



Effects of oil dispersant and oil on sorption and desorption of phenanthrene with Gulf Coast marine sediments



Yanyan Gong^a, Xiao Zhao^a, S.E. O'Reilly^b, Tianwei Qian^{a,c}, Dongye Zhao^{a,*}

^a Environmental Engineering Program, Department of Civil Engineering, Auburn University, Auburn, AL 36849, USA

^b Bureau of Ocean Energy Management, GOM Region, Office of Environment, New Orleans, LA 70123, USA

^c Institute of Environmental Science, Taiyuan University of Science and Technology, Taiyuan, Shanxi 030024, China

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ABSTRACT

Effects of a model oil dispersant (Corexit EC9500A) on sorption/desorption of phenanthrene were investigated with two marine sediments. Kinetic data revealed that the presence of the dispersant at 18 mg/L enhanced phenanthrene uptake by up to 7%, whereas the same dispersant during desorption reduced phenanthrene desorption by up to 5%. Sorption isotherms confirmed that at dispersant concentrations of 18 and 180 mg/L, phenanthrene uptake progressively increased for both sediments. Furthermore, the presence of the dispersant during desorption induced remarkable sorption hysteresis. The effects were attributed to added phenanthrene affinity and capacity due to sorption of the dispersant on the sediments. Dual-mode models adequately simulated sorption isotherms and kinetic data in the presence of the dispersant. Water accommodated oil (WAO) and dispersant-enhanced WAO increased phenanthrene sorption by up to 22%. This information is important for understanding roles of oil dispersants on the distribution and transport of petroleum PAHs in seawater-sediments.

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1. Introduction

Chemical dispersants have been widely used for mitigating oil spill impacts since the 1950s (Ramachandran et al., 2004). During the 2010 Deepwater Horizon (DWH) oil spill, 859 million liters (5.4 million barrels) of South Louisiana Sweet Crude oil were released, of which 731 million liters (4.6 million barrels) entered the Gulf of Mexico (Griffiths, 2012); and ~7.9 million liters of chemical dispersants (Corexit EC9500A and Corexit 9527A) were applied at the sea surface and near the 1500 m deep wellhead (Kujawinski et al., 2011).

Typically, oil dispersants are mixtures of anionic and nonionic surfactants and solvents. Oil dispersants are able to lower the oil–water interfacial tension, thereby breaking surface oil slicks into fine droplets and facilitating dispersion and dissolution of hydrophobic components of oil into the water column (Kujawinski et al., 2011; Ramachandran et al., 2004). Corexit 9527A consists of two nonionic surfactants (48%) and an anionic surfactant (35%) in an aqueous hydrocarbon solvent (17%) (Scelfo and Tjeerdema, 1991). Corexit EC9500A contains the same surfactants as Corexit 9527A, but it does not contain 2-butoxy ethanol, which is an ingredient in Corexit 9527A (George-Ares and Clark, 2000).

Polycyclic aromatic hydrocarbons (PAHs) are pollutants associated with oil spills that are of great concern due to their toxicity, mutagenicity, carcinogenicity, and persistence (Nam et al., 2008). The DWH oil contained ~3.9% PAHs by weight, and the incident released ~ 2.1×10^{10} g of PAHs into the Gulf of Mexico (Reddy et al., 2012).

Sorption and desorption affect the transport, physical and biological availabilities, toxicity, and ultimate fate of PAHs in the environment (Johnson et al., 2008). In the marine environment, suspended particulate matter (SPM) is a major transport medium for pollutants (Voice and Weber, 1983; Wu and Gschwend, 1986). Because of their hydrophobic nature, PAHs can be strongly sorbed to SPM and accumulate in bottom or coastal sediments through SPM-facilitated transport and settling (Yang et al., 2005), which can greatly alter the weathering rate and environmental fate of PAHs (Gearing et al., 1980).

Sediment organic matter (SOM) is the key component for sorption of hydrophobic compounds (Braidia et al., 2001; White and Pignatello, 1999). In addition to sorption, the extent and rate of desorption are also important factors in controlling physical/biological availabilities of sorbed contaminants (Pignatello and Xing, 1995). Yet, it remains unknown how oil dispersants affect such interactions between sediment particles and persistent oil components such as PAHs.

* Corresponding author.

E-mail addresses: zhaodan@auburn.edu, dzhao@eng.auburn.edu (D. Zhao).

