Chemosphere 172 (2017) 468–475

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

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

Yanyan Gong [a], [b], *, Dongye Zhao [b], **

[a] School of Environment, Guangzhou Key Laboratory of Environmental Exposure and Health, Guangdong Key Laboratory of Environmental Pollution and Health, Jinan University, Guangzhou, 510632, China
[b] Environmental Engineering Program, Department of Civil Engineering, Auburn University, Auburn, AL, 36849, USA

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.

ARTICLE INFO

Article history:
Received 25 October 2016
Received in revised form
14 December 2016
Accepted 3 January 2017
Available online 4 January 2017

Handling Editor: Caroline Gaus

Keywords:
Oil dispersant
PAHs
Ozonation
Oil weathering
Marine pollution

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.

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 polyethoxylae (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;

---

* Corresponding author. School of Environment, Guangzhou Key Laboratory of Environmental Exposure and Health, Guangdong Key Laboratory of Environmental Pollution and Health, Jinan University, Guangzhou, 510632, China.
** Corresponding author.
E-mail addresses: yanyangong@jnu.edu.cn (Y. Gong), zhaodon@auburn.edu (D. Zhao).

http://dx.doi.org/10.1016/j.chemosphere.2017.01.007
0045-6535/

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•) 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 μm 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 μg/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 μg/L and a pyrene solution of 60 μg/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 μg/L, and Corless et al. (1990) employed pyrene concentrations from 10 to 200 μg/L; and (2) the solubility of these two compounds in seawater. The solubility of phenanthrene and pyrene was measured to be 766 and 135 μg/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 μg/L or pyrene = 60 μg/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

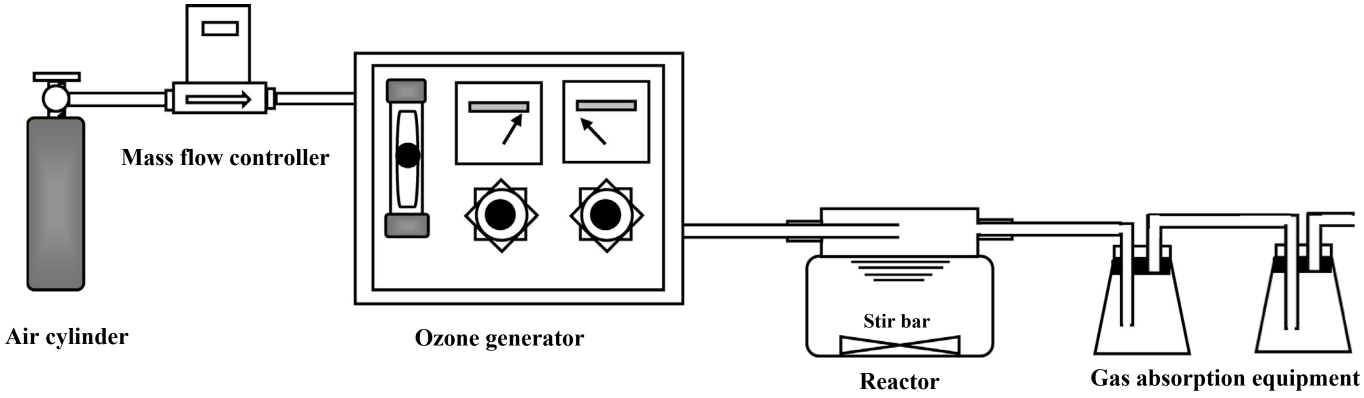

Fig. 1. Schematic of the experimental set-up including online ozone generation, ozonation reactor, and exhaust gas treatment apparatuses.

solution was sampled from the reactor at predetermined times and analyzed for phenanthrene/pyrene remaining. To investigate the effects of the dispersant, the tests were conducted in the presence of 0, 18, and 180 mg/L of Corexit EC9500A. The dispersant concentrations were calculated based on the initially added amounts of the dispersant. All experiments were conducted in duplicate at 22 ± 1 °C.

Experiments were also carried out in the glass reactor without phenanthrene/pyrene to determine the aqueous ozone concentrations. A phosphate buffer with a pH of 8.5 was prepared in DI water with 0.005 M NaH_2PO_4 and 0.005 M Na_2HPO_4. As the gaseous ozone passed through the surface of the reaction solution, samples were withdrawn at predetermined times. The ozone concentration was measured colorimetrically following the Indigo method (Bader and Hoigné, 1981). Ozone concentrations in the presence of 0, 18, and 180 mg/L of Corexit EC9500A in seawater were measured under otherwise identical conditions.

2.4. Effects of environmental factors on ozone degradation of pyrene in dispersant solutions

Effects of aqueous ozone concentration, pH, IS, and temperature were investigated through similar pyrene kinetic experiments in the presence of 18 mg/L of the dispersant. To study the ozone concentration effect, the aqueous ozone concentration was increased from 0.07 to 0.87 mg/L while the PAH and dispersant concentrations were kept fixed. To examine the pH effect, the initial solution pH was adjusted to 5.0 and 8.5 using 0.1 M HCl. After 2 h, the solution pH slightly changed to 5.3 and 8.2, respectively, probably due to the relatively low concentrations of pyrene (40 μg/L) and dispersant (18 mg/L) during the experiments. To test the IS effect, IS of the reaction solution was varied from 0.01 to 0.7 M. DI water was added to the original seawater IS (0.7 M) to dilute it down to 0.01 M. To investigate the temperature effect, the experiments were carried out at 10 and 22 °C, which represent the lowest and highest seawater temperatures in the Grand Bay area.

