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Weathering patterns of polycyclic aromatic hydrocarbons contained in submerged Deepwater Horizon oil spill residues when re-exposed to sunlight

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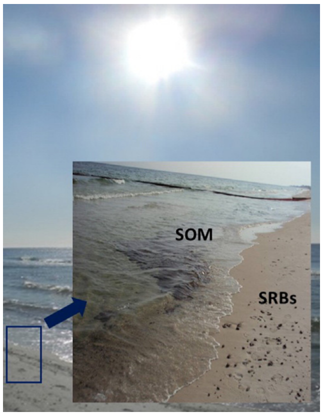
HIGHLIGHTS

- PAHs in DWH oil spill residues weathered significantly when re-exposed to sunlight.
- Sunlight induced weathering effects were higher for lower molecular weight PAHs.
- Sand particles in oil spill residues have the potential to inhibit photodegradation.

GRAPHICAL ABSTRACT



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ABSTRACT

The *Deepwater Horizon* (DWH) oil spill event released a large amount of sweet crude oil into the Gulf of Mexico (GOM). An unknown portion of this oil that arrived along the Alabama shoreline interacted with nearshore sediments and sank forming submerged oil mats (SOMs). A considerable amount of hydrocarbons, including polycyclic aromatic hydrocarbons (PAHs), were trapped within these buried SOMs. Recent studies completed using the oil spill residues collected along the Alabama shoreline have shown that several PAHs, especially higher molecular weight PAHs (four or more aromatic rings), are slowly weathering compared to the weathering levels experienced by the oil when it was floating over the GOM. In this study we have hypothesized that the weathering rates of PAHs in SOMs have slowed down because the buried oil was isolated from direct exposure to sunlight, thus hindering the photodegradation pathway. We further hypothesized that re-exposing SOMs to sunlight can reactivate various weathering reactions. Also, SOMs contain 75–95% sand (by weight) and the entrapped sand could either block direct sunlight or form large oil agglomerates with very little exposed surface area; these processes could possibly interfere with weathering reactions. To test these hypotheses, we completed controlled experiments to study the weathering patterns of PAHs in a field recovered SOM sample after re-exposing it to sunlight. Our experimental results show that the weathering levels of several higher molecular weight PAHs have slowed down primarily due to the absence of sunlight-induced photodegradation reactions. The data also show that sand particles in SOM material could potentially interfere with photodegradation reactions.

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1. Introduction

The *Deepwater Horizon* (DWH) accident, which occurred on April 20, 2010 released an estimated 5.3 × 10^8 kg of oil (Aeppli et al., 2012; McNutt et al., 2012) from the Macondo well (MC252) over a period of 87 days (Hayworth et al., 2015). It was estimated that about 26% of released oil remained in the water phase (Atlas and Hazen, 2011; Lehr et al., 2010; OSAT-1, 2010). This oil is expected to have distributed into various forms: a fraction would have been distributed into the water column and eventually transported into the deeper waters of Gulf of Mexico (GOM) (Chanton et al., 2015), a fraction deposited in the vicinity of the MC252 well, a fraction sank to the ocean bottom as marine snow (Gong et al., 2014; Passow et al., 2012), and the remaining oil was deposited along various GOM beaches (Lehr et al., 2010).

The oil spill residues deposited along Alabama's beaches were predominantly in the form of water-in-oil emulsion, a highly viscous and neutrally buoyant brownish material known as “mousse”. An unknown amount of this mousse interacted with suspended solids near the shoreline and sank, forming submerged oil mats (SOMs). SOMs were later fragmented by waves and other transport processes to form mobile surface residual oil balls (SRBs) (Dalyander et al., 2014; Hayworth et al., 2015; Liu et al., 2012; Michel et al., 2013; Urbano et al., 2013). The SRBs and SOMs are predominantly composed of sand (about 75 to 95% by mass) (Hayworth and Clement, 2011; OSAT-1, 2010; OSAT-2, 2011). The remnant oil trapped in SOMs and SRBs was found to contain various hazardous chemicals including polycyclic aromatic hydrocarbons (PAHs), which can be toxic to both human and ecological systems (Liu et al., 2012; Mulabagal et al., 2013; Urbano et al., 2013; Yin et al., 2015a).

PAHs are a group of organic compounds that contain two or more fused aromatic rings and are one of the most toxic classes of environmental compounds present in crude oils (Neff, 1979). Due to their carcinogenic and mutagenic properties, PAHs are classified as hazardous organic compounds (ATSDR, 1995; Mumtaz et al., 1996; Yin et al., 2015b). Several recent studies have shown that PAHs present in SOMs and SRBs found along the northern Gulf of Mexico shoreline appear to have very low weathering rates (Hayworth et al., 2015; McDaniel et al., 2015; Mulabagal et al., 2013; Natter et al., 2012; Turner et al., 2014; Yin et al., 2015b). The reason for these slow weathering rates is still not clear.