Due to the amphiphilic nature of surfactants, dispersants can cause contrasting effects on the sorption of PAHs by sediments (Cheng and Wong, 2006; Pan et al., 2009; Zhang and He, 2011). On one hand, a surfactant can increase the apparent solubility of PAHs through its hydrophobic tail which reduces sorption and favors desorption of PAHs. On the other hand, the sorption of surfactant on sediments enhances the partitioning of additional PAHs onto the immobilized surfactant. The overall effects of a dispersant would depend on the extent of these contrasting factors. Cheng and Wong (2006) observed that desorption of phenanthrene and pyrene from soil was enhanced in the presence of a nonionic surfactant (Tween 80) at concentrations higher than the critical micelle concentration (CMC), however, no significant desorption enhancement was evident in the surfactant concentration range of 0–7.5 mg/L. Pan et al. (2009) reported that the presence of 4.3 mg/L of an anionic surfactant increased sediment sorption of perfluorooctane sulfonate.

The overall goal of this study was to investigate effects of a model oil dispersant (Corexit EC9500A) on the distribution of a model PAH (phenanthrene) in a sediment–seawater system. The specific objectives were to: (1) investigate sorption and desorption behaviors of Corexit EC9500A with representative Gulf Coast marine sediments; (2) determine effects and mechanisms of the dispersant on sorption and desorption isotherms and kinetics of phenanthrene; and (3) evaluate effects of water accommodated oil (WAO) and dispersed WAO (DWAO) on sediment sorption of phenanthrene.

2. Materials and methods

2.1. Materials

Two marine sediments (0–30 cm) were collected at Grand Bay, AL, USA, in December 2010. The latitudes/longitudes of the two sites were 30.37926/88.30684 and 30.37873/88.30679, respectively. The sampling sites sit in the neighborhood with some sites affected by the DWH oil spill, such as Bayou La Batre and Dauphin Island (Fig. S1 in Supplementary materials (SM)). The wet sediments were placed in sealed plastic buckets and shipped within four hours to the lab and stored in a refrigerator (4 °C). The sediment samples were wet-sieved with seawater to obtain a size fraction of 75–840 µm and then air-dried for 7 days. The aggregates were broken by a ceramic mortar and pestle. Subsamples used for sorption/desorption experiments were oven dried for 6 h at 80 °C. These relatively moderate pre-treatments were necessary to eliminate interferences such as fine colloids, water-leachable compositions, and biological activities. While it was attempted to minimize alteration of the natural characteristics of the sediments, it is inevitable that the treated sediments may deviate from the original materials in the physical–chemical and biological properties. Therefore, cautions should be exercised when applying the research results to the natural marine sediments. In particular, the biological activities are eliminated in this work. The sediments were classified as loamy sand and sandy loam based on particle size analysis (Table S1). Seawater samples were collected from the top 30 cm of the water column from the same area. The seawater was first filtered through 0.45 µm membrane filters to remove suspended solids, and then sterilized at 121 °C for 35 min via autoclaving.

All chemicals used in this study were of analytical or higher grade. ¹⁴C-radiolabeled phenanthrene (in methanol) with a specific activity of 52.0 mCi/mmol (99.5% purity) was purchased from Moravex Biochemicals Inc. (Brea, CA, USA). Nonradioactive phenanthrene, methanol, and dichloromethane were purchased from Alfa Aesar (Ward Hill, MA, USA). Sodium azide (NaN₃) and sodium sulfate (Na₂SO₄) were obtained from Fisher Scientific (Fair lawn, NJ, USA). Corexit EC9500A was acquired through the courtesy of Nalco Company (Naperville, IL, USA). Table S2 in SM shows salient surfactant compositions of the dispersant. The CMC value of Corexit EC9500A was determined following the surface tension measurement method (Ahn et al., 2010). A surrogate Louisiana sweet crude oil was used. According to the manufacture, the oil is physically, chemically, and toxicologically similar to the Macondo Well crude oil in Mississippi Canyon Block 252.

2.2. Seawater and sediment analyses

Salient properties of the seawater sample are: pH = 8.8, dissolved organic carbon (DOC) = 0.43 mg/L, Cl⁻ = 18.55 g/L, NO₃⁻ = 2.55 g/L, SO₄²⁻ = 4.25 g/L, and an ionic strength of 0.7 M. Sodium azide was added to the seawater at 200 mg/L to minimize bacterial activity during batch sorption/desorption experiments. Sediment analysis was performed by the Soil Testing Laboratory at Auburn University. Method details have been described elsewhere (Gong et al., 2012). Table S1 in SM gives salient properties of the sediments. Tables S3–S6 and Section SM 2 show that 6 PAHs were detected at the ppb level in the filtered seawater, and 8 and 10 PAHs were detected at

ppb or sub-ppm levels in the unheated loamy sand and sandy loam sediments, respectively. Despite the oil exploration activities in the Gulf region and the DWH oil spill, the concentrations are relatively low. The reasons include: 1) The sampling sites were harbored in the ~250 m inlet within the bay area, 2) The sites were shielded by several naturally belt-shaped offshore islands such as the Dauphin Island and the Petit Bois Island, and 3) There have been fewer boating activities nearby. Upon the aforementioned heat treatments, all PAHs became undetectable presumably due to oxidation of the PAHs at elevated temperatures.

