In June 2011, the most serious oil spill to date occurred in an offshore oil field (Penglai 19-3, operated by ConocoPhillips China, Inc.) in the Bohai Sea. Approximately 723 barrels of oil and 2620 barrels of mineral oil-based drilling mud seeped into the sea (Li et al., 2015a); most of the oil was heavy oil. The majority of heavy oil is rich in carcinogenic compounds, the remains of which absorbed onto sediment particles (Agarwal and Liu, 2015). The oil concentration has exceeded 1.5 mg/g in the contaminated sediment of the Penglai 19-3 area and seawater oil concentration was >0.5 mg/L for the last 3 years. Although oil is insoluble, it is released slowly into the overlying water from contaminated sediments. The presence of oil components in water, even in small quantities, is considered a major concern for both environmental safety and public health (Saeed and Al-Mutairi, 1999). The monthly average water temperature of the Bohai Sea was 274 K to 298 K in 2011–2015 and average salinity was 32 psu. The potential factors affecting oil release from sediments are temperature, salinity, nutrients and dissolved organic matter (DOM).

Studies have shown that interactions between oil and sediments play an important role in the dispersion and degradation of spilled oil (Lee, 2002). Many hydrodynamic models were developed to simulate

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[*] Corresponding author at: College of Environment, Hohai University, Nanjing 210098, China.
E-mail address: hanlongxi999@163.com (L. Han).

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the migration and transformation of petroleum-derived contaminants into the soil/sediment–water system (Bandara et al., 2011; Pan et al., 2013). Much research has concentrated on the effects of controlling parameters, such as sediment particle size and concentration, organic matter content, oil properties, and salinity, on oil–sediment interactions (Gong et al., 2014a; Haftka et al., 2010; Rivas, 2006; Sorensen et al., 2014; Sterling et al., 2005; Sun et al., 2010). The sorption–desorption behavior of oil or polycyclic aromatic hydrocarbons (PAHs) onto soils/sediments has been investigated with batch experiments, Tenax beads, biosurfactants and oil dispersants during the last several decades (Cao et al., 2013; Cao et al., 2011; Poot et al., 2014; Portet-Koltalo et al., 2013; van Noort et al., 2003; Yang et al., 2014; Yu et al., 2011; Zhao et al., 2015). However, these studies could not evaluate the oil release process in a sediment–seawater system. Guo et al. (2011) studied the static release process of petroleum pollutants into a freshwater–sediments system described by a stagnant film model.

In this study, we investigated the oil release process and dynamics in a sediment–seawater system with reproductive heavy oil-contaminated sediment. The original sediment was obtained from Bohai Bay (Bohai Sea, northern China). The effects of temperature, salinity, pH and DOM on the process were investigated using conditions present in the Bohai Sea. Our results can be used to better understand the fate of heavy oil in contaminated sediment of the Penglai 19-3 area of the Bohai Sea.

2. Materials and methods

2.1. Oil-contaminated sediment

The sediment (1–10 cm deep) was recovered with a box sampler in the Bohai Sea (117Boh′15″E, 39°09′35″N), where the water depth is 4.5 m. The organic matter content was measured by potassium dichromate redox titration using a total carbon analyzer (GB 17378.5-2007). The mineralogical composition and particle size distribution were estimated by a BT-9300H laser particle size analyzer (Better, China). Physical and chemical properties of the sediment are shown in Table 1 and Fig. S1. After seashells and gravel were removed manually, the sediment was air-dried and passed through an 80 mesh sieve.

Heavy oil pumped from a platform in Bohai Bay oil field (China National Offshore Oil Corporation (CNOOC)) was used as the contamination source. Some known weights of the pretreated sediments were mixed with solutions of the heavy oil dissolved in *n*-hexane. The slurries were mixed thoroughly and air-dried at room temperature until the solvent evaporated completely to form the contaminated samples. Then, the contaminated sediments were aged at 4 °C in the dark for 60 days (Guo et al., 2011). Before use, the contaminated sediments were washed with artificial seawater (ASW) three times and air-dried to semi-dry in the dark.