2.5. Analytical methods

Phenanthrene and pyrene concentrations were determined using an HPLC system (HP series 1100, Hewlett Packard, CA, USA) equipped with a UV detector and a Zorbax SB-C18 column (150 × 468 mm). The mobile phase consists of 70% acetonitrile, 30% water, and 0.1% phosphoric acid. For phenanthrene, the injection volume was 80 μL, the mobile phase flow rate was 1.2 mL/min, and the optimal UV detection wavelength was found to be 250 nm, which afforded a phenanthrene detection limit of 4 μg/L. For pyrene, the injection volume was 100 μL, the mobile phase flow rate was 1.0 mL/min, and the optimal UV detection wavelength was determined to be 240 nm, which afforded a pyrene detection limit of 2.5 μg/L.

3. Results and discussion

3.1. Effects of oil dispersant on ozone oxidation of PAHs in seawater

The ozone oxidation of a given compound in water can be due to direct attack by molecular ozone and/or the indirect reaction with free radicals (Staehelin and Hoigne, 1985). The radicals are from the decomposition of ozone, which is initiated by the hydroxide ion or other substances present at trace concentrations. The pseudo-first order kinetic law was used to investigate the degradation kinetics of the PAHs (Ning et al., 2015; Lin et al., 2014):

$$\ln(C_t/C_0) = -kt \tag{1}$$

where C_0 and C_t are the reactant concentrations at irradiation time 0 and t, respectively, and k is an apparent rate constant. For phenanthrene, k is the rate constant due to direct O_3 oxidation, while for pyrene, k equals to the sum of the rate constants due to direct O_3 oxidation and indirect degradation by radicals such as hydroxyl radicals. The k value was obtained by fitting Eqn. (1) to the corresponding experimental kinetic data (Fig. 2).

Fig. 2a and b display an unusual two-stage kinetic profile (stage 1 and stage 2). For phenanthrene, a slow kinetic rate in the first 60 min with or without the dispersant was observed, which was followed by a much faster rate thereafter. Similarly, for pyrene, a slow initial reaction rate was observed in the first 45 min without dispersant and in the first 90 min with the dispersant, followed by a much faster rate. Accordingly, the pseudo-first order kinetic model was applied to the two stages separately to interpret the ozone degradation data. Table 1 lists the resultant kinetic parameters. For phenanthrene, the degradation rate constant in stage 1 (k_1) was determined to be 0.0141 min^{-1}, which increased to 0.0214 min^{-1} (a 52% increase) in stage 2. Likewise, the pyrene degradation rate constant in stage 2 (0.0643 min^{-1}) was 1.3 times greater than that in stage 1 (0.0285 min^{-1}). It is noteworthy that pyrene was more easily degraded than phenanthrene with much higher reaction rate constants in both stages. The difference can be attributed to the different degradation mechanisms. It has been reported that the oxidation of phenanthrene was primarily through the direct attack of ozone (Beltran et al., 1995), while the oxidation of pyrene involved both the direct reaction and the indirect reaction with radicals (Yao et al., 1998). Yao et al. (1998) reported that at the early

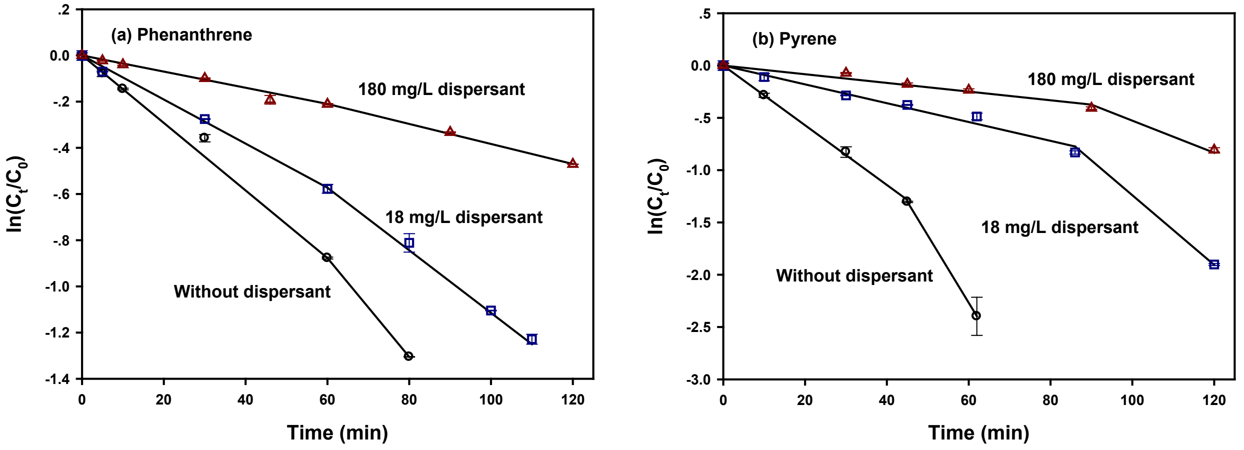

Fig. 2. First-order kinetic plots of **(a)** phenanthrene and **(b)** pyrene ozonation in seawater and in a monomeric dispersant solution (Corexit EC9500A = 18 mg/L) and micellar dispersant solution (Corexit EC9500A = 180 mg/L). Initial phenanthrene = 400 µg/L, initial pyrene = 60 µg/L, solution volume = 300 mL, solution pH = 8.0–8.5, temperature = 22 °C. Data plotted as mean of duplicates and the error bars (calculated as standard error) indicate data reproducibility.