2.3. Sorption and desorption of Corexit EC9500A by sediment

Batch experiments were conducted in duplicate to determine dispersant sorption isotherms with sandy loam using 43-mL glass vials with Teflon-lined caps. Each vial was first filled with 0.21 g of sandy loam mixed with 2 mL of seawater, and then filled with 40 mL of dispersant solutions, resulting in initial dispersant concentrations from 0 to 1080 mg/L. The mixtures were then equilibrated on an end-to-end rotator at 60 rpm kept at 21 ± 1 °C for 5 days. Then, the solids were separated from aqueous solution by centrifuging at 3000 rpm for 10 min, and aliquots (40 mL each) of the supernatants were pipetted out for surface tension analysis (CSC-Du Noüy Tensiometer, Central Scientific Company, Fairfax, VA, USA). The dispersant concentration was then determined based on the surface tension (SM 3 and Fig. S2). Control tests conducted without the sediments showed that the loss of dispersant due to sorption to the vial walls and septa was <5% in all cases. Dispersant uptake by the sediment (mg/g) was calculated based on the difference in initial and final aqueous dispersant concentrations.

To test sorption reversibility of the dispersant, desorption isotherm tests were carried out. Following the sorption equilibrium, 99% of the supernatant was replaced with an equal volume of dispersant-free seawater. To assure equal background compositions, the sediment-amended replacement seawater was first amended with the same sediment by mixing the sediment with seawater at the same sediment-to-water ratio as in sorption isotherm tests. The vials were then re-equilibrated for 7 days, and desorption isotherms were then obtained in the same manner.

2.4. Effects of dispersant on sorption/desorption kinetics of phenanthrene

A stock solution of nonradioactive phenanthrene was prepared at 1.4 g/L in methanol. The ¹⁴C-radiolabeled phenanthrene was diluted 10 times using methanol. The two solutions were then mixed at a volume ratio of 1:9 (¹⁴C-radiolabeled-to-nonradioactive phenanthrene), which was then diluted with seawater to a phenanthrene concentration of 630 µg/L.

Batch phenanthrene sorption kinetic tests were conducted in duplicate in 43-mL glass tubes with Teflon-lined caps. First, a known mass of sterilized sediments (1.05 g of loamy sand or 0.21 g of sandy loam) was mixed with 2 mL of seawater in each vial. The phenanthrene sorption was then initiated by adding 40 mL of the phenanthrene solution to each sediment–seawater suspension, which resulted in an initial phenanthrene concentration of 600 µg/L. Nearly zero headspace was maintained in the vials to minimize volatilization loss of phenanthrene. The volume fraction of methanol in all cases was <0.1% to avoid co-solvent effect. The vials were then sealed and rotated on an end-to-end rotator operated at 60 rpm in an incubator at 21 ± 1 °C. After the predetermined time intervals, vials were sacrificially centrifuged at 3000 rpm for 10 min to separate the solids from the solution. After 5 min, 1 mL of each supernatant was sampled and added to 10 mL of Ecoscint cocktail (National diagnostics, Atlanta, GA, USA) for liquid scintillation counting. To determine the dispersant effect, the kinetic tests were also carried out in the presence of 18 mg/L of Corexit EC9500A. Control experiments carried out without sediments showed that phenanthrene loss was consistently <4%.

Following the sorption equilibrium, phenanthrene desorption tests were initiated by replacing 99% of the supernatant with an equal volume of sediment-amended seawater. The vials were then mixed and sacrificially sampled in the same manner as in the sorption tests. To evaluate effects of the dispersant on the desorption rate and extent, four experimental scenarios were evaluated: (1) Phenanthrene was pre-sorbed onto the sediments without dispersant, then subjected to desorption without dispersant; (2) Sorption was the same as in scenario (1), but desorption was conducted with dispersant; (3) Phenanthrene was pre-sorbed on the sediments with dispersant, then subjected to desorption without dispersant; and (4) Sorption was the same as in scenario (3), but desorption with dispersant.

2.5. Effect of dispersant on sorption/desorption isotherms of phenanthrene

Sorption isotherm tests were conducted following the same protocols as described in Section 2.4 with an equilibration time of 5 days and a range of initial phenanthrene concentrations (0–864 µg/L). Isotherms were constructed in the presence of 0, 18 and 180 mg/L of the dispersant. Control tests without the sediments showed that the loss in phenanthrene and the dispersant was <5%. Following the sorption equilibrium tests, desorption isotherms were obtained by replacing 99% of each supernatant with an equal volume of the replacement fluid, and re-equilibrating the systems for 7 days. To test effects of the dispersant on sorption reversibility, the equilibrium tests were carried out according to the aforementioned four scenarios.

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