Dispersion, sorption and photodegradation of petroleum hydrocarbons in dispersant-seawater-sediment systems

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Xiao Zhao, Wen Liu, Jie Fu, Zhengqing Cai, S.E. O'Reilly [1], Dongye Zhao *

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

A B S T R A C T

This work examined effects of model oil dispersants on dispersion, sorption and photodegradation of petroleum hydrocarbons in simulated marine systems. Three dispersants (Corexit 9500A, Corexit 9527A and SPC 1000) were used to prepare dispersed water accommodated oil (DWAO). While higher doses of dispersants dispersed more n-alkanes and PAHs, Corexit 9500A preferentially dispersed C11–C20 n-alkanes, whereas Corexit 9527A was more favorable for smaller alkanes (C10–C16), and SPC 1000 for C12–C28 n-alkanes. Sorption of petroleum hydrocarbons on sediment was proportional to TPH types/fractions in the DWAOs. Addition of 18 mg/L of Corexit 9500A increased sediment uptake of 2–3 ring PAHs, while higher dispersant doses reduced the uptake, due to micelle-enhanced solubilization effects. Both dispersed n-alkanes and PAHs were susceptible to photodegradation under simulated sunlight. For PAHs, both photodegradation and photo-facilitated alkylation were concurrently taking place. The information can facilitate sounder assessment of fate and distribution of dispersed oil hydrocarbons in marine systems.

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1. Introduction

The 2010 Deepwater Horizon (DwH) oil spill released 7.94×10^8–1.11×10^9 L of Louisiana Sweet Crude (LSC) into the Gulf of Mexico (Reddy et al., 2012; Sammarco et al., 2013). The spilled oil contains saturated n-alkanes, polycyclic aromatic hydrocarbons (PAHs), and their alkylated homologs, with > 50% as low-molecular-weight petroleum hydrocarbons (methane and C2–C11 alkanes) (Ryerson et al., 2012). During the spill, elevated concentrations of oil components such as n-alkanes, PAHs (both parent and alkylated), benzene, toluene, ethylbenzene and xylene (BTEX) were detected in both surface and deepwater samples (Sammarco et al., 2013; Camilli et al., 2010; Diercks et al., 2010; Wade et al., 2011).

To mitigate the environmental impact, approximately 8.21×10^6 L of chemical dispersants (Corexit EC9500A and Corexit 9527A) were applied to break the oil slicks into fine droplets and disperse oil components into the water column (Kujawinski et al., 2011). While the dispersants were believed to have caused part of the surface oil slicks to "disappear", little is known on the effectiveness of the dispersants for various portions of petroleum hydrocarbons. In addition, information remains limited on the performance of these Corexit dispersants when compared to other oil dispersants.

Among various classes of petroleum hydrocarbons, n-alkanes are considered less toxic since the C-C linked chains are readily degradable, while aromatic oil components, especially PAHs, are much more toxic, carcinogenic and mutagenic, and can pose long-term threat to the ecological health (Turner et al., 2014). Large n-alkanes and PAHs are often more persistent in the environment and have been commonly detected in oil residuals near shorelines including salt marshes, sediments, coastal wetlands, oil mousse/tar balls and submerged oil mats (Turner et al., 2014; Liu et al., 2012; Yin et al., 2015a; Yin et al., 2015b).

Yet, five years after the spill, our knowledge on the distribution and weathering of the spilled oil remains rudimentary, not only because of the unprecedented magnitude of the spill and the massive amounts of dispersants applied, but also owing to the fact that the spilled oil experienced a unique series of complex processes following their release at a depth of 1500 m (Reddy et al., 2012). While oil in the water column appears vanished, weathered or persistent oil residuals remain in the coastal sediment, such as sediment at Bay Jimmy and the barrier islands near Grand Isle, LA (Turner et al., 2014).

Typically, oil released in the environment undergoes a variety of weathering processes including evaporation, dissolution, dispersion, photochemical oxidation, water–oil emulsification, bio-degradation and sorption onto suspended particulate materials (Wang and Fingas, 1997). While limited field data have indicated some general weathering trend of persistent oil components (Turner et al., 2014), information on the weathering rate, extent and mechanisms has been lacking. Based on the oil budget calculator developed by the Department of Interior (DOI) and the National Oceanic and Atmospheric Administration (NOAA), the direct recovery from the wellhead, burning and skimming removed

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* Corresponding author.
  E-mail address: zhaodon@auburn.edu (D. Zhao).
[1] Bureau of Ocean Energy Management, GOM Region, Office of Environment, New Orleans, LA 70123, USA.