Table 1
Pseudo-first order ozone oxidation rate constants for phenanthrene and pyrene in the absence or presence of Corexit EC9500A. Errors refer to the standard error.

Corexit EC9500A (mg/L)	Phenanthrene				Pyrene			
	0-60 min		60-120 min		0-45 min without dispersant or 0–90 min with dispersant		45-120 min without dispersant or 90–120 min with dispersant	
	k_1 (min^{-1})	R^2	k_2 (min^{-1})	R^2	k_1 (min^{-1})	R^2	k_2 (min^{-1})	R^2
0	$(1.41 \pm 0.01) \times 10^{-2}$	0.990	$(2.14 \pm 0.03) \times 10^{-2}$	1	$(2.85 \pm 0.06) \times 10^{-2}$	0.999	$(6.43 \pm 1.04) \times 10^{-2}$	1
18	$(0.96 \pm 0.02) \times 10^{-2}$	0.997	$(1.32 \pm 0.05) \times 10^{-2}$	0.998	$(0.90 \pm 0.01) \times 10^{-2}$	0.978	$(3.15 \pm 0.07) \times 10^{-2}$	1
180	$(0.35 \pm 0.01) \times 10^{-2}$	0.997	$(0.43 \pm 0.01) \times 10^{-2}$	0.999	$(0.42 \pm 0.01) \times 10^{-2}$	0.958	$(1.34 \pm 0.04) \times 10^{-2}$	1

Note: k_1 and k_2 (min^{-1}): ozone oxidation rate constant in stage 1 and stage 2, respectively; R^2: coefficient of determination, $R^2 = 1 - \frac{\sum_i (y_i - y_{i(predict)})^2}{\sum_i (y_i - \bar{y})^2}$, where y_i and $y_{i(predict)}$ are observed data and model values, respectively, and $\bar{y}$ is the mean of the observed data.

stage of ozonation, the ring cleavage of pyrene first occurred at the 4, 5 positions, forming phenanthrene-type products; upon further ozonation, pyrene and the phenanthrene-type products were further degraded, resulting in an increase in the concentrations of biphenyl-type products.

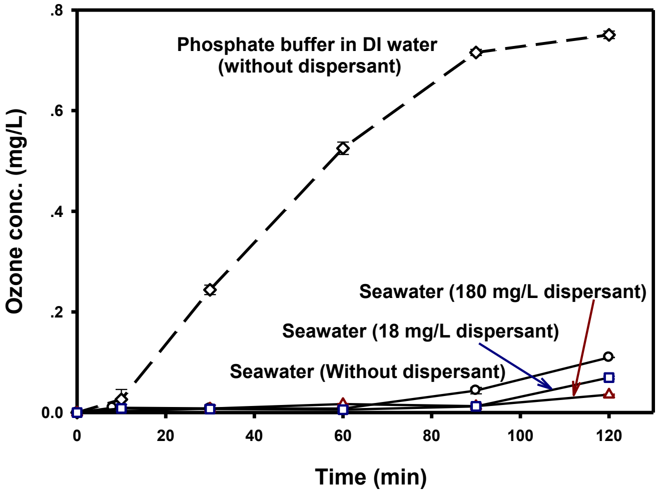

Fig. 3. Concentration histories of aqueous ozone in the reactor systems with different media: DI water, seawater, a monomeric dispersant solution (Corexit EC9500A = 18 mg/L), and micellar dispersant solution (Corexit EC9500A = 180 mg/L). Solution volume = 300 mL, solution pH = 8.5, temperature = 22 °C. Data plotted as mean of duplicates and the error bars (calculated as standard error) indicate data reproducibility.

The two-stage degradation kinetics were in consistent with the dissolved ozone concentration changes in the seawater (without phenanthrene/pyrene) over the reaction time (Fig. 3). The overall ozonation rates of both phenanthrene and pyrene increased with the increment in the residual ozone concentration. During the first 60 min, the aqueous ozone concentration remained constant at ~0.008 mg/L probably due to the initial ozone demand, i.e., reactions with other chemical compositions (e.g., DOM and sulfide compounds) in seawater (Liu et al., 2001), which can be revealed by comparing with the much higher ozone level when DI water was used as the control. After the initial ozone consumption, the ozone concentration sharply increased to 0.04 mg/L at 90 min, and further to 0.11 mg/L at 120 min. In dilute aqueous solutions, the self-decomposition of ozone is very important compared to the consumption of ozone by organic compounds, as such, a smaller percentage of applied ozone would go to the oxidation of the target chemicals (Yao et al., 1998). Since the ozonation of phenanthrene was mainly direct ozonation, the degradation was slower in the first 60 min at low ozone concentrations and faster thereafter at high ozone concentrations. While for pyrene, the degradation was slower in the first 45 min and faster thereafter probably due to the contributions of both direct and indirect ozonation.

