



Effects of oil dispersant on ozone oxidation of phenanthrene and pyrene in marine water



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HIGHLIGHTS

- Oil dispersant inhibits phenanthrene and pyrene ozone oxidation in seawater.
- Ozonation shows a two-stage kinetics and follows first-order rate law.
- Ozonation rate for pyrene is faster than that for phenanthrene.
- Lower pH and temperature and higher ozone concentration favor pyrene ozonation.

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ABSTRACT

This work investigated effects of a popular oil dispersant (Corexit EC9500A) on oxidation of phenanthrene and pyrene (two model polycyclic aromatic hydrocarbons) in Gulf coast seawater under simulated atmospheric ozone. The degradation data followed a two-stage pseudo-first order kinetics, a slower initial reaction rate followed by a much faster rate in longer time. The ozonation rate for pyrene was faster than that for phenanthrene. The presence of 18 and 180 mg/L of the dispersant inhibited the first-order degradation rate by 32–80% for phenanthrene, and 51–85% for pyrene. In the presence of 18 mg/L of the dispersant, the pyrene degradation rate increased with increasing ozone concentration, but decreased with increasing solution pH and temperature, while remained independent of ionic strength. For the first time, the results indicate that atmospheric ozone may play a significant role in the weathering of dispersed persistent oil components in natural and engineered systems.

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1. Introduction

The 2010 Deepwater Horizon (DwH) oil spill lasted for 84 days and leaked approximately 795 million liters (5 million barrels) of Louisiana sweet crude oil from the seabed into Gulf of Mexico (GOM) waters, affecting the seawater column, the benthos, and commercial seafood (Sammarco et al., 2013). One of the strategies used during the oil spill to mitigate the environmental impacts was

the application of oil dispersants. During the spill, around 6.8 million liters of Corexit EC9500A and 1.1 million liters of Corexit EC9527A were applied to the sea surface and at the wellhead (Kujawinski et al., 2011) to disperse the spilled oil. Typically, oil dispersants are a mixture of anionic and nonionic surfactants and solvents, which can lower the oil-water interfacial tension, thereby breaking oil slicks into fine droplets and facilitating dispersion and dissolution of oil components into the water column. For instance, Corexit EC9500A contains 48% of three nonionic surfactants (sorbitan monooleate (Span 80), sorbitan monooleate polyethoxylate (Tween 80), and sorbitan trioleate polyethoxylate (Tween 85)) and 35% of an anionic surfactant (sodium dioctyl sulfosuccinate (SDSS)) dissolved in 17% of aqueous hydrocarbon solvent, i.e., a mixture of 1-(2-butoxy-1-methylethoxy)-2-propanol, 1,2-propanediol, and hydrotreated light distillates (petroleum) (Gong et al., 2014a,b;

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Scelfo and Tjeerdema, 1991).

Polycyclic aromatic hydrocarbons (PAHs) are a class of important oil hydrocarbons that are of great environmental concern due to their potential toxicity and environmental persistency (Nam et al., 2008). The BP's Macondo well oil contained approximated 3.9% of PAHs by weight. The DwH oil spill released approximately 2.1×10^7 kg of PAHs into the Gulf of Mexico (Reddy et al., 2012).

Once released into the environment, PAHs undergo a number of physical and chemical processes, such as dissolution and volatilization (Liu et al., 2012), adsorption (Yang et al., 2005), bioaccumulation (Baumard et al., 1998), biodegradation (Baumard et al., 1998), and photodegradation (D'Auria et al., 2009). Another potentially important, yet overlooked, abiotic process affecting the fate of PAHs in the Gulf coast is oil degradation by tropospheric ozone, which is produced by reaction of sunlight with volatile organic compounds and nitrogen oxides in air. High levels of ozone have been widely reported at the ground level along the Gulf coast. For example, based on the 2010 monitoring data, the 8-h ozone level in Alabama air ranged from 60 to 92 ppb (EPA, 2015). Ozone levels over an oil slick may be much higher than the normal value due to the heavy evaporation of hydrocarbons from leaked oil reaching the surface (Ryerson et al., 2011).

Ozone is one of the most effective oxidants ($E_0 = +2.07$ V) and has been widely applied to degrade various organic chemicals including PAHs in engineered processes (Broséus et al., 2009; Chelme-Ayala et al., 2011; Liu et al., 2014; Márquez et al., 2014). Two primary mechanisms have been proposed for ozone oxidation of PAHs: (1) direct attack by O_3 via cycloaddition or electrophilic reaction; and (2) indirect attack by free radicals (primarily hydroxyl radical, $OH\bullet$) resulting from decomposition of ozone (Masten and Davies, 1994; Zhao et al., 2011). Beltran et al. (1995) examined the role of hydroxyl radical scavengers on ozone oxidation of fluorene, phenanthrene, and acenaphthene in aqueous solutions, and concluded that the ozonation of fluorene was due to both direct and hydroxyl radical reactions while phenanthrene and acenaphthene was only due to direct reactions with ozone.