17%, 5% and 3% of spilled oil, respectively (Lubchenco, 2010), natural evaporation and dissolution during the travel from wellhead to the gulf surface/shoreline took 25%, chemical dispersion and natural dispersion accounted for 8% and 16% of the oil removal, respectively, and the residual (26%) was believed to be on or below the surface in forms of light sheen or tar balls.

Typically, the solubilities of light crude and heavy crude are 10–50 and 5–30 mg/L, respectively (Fingas, 2012). Petroleum n-alkanes are sparingly soluble, and the longer the hydrocarbon chain, the less soluble (Diallo et al., 1994). Likewise, lower molecular weight PAHs such as naphthalene and phenanthrene are considered a major soluble fraction of petroleum PAHs (Gong et al., 2014a; Zhao et al., 2015). Both n-alkanes and PAHs can be effectively solubilized via commonly used surfactants (Bruheim et al., 1999; Edwards et al., 1991). Both surfactants and solvents in dispersants are responsible for dispersing petroleum hydrocarbons. According to studies on 8 EPA approved dispersants, researchers observed that at a dispersant-oil ratio (DOR) of 1:10, the total petroleum hydrocarbons (TPHs) in the water column ranged from 6.8 mg/L with the least effective dispersant (JD-2000) to 1800 mg/L with the most effective ZI-400 (Hemmer et al., 2011). In the presence of Corexit 9500A at a DOR of 1:100, the concentration of total n-alkanes was increased from 73 to 5492 μg/L (Özhan et al., 2014). Corexit EC9500A can also effectively solubilize both parent PAHs and their alkylated homologs (Zhao et al., 2015; Gong et al., 2014b). However, there is limited information on the selectivity of oil dispersants toward various fractions or types of petroleum hydrocarbons including those of different M.W. and molecular structures.

Sorption of petroleum hydrocarbons onto suspended particulate matter or sediments has been recognized as an important process for oil transport (Gong et al., 2014a). In sediment-water systems, the distribution of petroleum hydrocarbons between sediment and water is often governed by the sediment organic matter (SOM) content and properties of the oil hydrocarbons. The introduction of an oil dispersant can pose some contrasting effects on the sorption behavior of oil components: First, a dispersant may preferentially disperse different fractions or types of oil hydrocarbons into the water column, as such, only these dispersed fractions can reach and be sorbed onto sediment; Second, dissolved dispersant molecules or micelles enhance solubilization of petroleum hydrocarbons, preventing the hydrocarbons from being sorbed by sediment; and Third, surfactants molecules can also be sorbed on the sediment surface and act as an added sorption sink for petroleum hydrocarbons, resulting in more uptake (known as adsolubilization) of petroleum hydrocarbons. Zhao et al. (Zhao et al., 2015) also found that such contrasting effects (solubilization versus adsolubilization) are dependent on the DOR. However, little is known about the sediment sorption of dispersed oil hydrocarbons.

Photodegradation under solar irradiation is an important natural weathering process for petroleum hydrocarbons in marine systems. Yet the photodegradation rate and extent may vary for different types or portions of dispersed petroleum hydrocarbons (DPHs). For example, petroleum n-alkanes are readily biodegraded but are recalcitrant to sunlight irradiation due to their poor ability to absorb UV (Tjessem and Aaberg, 1983). Theoretically, PAHs are intrinsically more stable considering that the π electrons are delocalized over the aromatic rings. Yet, PAHs are photochemically more reactive owing to their ability to absorb light in the UV region, and direct photolysis has been known to be the main mechanism associated (Plata et al., 2008). Interestingly, when various PAHs are mixed with n-alkanes (1:100 mol/mol) and irradiated under UV, photoalkylation can occur readily, resulting in alkylated PAHs (Mahajan et al., 2003). However, little is known on the photodegradation of DPHs.