Fig. 2 shows that the ozonation rates of phenanthrene and pyrene decreased with increasing dispersant concentration. At 60 min, 64% of phenanthrene was degraded when no dispersant was present, and the degradation was lowered to 48% and 19%, respectively, in the presence of 18 and 180 mg/L of the dispersant. The rate constant k_1 of phenanthrene was suppressed from 0.0141 min^{-1} (without dispersant) to 0.0096 min^{-1} (by 32%) (with 18 mg/L dispersant) and to 0.0035 min^{-1} (by 75%) (with 180 mg/L dispersant), and k_2 from 0.0214 min^{-1} (without dispersant) to 0.0132 min^{-1} (by 38%) (with 18 mg/L dispersant) and 0.0043 min^{-1} (by 80%) (with 180 mg/L dispersant). Similar retardation phenomena were also observed for pyrene. Within 60 min, the degradation of pyrene was decreased from 82% without dispersant to 38% and 21% with 18 and 180 mg/L of the dispersant, respectively. k_1 of pyrene was suppressed from 0.0285 min^{-1} (without dispersant) to 0.0090 min^{-1} (by 68%) (with 18 mg/L dispersant) and to 0.0042 min^{-1} (by 85%) (with 180 mg/L dispersant), and k_2 from 0.0643 min^{-1} (without dispersant) to 0.0315 min^{-1} (by 51%) (with 18 mg/L dispersant) and to 0.0134 min^{-1} (by 79%) (with 180 mg/L dispersant).

The dispersant Corexit EC9500A can affect the oxidation of PAHs in two contrasting ways. On the one hand, the dispersant may accelerate the degradation by lowering the surface tension, which may reduce the gas transfer barrier between the ozone gas phase and the liquid phase, and thereby leading to an increase in the soluble ozone concentration in the solution (Chu et al., 2006); on the other hand, the dispersant itself can compete for the reactive ozone and free radicals resulting in a decrease in the aqueous ozone concentration and thereby reduced ozonation rate (Amat et al., 2007; Ikehata and El-Din, 2004). The overall effect depends on the extent of these two contrasting effects. Fig. 3 compares the changes of the aqueous ozone concentration during the reaction period in seawater with or without the dispersant. Within 120 min, the ozone concentration was decreased from 0.11 mg/L in dispersant-free seawater to 0.07 mg/L in the 18 mg/L dispersant solution and further to 0.03 mg/L in the 180 mg/L dispersant solution. In this study, the inhibitive effects outweighed the promoting effects.

In addition, at the dispersant concentration of 180 mg/L, which is much higher than the CMC value (22.5 mg/L), the dispersant can further inhibit the ozone degradation through the “cage effect”, i.e., the accumulation of pyrene in the micelles, which inhibit access of ozone and free radicals to pyrene due to elevated mass transfer resistance (Chu and Jia, 2009; Zhang et al., 2011).

3.2. Influence of reaction conditions on ozonation of pyrene in dispersant solution

The ozone degradation kinetics of pyrene in the presence of 18 mg/L of Corexit EC9500A was tested as a function of dissolved ozone concentration, pH, IS, and temperature. The first-order rate constants of k_1 and k_2 are listed in Table 2.

3.2.1. Effects of ozone concentration

Fig. 4 shows the pyrene degradation kinetic data at various concentrations of ozone. As the aqueous ozone concentration increased from 0.07 to 0.87 mg/L, the rate constant k_1 increased from 0.0090 to 0.0637 min^{-1} (a factor of 6), and k_2 boosted from 0.0315 to 0.290 min^{-1} (by 8 times), respectively. Apparently, the pyrene oxidation rate is proportional to the aqueous ozone concentration even though 18 mg/L of the dispersant was competing for the reactive species.

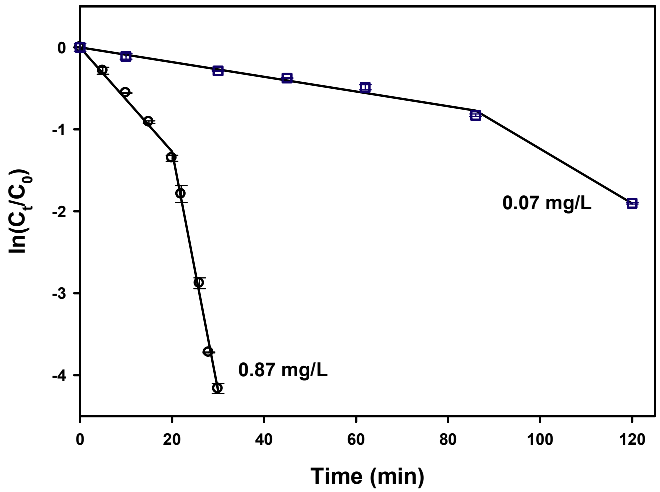

Fig. 4. Effects of aqueous ozone concentration on ozone degradation of pyrene in 18 mg/L dispersant solution. Data plotted as mean of duplicates and the error bars (calculated as standard error) indicate data reproducibility.

3.2.2. Effects of pH

pH has a significant influence on the ozonation of pyrene in the dispersant solutions. Fig. 5 presents effects of pH on ozone degradation of pyrene. The rate constant k_1 increased from 0.0637 to 0.117 min^{-1} (an 83% increase), and k_2 increased from 0.290 to 0.779 min^{-1} (by 1.68 times) as the pH decreased from 8.5 to 5.0.

Solution pH significantly influences ozone decomposition in water. As pH increased, ozone decomposition occurs via the following five-step chain reactions as shown in Eqns. (2)–(6) (Kasprzyk-Hordern et al., 2003):

$$O_3 + H_2O \rightarrow 2HO^{\bullet} + O_2 \quad (2)$$

$$O_3 + OH^{-} \rightarrow HO_2^{\cdot} + O_2^{\bullet -} \quad (3)$$

$$O_3 + HO^{\bullet} \rightarrow HO_2^{\cdot} + O_2 \leftrightarrow O_2^{\bullet -} + H^{+} \quad (4)$$

$$O_3 + HO_2^{\cdot} \rightarrow 2O_2 + HO^{\bullet} \quad (5)$$

$$2HO_2^{\bullet} \rightarrow O_2 + H_2O_2 \quad (6)$$

It is evident that under alkaline conditions, ozone decomposition is elevated, resulting in more free radicals including hydroxyl radicals ($HO^{\bullet}$) and superoxide ($O_2^{\bullet -}$), which favors the indirect

Table 2
Pseudo-first order rate constants for pyrene ozone degradation in 18 mg/L dispersant solutions as a function of dissolved ozone concentration, pH, IS, and temperature. Errors refer to the standard error.

