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Effect of temperature and dispersant (COREXIT® EC 9500A) on aerobic biodegradation of benzene in a coastal salt marsh sediment

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HIGHLIGHTS

- Benzene degradation was 6 time faster under aerobic than anaerobic condition.
- Benzene degradation was in an order of 20 °C > 10 °C > 30 °C in a saline environment.
- Dispersant shows an inhibitory effect on benzene degradation.

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ABSTRACT

The coastal ecosystem in the northern Gulf of Mexico (GoM) has been seriously impacted by the 2010 BP oil spill. Two experiments were conducted to study the effect of temperature and addition of the dispersant on biodegradation of benzene, as a representative of petroleum hydrocarbon, in a coastal salt marsh sediment under aerobic conditions. The results show that benzene biodegradation was approximately 6 time faster under aerobic conditions (Eh > +300 mV) than under anaerobic iron-reduction conditions (+14 mV < Eh < +162 mV). Benzene biodegradation in response to temperature was in an order of 20 °C > 10 °C > 30 °C as expected in a saline environment. Application of the dispersant caused initial fluctuations of benzene vapor pressure during the incubation due to its hydrophobic and hydrophilic nature of the molecules. Presence of the dispersant shows an inhibitory effect on benzene biodegradation, and the inhibition increased with concentration of the dispersant. The Gulf coast sediment seems in a favorable scenario to recover from the BP oil spill with an average temperature around 20 °C in spring and fall season. Application of the dispersant may be necessary for the oil spill rescue operation, but its side effects may deserve further investigations.

1. Introduction

The 2010 BP (British Petroleum) oil spill in the Gulf of Mexico (GoM) was unprecedented with approximately 4.9 million barrels of petroleum hydrocarbons released into the ocean (BP, 2010; NOAA, 2010). This is equivalent to spilling 0.5 mL crude oil on every square meter of the GoM (1.6 million km^2) that is larger than all five Gulf States combined (1.3 million km^2). In addition, approximately 7 million L of dispersants (mainly COREXIT EC9500A and some COREXIT EC9527A) were applied in response to the oil spill, among which 3 million L were allocated to the oil wellhead at the sea floor and 4 million L on the Gulf surface (National Commission on the BP Deepwater Horizon Oil Spill and Offshore Drilling, 2010). Initial survey shows that 1773 km of GoM shoreline was significantly oiled, of which 45% was coastal marsh (Michel et al., 2013). Louisiana alone accounts for 40% of the total wetlands in mainland US (Richardson and Pahl, 2006), and generates 30% of the nation's seafood production (Day et al., 2005). As a transition zone from terrestrial to marine ecosystems, coastal wetlands play a critical role in maintaining the ecosystem integrity of the Gulf of Mexico. However, presence of oil and dispersant and their degradation products provides additional stresses that affect the survival and ecological functions of the coastal wetlands. The environmental and human health impacts from this oil spill may take decades to unveil.

Recovery of ecological services from the coastal wetlands largely relies on a significant removal of oil toxicity. Bioremediation is the

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most effective treatment for removing oil pollutants, a major conclusion from a joint Exxon-USEPA-State of Alaska monitoring effort (Atlas, 1991). Both aerobic (Atlas, 1981) and anaerobic (Chakraborty and Coates, 2004; Phelps and Young, 2001) mechanisms have been studied for the biodegradation of petroleum hydrocarbons. During this process, complex petroleum compounds are degraded to volatile components, and further to gaseous end products of carbon dioxide (CO_2) and possibly methane (CH_4) (Masumoto et al., 2012). Aerobic oil degradation has been deemed more effective due to the presence of oxygen (O_2). Documented recovery of petroleum contaminated marsh is more rapid in the warmer Gulf coast than the boreal regions (Cross et al., 2003; Van Stempvoort et al., 2004). Even in the same region, seasonal temperature changes will have significant impacts on the efficiencies of oil biodegradation.

Using benzene as a representative petroleum hydrocarbon, we conducted two experiments to explore the potential of stimulating oil biodegradation in the Gulf coast marsh sediments under anaerobic conditions. The first study explored if a pre-exposure of benzene to a salt marsh sediment could stimulate biodegradation of benzene in a later-exposure (Yu et al., 2012). The second study explored the possibility of nitrate amendment (as a nutrient and an electron acceptor) to stimulate benzene degradation in coastal marsh sediments with a salinity gradient (Tao and Yu, 2013). Both attempts showed little improvement in benzene biodegradation in the marsh sediments. To complement existing knowledge, the objectives of this study were to study benzene biodegradation in a salt marsh sediment under aerobic conditions, and (1) the effect of temperature, and (2) the effect of oil dispersant.