When crude oil is released into the marine environment it undergoes various natural weathering processes including spreading, advection, volatilization, dissolution, photodegradation, emulsification, sedimentation and microbial degradation (Dutta and Harayama, 2000; Ehrhardt et al., 1992; Garrett et al., 1998; Guo and Wang, 2009; Hall et al., 2013; Hamoda et al., 1989; NRC, 2003; Prince et al., 2003; Wang et al., 2005). Volatilization is one of the most important weathering processes in many oil spill incidents and it can greatly reduce the volume of the spilled oil (Fingas, 1997).

Photodegradation is another important weathering process that can transform PAHs present in crude oil. Photodegradation typically yields by-products that have higher polarity and water solubility and thus photodegradation reactions can enhance the net dissolution rates of PAHs and other chemicals (Dutta and Harayama, 2000; Lee, 2003). Photodegradation can also increase the susceptibility of crude oil to microbial degradation (Dutta and Harayama, 2000). However, photodegradation could also increase the net environmental toxicity by making the oil more bioavailable to marine biota (Lee, 2003).

Past studies have shown that PAHs trapped in the DWH oil spill residues are amenable to photodegradation (Aeppli et al., 2012; Hall et al., 2013; Radović et al., 2014). A recent field study completed by Yin et al. (2015b) using DWH oil spill residues recovered from the Alabama shoreline has indicated that PAHs in these residues should have undergone considerable weathering including volatilization, dissolution and photodegradation when the oil was floating over the GOM waters while transiting from the wellhead to the shoreline. This study has also shown that the net weathering rate appears to have slowed down considerably once the oil was submerged forming SOMs (Yin et al., 2015b).

In this study we have hypothesized that the weathering rates of PAHs in SOMs have slowed down because the buried SOMs were isolated from the sunlight hindering one of the major weathering pathways, photodegradation. Note, we use the phrases “*weathering levels or rates have slowed down*” or “*low weathering levels or rates*” to imply that the weathering processes have slowed down when compared to those experienced by the DWH oil when it was floating over the open ocean while transiting from the wellhead to the GOM shoreline. We have also hypothesized that re-exposing SOMs to sunlight would reactivate photodegradation reactions, which will increase the net weathering rate. Furthermore, SOMs contain 75% to 95% inert sand by weight, and the inert sand could either physically block sunlight or could allow oil to agglomerate over sand particles and reduce the surface area; these processes could possibly inhibit photodegradation and other weathering processes. The objective of this effort is to test these hypotheses by conducting controlled laboratory experiments using a SOM sample recovered from a field site in Gulf Shores, Alabama, USA. While others have investigated photodegradation of various types of PAHs in the past, our study is unique because, to the best of our knowledge, this is the first study that has conducted sunlight re-exposure experiments using SOM samples related to the DWH oil spill. This work is significant because DWH oil spill residues in the form of SOMs and SRBs continue to be present along the GOM shoreline (Hayworth et al., 2015; Yin et al., 2015b). Therefore, it is important to understand various environmental processes that can degrade these residues. The results of this study can help understand how the PAHs trapped in SOMs and SRBs could degrade over time when periodically re-exposed to sunlight while they are transported in shallow waters or deposited along the shoreline.

2. Experimental

2.1. Samples

MC252 reference crude oil was supplied by British Petroleum (BP) and is referred to as “*DWH reference oil*.” The SOM (commonly known as tarmat) sample used was collected by our team during a joint excavation survey completed by the U.S. Coast Guard, Alabama Department of Environmental Management (ADEM) and Auburn University. This survey was completed about three weeks after the Tropical Storm Lee, which mobilized buried oil and deposited large amounts of SRBs on Alabama's beaches, as it made landfall during the first week of September 2011. Following this meteorological event, field observations indicated the presence of a buried SOM within 50 m from the shoreline located about a mile west of the Lagoon Pass located in Gulf Shores, Alabama, USA. A field survey was completed at this site on September 24, 2011 to excavate this SOM using a long-arm excavator. The GPS coordinates for this site are: N30.24 and W87.74. After about 4 h of excavation our team was able to dig out a SOM buried under 1 to 2 m of sand about 20 to 30 m from the shoreline (see Figure S1). Multiple split samples (field sample name: TRB2011) of the SOM material were shared between the three teams. The Auburn University sample, designated as TRB2001-AUClement, was used as the reference SOM sample in this study. This SOM is an ideal sample for the sunlight re-exposure experiment since this oil spill sample was excavated from a depth of over 1 of 2 m; it is highly unlikely that the residual oil in this sample was ever exposed to the sunlight after it was submerged to form the SOM.

2.2. Materials

Dichloromethane and hexane used in this study were of analytical grade or higher. The solvents, silica gel (60–200 μm), and anhydrous sodium sulfate (ACS grade) were purchased from VWR International (Suwanee, GA). C_{30} ββ-hopane (17β(H),21β(H)-hopane) standard