Initial pyrene concentration (μg/L)	Reaction conditions in 18 mg/L dispersant solution		k_1 (min^{-1})	R^2	k_2 (min^{-1})	R^2
60	Ozone concentration (mg/L)	0.87	(6.37 ± 0.11) × 10^{-2}	0.986	(29.02 ± 0.43) × 10^{-2}	0.992
60		0.07	(0.90 ± 0.01) × 10^{-2}	0.978	(3.15 ± 0.07) × 10^{-2}	1
60	pH	5.0	(11.68 ± 1.08) × 10^{-2}	0.992	(77.86 ± 12.08) × 10^{-2}	0.971
60		8.5	(6.37 ± 0.11) × 10^{-2}	0.986	(29.02 ± 0.43) × 10^{-2}	0.992
60	IS (M)	0.01	(7.15 ± 0.76) × 10^{-3}	0.980	(29.76 ± 1.96) × 10^{-2}	1
60		0.70	(6.37 ± 0.11) × 10^{-2}	0.986	(29.02 ± 0.43) × 10^{-2}	0.992
60	Temperature (°C)	10	(8.93 ± 0.08) × 10^{-2}	0.978	(64.30 ± 0.99) × 10^{-2}	1
60		22	(6.37 ± 0.11) × 10^{-2}	0.986	(29.02 ± 0.43) × 10^{-2}	0.992

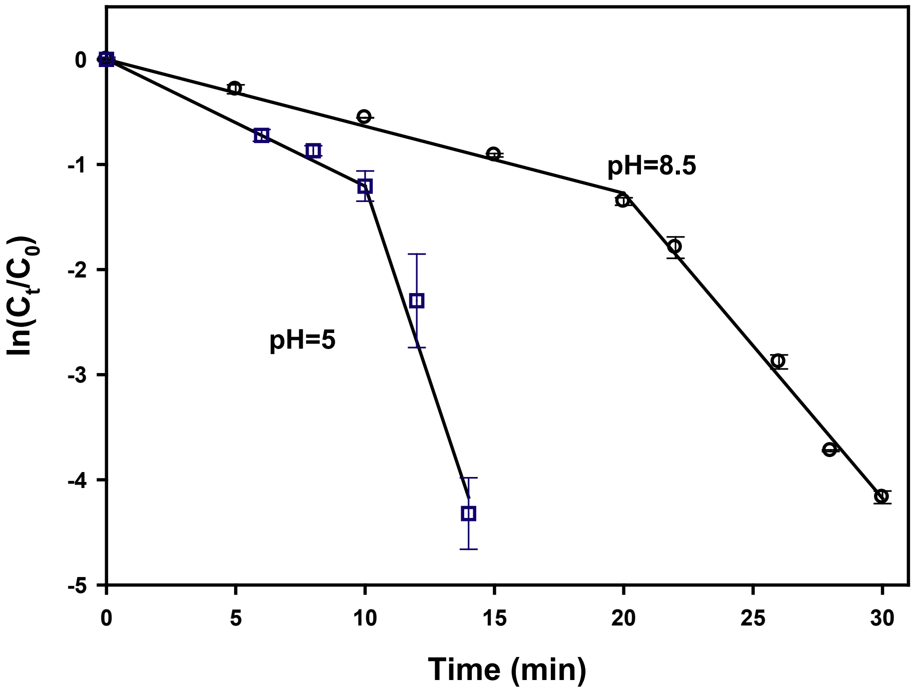

Fig. 5. Effects of pH on ozone degradation of pyrene in 18 mg/L dispersant solution. Data plotted as mean of duplicates and the error bars (calculated as standard error) indicate data reproducibility.

degradation of pyrene. However, the gain in the indirect ozonation is at the expense of a loss in direct ozonation. Based on our observations in this case, it was estimated that the loss in direct ozonation outweighed the gain in the indirect reactions, resulting in a net decrease in the overall pyrene degradation rate at the higher pH. Further work is needed to more accurately quantify the relative contributions of direct and indirect ozonation to pyrene degradation. Different from our findings, Beltran et al. (1995) investigated effects of pH on oxidation rate of fluorene by ozone and found that the increase of pH led to an increase in the oxidation rate. This inconsistency may be attributed to the dispersant which might compete for the radicals more fiercely than for the ozone.