The ozonation efficiency of PAHs in water depends on several factors including ozone concentration, pH, and temperature (Beltran et al., 1995). Beltran et al. (1995) observed that the oxidation rate of fluorene increased with increasing ozone partial pressure from 116 to 1015 Pa, with increasing pH from 2 to 12, and with increasing reaction temperature from 4 to 20 °C. However, little is known on the effects of oil dispersants on the ozone oxidation kinetics of PAHs. Moreover, the influences of other factors such as aqueous ozone concentration, pH, ionic strength (IS), and temperature on PAHs degradation in the presence of oil dispersant have not yet been explored.

The overall goal of this study was to determine effects of a stereotype oil dispersant (Corexit EC9500A) on the ozone degradation rates of PAHs in seawater. Phenanthrene and pyrene were selected to represent typical oil-related PAHs. The specific objectives were to: (1) investigate effects of various concentrations of the dispersant on the ozone degradation rate of phenanthrene and pyrene in seawater; and (2) examine effects of aqueous ozone concentration, pH, IS, and temperature on ozone degradation of pyrene in dispersant solutions.

2. Materials and methods

2.1. Materials

Seawater was collected from the top 30 cm of the water column from Grand Bay, AL, USA in December, 2010. The latitudes/longitudes of the sampling site were 30.37926/88.30684. The seawater

sample was stored in sealed containers at 4 °C in the refrigerator. Before use, the seawater was first passed through 0.45 μ m membrane filters of cellulose acetate to remove suspended solids, and then sterilized at 121 °C for 35 min via autoclaving. Separate tests confirmed that the membrane filters did not retain phenanthrene or pyrene in the solutions. Detailed properties of the seawater sample have been described elsewhere (Gong et al., 2015; Gong et al., 2014b). In brief, pH of the seawater was 8.8, dissolved organic matter (DOM) was 0.43 mg/L as total organic carbon (TOC), and IS was 0.7 M. Phenanthrene and pyrene in the seawater were 0.0029 and 0.0028 μ g/L, respectively.

All chemicals used in this study were analytical grade or higher. Phenanthrene, pyrene, and methanol were purchased from Alfa Aesar (Ward Hill, MA, USA). NaOH and NaCl were obtained from Fisher Scientific (Fair lawn, NJ, USA). Acetonitrile (HPLC grade) was purchased from EMD Millipore Corporation (Billerica, MA, USA). HCl was acquired from BDH Aristar (West Chester, PA, USA). Corexit EC9500A was acquired through the courtesy of Nalco Company (Naperville, IL, USA). The critical micelle concentration (CMC) of Corexit EC9500A was determined to be 22.5 mg/L from our prior work (Gong et al., 2014b).

2.2. Experimental apparatus

A schematic of the experimental set-up for ozonation is depicted in Fig. 1. Ozone was generated from dry and pure air using an A2Z ozone generator (Model HB5735B, A2Z Ozone Inc., Louisville, Kentucky, USA), which is able to generate a maximum of 1 g ozone h^{-1} . Gaseous ozone was passed through the surface of the reaction solution which was continuously mixed using a magnetic stirrer and a stir bar. The flow of ozone into the reactor was regulated at 500 mL/min using an Aalborg mass flow controller (Model GFC17, Orangeburg, New York, USA). Ozone concentration in the gas phase was analyzed by an ozone monitor M106-L (2B Technologies, Inc., Boulder, CO, USA) through measuring the ultra violet absorbance at 254 nm. Excess ozone was passed into two gas absorption bottles containing 2% KI solution. All tubes from the ozone generator to the reactor and the gas absorption bottles were made of Teflon to avoid adsorption of the gas.

2.3. Effects of dispersant on ozone oxidation of phenanthrene and pyrene

Separate stock solutions of phenanthrene (1.4 g/L) and pyrene (0.3 g/L) were prepared in methanol, which were shaken overnight to assure complete dissolution. Then, the solutions were diluted with seawater to obtain a phenanthrene solution of 400 μ g/L and a pyrene solution of 60 μ g/L, respectively, to simulate PAHs-contaminated seawater during and after the DwH oil spill. The concentrations chosen here are based on: (1) the values reported in previous studies which investigated the ozone oxidation of PAHs. For instance, Beltran et al. (1995) used a phenanthrene concentration of 516 μ g/L, and Corless et al. (1990) employed pyrene concentrations from 10 to 200 μ g/L; and (2) the solubility of these two compounds in seawater. The solubility of phenanthrene and pyrene was measured to be 766 and 135 μ g/L in the seawater.

Batch ozone degradation kinetic tests were carried out in a well-controlled glass reactor with a surface area of 78 cm^2 and a volume of 650 mL. In each batch, the reactor was filled with 300 mL of a seawater solution (phenanthrene = 400 μ g/L or pyrene = 60 μ g/L), and stirred gently with a magnetic stirrer to simulate the ocean wave actions and maintain uniform PAHs distribution. Control tests (carried out without turning on the ozone generator) indicated that phenanthrene/pyrene loss due to volatilization and sorption to the reactor wall was negligible. During the tests, 1 mL each of the

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