The overall goal of this work was to preliminarily investigate the dispersant-facilitated dissolution, sorption/desorption and photodegradation of petroleum hydrocarbons in simulated DPH-seawater-sediment systems. The specific objectives were to: (1) investigate effects of three model dispersants (Corexit 9500A, Corexit 9527A and SPC 1000) on the dispersion of various types and fractions of petroleum hydrocarbons, (2) determine effects of the dispersants on sediment sorption/desorption of DPHs, and (3) explore the photodegradation potential of DPHs under simulated solar irradiation.

2. Materials and methods

2.1. Chemicals and materials

Chromatographic grade acetone, hexane and dichloromethane (DCM) were purchased from Fisher Scientific (Fair lawn, NJ, USA). Silica gel (60–200 μm) was acquired from Sigma-Aldrich (St. Louis, MO, USA) and was activated prior to each use. Sodium azide (NaN_3) of analytical grade was obtained from Fisher Scientific. Dispersants Corexit EC9500A and Corexit 9527A were acquired per courtesy of Nalco Company (Naperville, IL, USA), whereas SPC 1000 was purchased from Polychemical Corporation (Chestnut Ridge, NY, USA). A standard reagent consisting of 16 EPA listed PAHs, a standard of n-alkanes mixtures (C9–C40), Pristane (Pr), Phytane (Ph), two internal standards (5α-androstane for n-alkanes and fluorene-d_{10} for PAHs), and surrogate standards (mixture of naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10} and benzo(a)pyrene-d_{12}) were purchased from Supelco (Bellefonte, PA, USA).

Activation of the silica gel was performed following an established protocol (Wang et al., 1994). The silica gel was rinsed three times with acetone, hexane and DCM sequentially. Following initial air-drying, the sample was heated in the oven at 50°°C for 8 h and subsequently at 180 °C for 20°h to obtain the activated silica gel.

A surrogate LSC oil was acquired through courtesy of BP (Houston, TX, USA). Before use, 1 L of crude oil was artificially weathered by purging the oil with air in a flask in dark at a pressure of 18 psi for 4 weeks to eliminate the lighter compounds, which simulates the loss of volatile compounds at sea surface shortly following an oil spill (Li et al., 2009). Upon the weathering process, the LSC lost 33% of its initial mass, and its density increased from 0.81 to 0.91 g/cm^3.

2.2. Seawater and sediment samples

Seawater was collected from the top 30 cm of water column at Grand Bay, AL, USA (N30.38/W88.18) in October 2012. Before use, the sample was filtered through a membrane (0.45 μm) filter to remove suspended solids, and then sterilized through autoclaving at 121°°C for 35 min. The salient properties of the treated seawater include: pH = 7.86, dissolved organic carbon (DOC) = 0.82 mg/L, salinity = 3.5 wt.%, Cl$^-$ = 13.45 g/L, NO$_3^-$ = 2.85 g/L and SO$_4^{2-}$ = 4.25 g/L. Detailed analytical methods have been provided elsewhere (Zhao et al., 2015). The treated seawater was free of n-alkanes and PAHs.

A loamy sand sediment was sampled at N30.37926/W88.30684 of the same area. The sediment was wet-sieved with seawater to obtain a fraction of 75–840 μm and then air-dried for 7 days. The sample was further oven-dried for 6 h at 80 °C before use. Sediment analyses were performed by the Soil Testing Laboratory at Auburn University, and the method details have been described elsewhere (Zhao et al., 2015). Table S1 in the Supplementary Materials (SM) gives salient properties of the sediments. The total n-alkanes and PAHs in the sediment were determined to be 0.139 μg/g and 0.037 μg/g, respectively.

2.3. Dispersion of petroleum hydrocarbons at various DORs

Water accommodated oil (WAO) and dispersant-enhanced WAO (DWAO) were prepared following the method by Singer et al. (Singer et al., 2000). In brief, WAO was prepared in 2200 mL glass aspirator bottles containing a hose bib fitted with silicon tubing and clamp at the bottom of the vessels. Each bottle was filled with 1760 mL of the seawater, leaving a 20% headspace. About 8.8 mL of the artificially weathered LSC was carefully added to the seawater using a glass syringe (oil: seawater