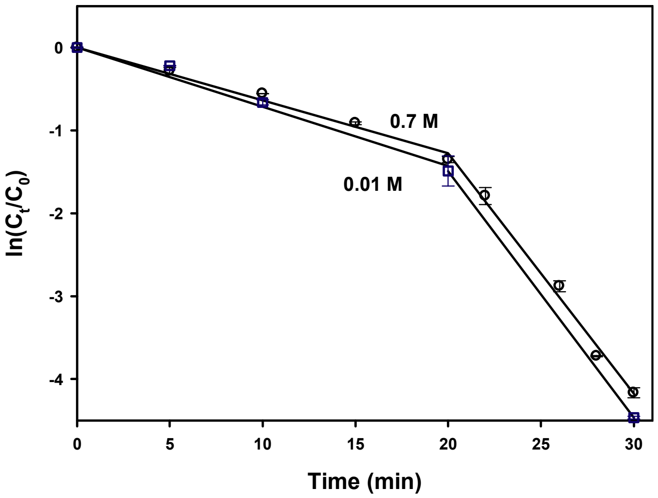

Fig. 6. Effects of IS on ozone degradation of pyrene in 18 mg/L dispersant solution. Data plotted as mean of duplicates and the error bars (calculated as standard error) indicate data reproducibility.

3.2.3. Effects of IS

Fig. 6 shows that increasing IS from 0.01 to 0.70 M did not significantly affect the degradation rate of pyrene in the dispersant solution (for k_1: $p = 0.414$, and for k_2: $p = 0.748$ at the 0.05 level of significance).

At elevated IS, NaCl can compete for dissolved ozone and radicals with pyrene, resulting in a slower degradation rate. In the experimental pH of 8.5, the following reactions can take place (Muthukumar and Selvakumar, 2004):

$$NaCl \leftrightarrow Na^{+} + Cl^{-} \tag{7}$$

$$Cl^{-} + OH^{\bullet} \rightarrow Cl^{\bullet} + OH^{-} \tag{8}$$

$$Cl^{-} + Cl^{\bullet} \rightarrow Cl_2 + e^{-} \tag{9}$$

In addition, elevated IS can increase the interfacial concentration of pyrene at the ozone-solution interface, resulting in a faster degradation rate.

In the presence of the dispersant, some of the lighter and less-soluble components in the dispersant (e.g., Span 80) may accumulate more PAH to the top layer of the water column, which is conducive to the contact and reactions with ozone in the headspace air. However, the dispersant also tends to offset the salting out effect due to lowered surface tension and enhanced solubilization of the PAH. Moreover, elevated IS may push more pyrene to the dispersant/solvent cages. In this study, all these contrasting effects of IS in the presence of the dispersant appeared to have mutually offset. As a result, the overall effect on the reaction rate was insignificant.

3.2.4. Effects of temperature

The effect of temperature on the oxidation rate of pyrene by ozone was investigated at pH 8.5. Fig. 7 shows that decreasing temperature from 22 to 10 °C enhanced the rate constant k_1 from

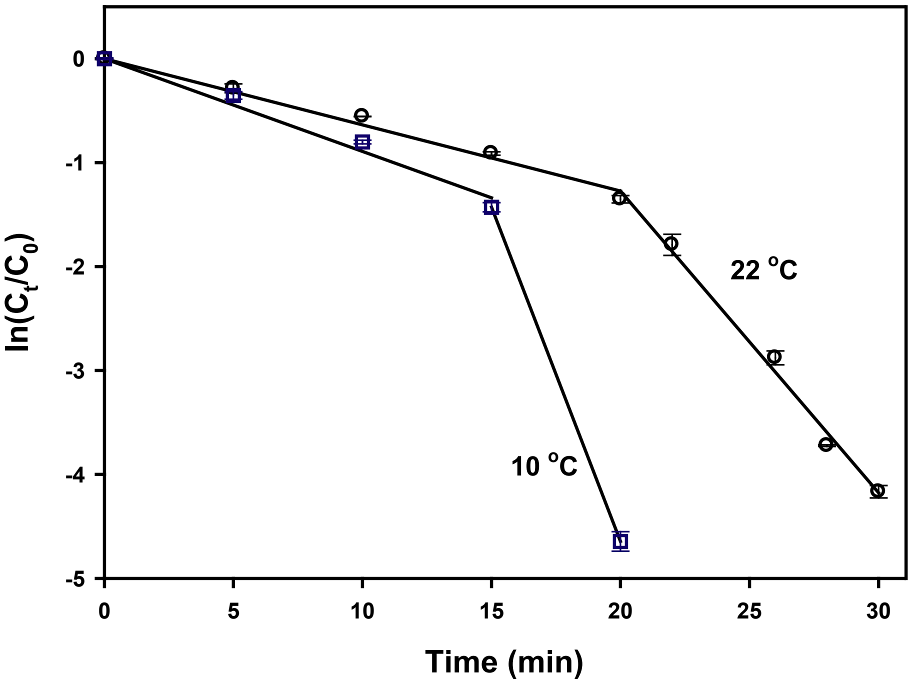

Fig. 7. Effects of temperature on ozone degradation of pyrene in 18 mg/L dispersant solution. Data plotted as mean of duplicates and the error bars (calculated as standard error) indicate data reproducibility.

0.0637 to 0.0893 min^{-1} ($p = 0.003$), and k_2 from 0.290 to 0.643 min^{-1} ($p = 0.001$), respectively.

Higher temperature accelerates the molecular collision rate, increases the reaction rate constant and the volumetric mass transfer coefficient, accelerating the degradation rate (Zhao et al., 2004), however, it decreased the solubility of ozone, and thereby, inhibited the production of radicals (Beltran et al., 1995). Zhao et al. (2004) reported a modest decrease in the conversion of cationic red X-GRL dye from 88, 86, to 85% as the temperature increased from 15, 20 to 25 °C. The much enlarged effect observed in our study can be attributed to the dispersant effects: (1) competition of the dispersant with pyrene for free radicals and ozone, and (2) interactions between pyrene and the dispersant.