2. Materials and methods

2.1. Sediment and oil dispersant sample

A salt marsh sediment sample (top 30 cm and composite from 5 locations) was taken in Louisiana coast near Lake Pontchartrain (N30° 08.78′, W89° 44.67’). Major plant species at the sampling site were *Spartina alterniflora* and *Spartina patens*. The composite sediment sample was put in an ice cooler and immediately shipped to the laboratory. The sample was stored in a refrigerator (4 °C) less than a month before the experiment. One-liter dispersant sample, COREXIT® EC 9500A, was obtained from Nalco Environmental Solution LLC (Sugar Land, TX) with agreement to use for this study. Brief physical and chemical characteristics of the sediment and dispersant are summarized in Table 1. More detailed characteristics of the sediment are available in previous publications (Yu et al., 2012; Tao and Yu, 2013).

Table 1
Basic characteristics of the salt marsh sediment and dispersant.

Sample	Characteristics	Values
Salt marsh sediment		
	Texture	Silty Clay Loam
	Sand	11%
	Silt	57%
	Clay	32%
	Total carbon	7.2%
	Total nitrogen	0.43%
	Iron	$19.91\ g\ kg^{-1}$ dry sediment
	Manganese	$0.12\ g\ kg^{-1}$ dry sediment
	Sulfur	$5.30\ g\ kg^{-1}$ dry sediment
	Salinity	12‰ (ppt)
	pH	7.0
Oil dispersant		
	Distillates, hydro-treated light	10–30%
	Organic sulfonic acid salt	10–30%
	Propylene glycol	1–5%
	Density	$0.95\ kg\ L^{-1}$ at 15.6 °C.
	pH	6.2

2.2. Experimental setup

Two batches of experiment were conducted, one for studying the effect of temperature and the other for studying the effect of dispersant on benzene biodegradation in the sediment. For all experiments, a sediment slurry was made by mixing 40 g (wet weight) sediment and 80 mL water of the same salinity as at the sampling site. Saturated saline water (36 ppt, ‰) was made by dissolving sea salt (Instant Ocean, Spectrum Brands Inc.) into D.I. water, and was later diluted to a final salinity of 12 ppt for the experiments. The experimental unit was a 237-mL wide-mouth glass bottle with a screw cap sealed with Teflon tape to prevent gas leakage. A hole was drilled in the middle of the cap, and then a rubber stopper was installed for introducing benzene/dispersant to the sediment slurries and later for gas sampling from headspace of the bottle during incubation. All experimental treatments were prepared without replacing the headspace air in the bottles (note: headspace air can be replaced with pure nitrogen gas for an anaerobic incubation) to ensure that benzene biodegradation was under aerobic conditions. Approximately half of the incubation bottle as headspace volume provided sufficient O_2 (ambient concentration 21%) to support microbial aerobic respiration in a 4-week incubation.

For the experimental batch studying the temperature effect, 9 sediment slurry bottles were prepared for three temperature treatments (Temp - 10, Temp - 20, and Temp - 30) incubated in three separate water bathes, and three replicates were applied for each treatment. The selected temperatures represent the mean air temperature in winter (10 °C), spring/fall (20 °C) and summer (30 °C) at the sampling location, respectively (Yu et al., 2008). After all bottles were capped, 1-mL benzene (>99.8% purity, analytical grade, Sigma-Aldrich Chemical Company) was injected to each sediment slurry using a micro-syringe through the rubber stopper of the bottle.

For the experimental batch studying the dispersant effect, 12 sediment slurry bottles were prepared. Four treatments with three replicates were applied, including Control (no dispersant), B:D = 10:1 (benzene: dispersant = 10:1), B:D = 20:1 (benzene: dispersant = 20:1), and B:D = 40:1 (benzene: dispersant = 40:1). For all treatments (including the batch for studying the temperature effect), the quantity of benzene applied was the same (1 mL). The sediment had 72% water content before the experiment. With 1 mL benzene (density $0.88\ g\ mL^{-1}$) addition, it is equivalent to 78.6 mg benzene per g dry sediment. Solubility of benzene in water varies slightly (Arnold et al., 1958) with temperature (about $1.8\ g\ L^{-1}$ in a range of 10–30 °C). Approximately 20% of the added benzene was dissolved in the water phase of the sediment slurry, with the remaining 80% subject to be dispersed by the dispersant. A mixture of benzene and dispersant (10:1) was serially diluted to 20:1 and 40:1 and injected to each corresponding treatment using a micro-syringe. To monitor potential fluctuations of pH and redox potential (Eh) during the incubation and effect of the dispersant addition, another 12 bottles with the same four treatments were prepared. This is because uncovering the bottles for the pH and Eh measurements would unavoidably cause loss of benzene from the system. This experimental batch was conducted only under room temperature (20 °C).

All sediment slurries with different treatments were thoroughly mixed on a rotary shaker for 2 h to allow the system to reach equilibrium, and were incubated for approximately a month in the dark except for gas sampling and for pH/Eh measurement. Benzene