2.2. Static release experiments

The ASW was prepared, which served as the overlying water in our release experiments. The semi-dry polluted sediments (contamination concentrations of 464, 734, 1239, 2317, 4382 and 9196 mg/kg) were placed at the bottom of 1000-mL glass cylinders. The sediment thickness was 5 cm, and the overlying water height was 30 cm (~1000 mL); this was the static release system. Finally, NaN_3 was added to the solution to inhibit the growth of microorganisms (Lou et al., 2012). The glass cylinders were sealed and put into a 283 ± 2 K temperature controlled box to avoid light. The oil content of the middle overlying water layer was measured at regular intervals, and the oil release amounts from the sediment samples were determined based on the oil content in that layer.

Table 1
Physical and chemical properties of the sediments.

Clay (%)	Silt (%)	Sand (%)	Organic matter (%)	Oil (10^{-6})	Moisture content (%)
41.36	55.16	3.48	0.331	222	38.4

2.3. Environmental factor tests

The static oil release tests only varied one factor, temperature, salinity, pH or DOM. However, in the environmental factor test, all of these parameters were adjusted with the sediment pollution level set at 1239 mg/kg. The reaction temperatures used were 275 ± 2 K, 283 ± 2 K, and 298 ± 2 K. The salinity of the overlying water was 2 and 32 psu, and the pH values were 5.0, 7.0, and 10.0.

The DOM was extracted from organic fertilizer (collected from Beitang field, Tanggu, Tianjin, China) for 30 min with distilled water (solid:water = 1:10) at 200 rpm in the dark. The suspensions were centrifuged for 30 min at 1500 × *g* and filtered through 0.45 μm polysulfone membrane filters (Lou et al., 2012). The pH value of the DOM solution was adjusted to 7.0 before conducting the experiment. The DOM solution was added to vials of ASW (the overlying water), for total organic carbon (TOC) values of 0, 1.5, 3.0, 4.5 mg/L.

2.4. Oil analysis

The oil concentration in the overlying water and sediments was measured with ultraviolet spectrophotometry (T6 New Century, PERSEE, China) according to the GB 17378.4-2007 and GB 17378.5-2007 procedures. The sediment pollution level was monitored before each test at a wavelength of 225 nm. Two replicates were performed. All data were subjected to variance analysis with ORIGIN 8.0.

3. Results and discussion

3.1. Heavy oil release dynamics

The release kinetic curves of the sediment samples at contamination levels of 464, 734, 1239, 2317, 4382 and 9196 mg/kg are shown in Fig. 1. Generally, the oil release process occurred in two stages. Oil was desorbed from the sediment into the pore water and then diffused to the overlying water. Most of the hydrophobic components in the sediment and soil were adsorbed onto particles, organic matter, and black carbon. The amount dissolved in pore water is generally very low (Liu et al., 2004; Wang et al., 2011; Mathialagan and Viraraghavan, 2009). The decisive step in the oil release process was desorption in agreement with Huang and Ren (2004) and Cao and Shu (1999), but contrasts with the findings of Guo et al. (2011). One of the most widely used models for the adsorption–desorption of solute in liquid solution is the Lagergren first-order (LFO) equation, which is well-suited for explaining liquid–solid adsorption–desorption kinetics (Tseng et al., 2010). The LFO equation is most appropriate for describing the adsorption–desorption process with an ideal surface layer, dominated by rapid adsorption/desorption (Chang, 2013).

In our experiments, the underlying sediment absorbed large amounts of heavy oil. The oil was desorbed mainly from low-energy binding sites on the particle surface, through which the concentration of oil in water reached equilibrium rapidly. The desorption of oil bound to high-energy sites on the particle surface or on the surface of organic matter, particularly black carbon, did not occur. The main desorption process was rapid, slow desorption was negligible. The LFO equation is well suited to simulate the desorption kinetics of heavy oil release in the sea–sediment system in this experiment.

$$\frac{dq_t}{dt} = k_1(q_s - q_t) \tag{1}$$

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