4. Conclusions

This study investigated effects of a stereotype oil dispersant Corexit EC9500A on ozone oxidation of phenanthrene/pyrene in the seawater. The primary findings are summarized as follows:

1. Ozone can effectively degrade phenanthrene and pyrene with or without the dispersant. In the dispersant solutions, the ozone degradation followed a two-stage first order kinetics, i.e., a slower initial degradation rate followed by a much faster rate thereafter. Pyrene was more easily degraded than phenanthrene based on the reaction rate constants.
2. The presence of 18 and 180 mg/L of the dispersant inhibited the phenanthrene and pyrene degradation. The rate constant k_1 of phenanthrene was suppressed by 32% and 75%, and k_2 by 38% and 80%, respectively, at 18 and 180 mg/L of the dispersant. Similarly, k_1 of pyrene was suppressed by 68% and 85%, and k_2 was reduced by 51% and 79%, respectively.
3. The pyrene degradation rate constants (k_1 and k_2) in the 18 mg/L dispersant solution increased by 6 and 8 times when the aqueous ozone concentration was raised from 0.07 to 0.87 mg/L. Decreasing pH from 8.5 to 5.0 increased k_1 value by 83% and k_2 by 1.68 times. Decreasing temperature from 22 to 10 °C enhanced degradation rate constants of k_1 and k_2 by 40% and 1.2 times, respectively. The effect of IS in the range of 0.01–0.70 M was insignificant.

The results provide useful information for understanding the roles of oil dispersants on environmental weathering/degradation and fate of persistent oil components in natural and engineered systems.

Acknowledgements

The research was partially supported by MESC BP-GRI and the U.S. Department of the Interior Bureau of Ocean Energy Management.

References

Amat, A.M., Arques, A., Miranda, M.A., Vincente, R., Segui, S., 2007. Degradation of two commercial anionic surfactants by means of ozone and/or UV irradiation. Environ. Eng. Sci. 24, 790–794.
Bader, H., Hoigné, J., 1981. Determination of ozone in water by the indigo method. Water Res. 15, 449–456.
Baumard, P., Budzinski, H., Garrigues, P., Sorbe, J.C., Burgeot, T., Bellocq, J., 1998. Concentrations of PAHs (polycyclic aromatic hydrocarbons) in various marine organisms in relation to those in sediments and to trophic level. Mar. Pollut. Bull. 36, 951–960.
Beltran, F.J., Ovejero, G., Encinar, J.M., Rivas, J., 1995. Oxidation of polynuclear aromatic hydrocarbons in water. 1. Ozonation. Ind. Eng. Chem. Res. 34, 1596–1606.
Broséus, R., Vincent, S., Aboulfadl, K., Daneshvar, A., Sauvé, S., Barbeau, B., Prévost, M., 2009. Ozone oxidation of pharmaceuticals, endocrine disruptors and pesticides during drinking water treatment. Water Res. 43, 4707–4717.
Chelme-Ayala, P., El-Din, M.G., Smith, D.W., Adams, C.D., 2011. Oxidation kinetics of two pesticides in natural waters by ozonation and ozone combined with hydrogen peroxide. Water Res. 45, 2517–2526.
Chu, W., Chan, K.H., Graham, N.J.D., 2006. Enhancement of ozone oxidation and its associated processes in the presence of surfactant: degradation of atrazine. Chemosphere 64, 931–936.
Chu, W., Jia, J., 2009. The photodegradation and modeling of a typical NAPL, trichloroethene, by monochromatic UV irradiations. Environ. Sci. Technol. 43, 1455–1459.

Corless, C.E., Reynolds, G.L., Graham, N.J.D., Perry, R., 1990. Ozonation of pyrene in aqueous solution. Wat. Res. 24, 1119–1123.

D'Auria, M., Emanuele, L., Racioppi, R., Velluzzi, V., 2009. Photochemical degradation of crude oil: comparison between direct irradiation, photocatalysis, and photocatalysis on zeolite. J. Hazard. Mater. 164, 32–38.

EPA (2015) Monitor values report. Retrieved on July 23, 2015, from http://www.epa.gov/airdata/ad_rep_mon.html.

Gong, Y., Fu, J., O'Reilly, S.E., Zhao, D., 2015. Effects of oil dispersants on photodegradation of pyrene in marine water. J. Hazard. Mater. 287, 142–150.

Gong, Y., Zhao, X., Cai, Z., O'Reilly, S.E., Hao, X., Zhao, D., 2014a. A review of oil, dispersed oil and sediment interactions in the aquatic environment: influence on the fate, transport and remediation of oil spills. Mar. Pollut. Bull. 79, 16–33.

Gong, Y., Zhao, X., O'Reilly, S.E., Qian, T., Zhao, D., 2014b. Effects of oil dispersant and oil on sorption and desorption of phenanthrene with Gulf Coast marine sediments. Environ. Pollut. 185, 240–249.

Ikehata, K., El-Din, M.G., 2004. Degradation of recalcitrant surfactants in wastewater by ozonation and advances oxidation processes: a review. Ozone-Sci. Eng. 26, 327–343.

Kasprzyk-Hordern, B., Ziolek, M., Nawrocki, J., 2003. Catalytic ozonation and methods of enhancing molecular ozone reactions in water treatment. Appl. Catal. B-Environ 46, 639–669.

Kujawinski, E.B., Kido Soule, M.C., Valentine, D.L., Boysen, A.K., Longnecker, K., Redmond, M.C., 2011. Fate of dispersants associated with the Deepwater Horizon oil spill. Environ. Sci. Technol. 45, 1298–1306.

Lin, C., Zhang, W., Yuan, M., Feng, C., Ren, Y., Wei, C., 2014. Degradation of polycyclic aromatic hydrocarbons in a coking wastewater treatment plant residual by an O_3/ultraviolet fluidized bed reactor. Environ. Sci. Pollut. Res. 21, 10329–10338.

Liu, Q., Schurter, L.M., Muller, C.E., Aloisio, S., Francisco, J.S., Margerum, D.W., 2001. Kinetics and mechanisms of aqueous ozone reactions with bromide, sulfite, hydrogen sulfite, iodide, and nitrite ions. Inorg. Chem. 40, 4436–4442.

Liu, Y., Li, X., Liu, J., Shi, C., Zhu, A., 2014. Ozone catalytic oxidation of benzene over AgMn/HZSM-5 catalysts at room temperature: effects of Mn loading and water content. Chin. J. Catal. 35, 1465–1474.

Liu, Z., Liu, J., Zhu, Q., Wu, W., 2012. The weathering of oil after the Deepwater Horizon oil spill: insights from the chemical composition of the oil from the sea surface, salt marshes and sediments. Environ. Res. Lett. 7, 035302.

Márquez, G., Rodríguez, E.M., Maldonado, M.I., Álvarez, P.M., 2014. Integration of ozone and solar TiO_2-photocatalytic oxidation for the degradation of selected pharmaceutical compounds in water and wastewater. Separ. Purif. Technol. 136, 18–26.

Masten, S.J., Davies, S.H., 1994. The use of ozonation to degrade organic contaminants in wastewaters. Environ. Sci. Technol. 28, 180A–185A.

Muthukumar, M., Selvakumar, N., 2004. Studies on the effect of inorganic salts on decolouration of acid dye effluents by ozonation. Dyes Pigments 62, 221–228.

Nam, J.J., Thomas, G.O., Jaward, F.M., Steinnes, E., Gustafsson, O., Jones, K.C., 2008. PAHs in background soils from Western Europe: influence of atmospheric deposition and soil organic matter. Chemosphere 70, 1596–1602.

Ning, X.a., Shen, L., Sun, J., Lin, C., Zhang, Y., Yang, Z., Chen, S., 2015. Degradation of polycyclic aromatic hydrocarbons (PAHs) in textile dyeing sludge by O_3/H_2O_2 treatment. RSC Adv. 5, 38021–38029.

Reddy, C.M., Arey, J.S., Seewald, J.S., Sylva, S.P., Lemkau, K.L., Nelson, R.K., Carmichael, C.A., McIntyre, C.P., Fenwick, J., Ventura, G.T., Van Mooy, B.A.S., Camilli, R., 2012. Science Applications in the Deepwater Horizon Oil Spill Special Feature: Composition and Fate of Gas and Oil Released to the Water Column during the Deepwater Horizon Oil Spill. PNAS, p. 1101242108.

Ryerson, T.B., Aikin, K.C., Angevine, W.M., Atlas, E.L., Blake, D.R., Brock, C.A., Fehsenfeld, F.C., Gao, R.S., de Gouw, J.A., Fahey, D.W., Holloway, J.S., Lack, D.A., Lueb, R.A., Meinardi, S., Middlebrook, A.M., Murphy, D.M., Neuman, J.A., Nowak, J.B., Parrish, D.D., Peischl, J., Perring, A.E., Pollack, I.B., Ravishankara, A.R., Roberts, J.M., Schwarz, J.P., Spackman, J.R., Stark, H., Warneke, C., Watts, L.A., 2011. Atmospheric emissions from the Deepwater Horizon spill constrain air-water partitioning, hydrocarbon fate, and leak rate. Geophys. Res. Lett. 38, L07803.

Sammarco, P.W., Kolian, S.R., Warby, R.A.F., Bouldin, J.L., Subra, W.A., Porter, S.A., 2013. Distribution and concentrations of petroleum hydrocarbons associated with the BP/Deepwater Horizon oil spill, Gulf of Mexico. Mar. Pollut. Bull. 73, 129–143.

Scelfo, G.M., Tjeerdema, R.S., 1991. A simple method for determination of Corexit 9527 in natural waters. Mar. Environ. Res. 31, 69–78.

Staehelin, J., Hoigne, J., 1985. Decomposition of ozone in water in the presence of organic solutes acting as promoters and inhibitors of radical chain reactions. Environ. Sci. Technol. 19, 1206–1213.

Yang, G., Zhao, Y., Lu, X., Gao, X., 2005. Adsorption of methomyl on marine sediments. Colloid. Surf. A 264, 179–186.

Yao, J., Huang, Z., Masten, S.J., 1998. The ozonation of pyrene: pathway and product identification. Water Res. 32, 3001–3012.

Zhang, Y., Wong, J.W.C., Liu, P., Yuan, M., 2011. Heterogeneous photocatalytic degradation of phenanthrene in surfactant solution containing TiO_2 particles. J. Hazard. Mater. 191, 136–143.

Zhao, W., Liao, Q., Zhang, J., Yang, Y., Dai, J., Zhao, D., 2011. Oxidation of cationic Red X-GRL by ozonation combined with UV radiation in aqueous solution: degradation, kinetics, and modeling. Chem. Eng. J. 171, 628–639.

Zhao, W., Shi, H., Wang, D., 2004. Ozonation of Cationic Red X-GRL in aqueous solution: degradation and mechanism. Chemosphere 57, 1189–1199.