



Degradation of petroleum hydrocarbons in seawater by simulated surface-level atmospheric ozone: Reaction kinetics and effect of oil dispersant



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ARTICLE INFO

Keywords:

Atmospheric ozone
Ozonation
Oil spill
Oil dispersant
Oil weathering
Petroleum hydrocarbon

ABSTRACT

Oil degradation by surface-level atmospheric ozone has been largely ignored in the field. To address this knowledge gap, this study investigated the ozonation rate and extent of typical petroleum compounds by simulated surface-level ozone, including total petroleum hydrocarbons (TPHs), *n*-alkanes, and polycyclic aromatic hydrocarbons (PAHs). Moreover, the work explored the effect of a prototype oil dispersant, Corexit EC9500A, on the ozonation rate. Rapid oxidation of TPHs, *n*-alkanes and PAHs was observed at various gaseous ozone concentrations (i.e. 86, 200 and 300 ppbv). Generally, the presence of the oil dispersant enhanced ozonation of the oil compounds. The addition of humic acid inhibited the reaction, while increasing salinity accelerated the degradation. Both direct ozonation by molecular ozone and indirect oxidation by ozone-induced radicals play important roles in the degradation process. The findings indicate that ozonation should be taken into account in assessing environmental fate and weathering of spilled oil.

1. Introduction

The 2010 Deepwater Horizon (*DwH*) oil spill released > 795 million L of Louisiana Sweet Crude (LSC) oil into the Gulf of Mexico (Camilli et al., 2010; Reddy et al., 2012; Sammarco et al., 2013). As a result, high concentrations of oil compounds in the water column were detected following the spill. For instance, Camilli et al. (2010) reported that the concentration of mono-aromatic petroleum hydrocarbons in the affected seawater exceeded 50 mg/L, and Reddy et al. (2012) observed that the light aromatic hydrocarbons (benzene, toluene, ethylbenzene, and total xylenes) reached up to 78 mg/L. The *DwH* oil contained ~3.9% total polycyclic aromatic hydrocarbons (TPAHs), ~1.5% alkylated PAHs, and ~15.3% *n*-alkanes by weight; as such, the incident released approximately $\sim 2.1 \times 10^7$ kg of TPAHs, $\sim 7.9 \times 10^6$ kg of alkylated PAHs, and $\sim 8.1 \times 10^7$ kg of *n*-alkanes into the Gulf of Mexico (Reddy et al., 2012).

As an emergency mitigation measure, two chemical dispersants, Corexit EC9500A (6.8 million L) and Corexit EC9527A (1.1 million L) were applied at the wellhead and on the seawater surface to disperse

the oil slicks into the water column (Kujawinski et al., 2011). As a result, it was estimated that 16% of the spilled oil was dispersed by chemical dispersants (Ramseur, 2010). While several recent studies have reported that oil dispersant enhanced degradation of oil, particularly *n*-alkanes, under conditions relevant to the northern Gulf of Mexico, a thorough understanding of the process and mechanisms is needed (Bacosa et al., 2015; Liu et al., 2016).

A number of physical, chemical and biological processes can affect the fate and transport of spilled oil, including spreading, drifting, evaporation and dissolution (Liu et al., 2012, 2017; Ryerson et al., 2011), dispersion of oil droplets into the water column (Conmy et al., 2014; Kleindienst et al., 2015), interactions of dissolved and dispersed oil compounds with suspended particulate matter and sediment particles (Fu et al., 2014; Gong et al., 2014; Zhao et al., 2015; Zhao et al., 2016), sorption (Gong et al., 2014; Zhao et al., 2015; Zhao et al., 2016), bioaccumulation and biodegradation (Baumard et al., 1998), and photodegradation (Gong et al., 2015; Zhao et al., 2016). Another potentially significant oil weathering process is oxidation by atmospheric ozone (O₃). However, ozonation has been completely ignored in

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<https://doi.org/10.1016/j.marpolbul.2018.07.047>

Received 16 February 2018; Received in revised form 4 July 2018; Accepted 17 July 2018

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estimating oil budget and in assessing the fate and weathering of spilled oil despite the known high reactivity and fairly high concentrations of atmospheric ozone at the ground or sea level.

Typically, surface-level ozone is formed through photochemical reactions involving volatile organic compounds (VOCs) and nitrogen oxides (Haagen-Smit et al., 1953). High levels of ozone have been widely detected at the ground level along the Gulf of Mexico coast. For instance, based on 2002–2013 monitoring data, the 8-hour average ozone in Alabama air ranged from 60 to 92 ppbv (ADEM, 2016). Nationally, the average of the fourth highest daily maximum 8-h ozone level had consistently exceeded the National Ambient Air Quality Standards (NAAQS) of 75 ppbv from 1986 through 2016 (EPA, 2017). It is noted that the ozone levels over an oil slick may be much higher than in the bulk air due to the extensive evaporation of volatile hydrocarbons from the oil slick (Ryerson et al., 2011).

Ozone is a well-known strong oxidant ($E^0 = +2.07$ V) and relatively strong electrophile (Yu et al., 2007). In engineered processes, ozone has been widely used to degrade various organic compounds, including PAHs (Chelme-Ayala et al., 2011; Lin et al., 2014; von Gunten, 2003) and *n*-alkanes (Masten and Davies, 1994; von Gunten, 2003; Yu et al., 2007). In general, ozonation of organic compounds (e.g., *n*-alkanes and PAHs) can take place in the following fashions: 1) direct attack by molecular O₃ on the σ -bond between C and H atoms via 1,3-dipolar insertion for alkanes or via cycloaddition or electrophilic reactions for PAHs (Hellman and Hamilton, 1974); and 2) indirect attack by free radicals (primarily hydroxyl radicals, \cdot OH) (Masten and Davies, 1994; Zhao et al., 2004, 2011). Therefore, it is reasonable to postulate that oxidation under atmospheric ozone is an important natural weathering process for petroleum hydrocarbons.

Oil dispersants are complex mixtures of anionic, nonionic surfactants, and solvents (Board and Council, 1989; Gong et al., 2014). Corexit EC9500A consists of three nonionic surfactants including ethoxylated sorbitan mono- and trioleates and sorbitan monooleate (commercially known as Tween 80, Tween 85, and Span 80) and an anionic surfactant, namely, sodium dioctyl sulfosuccinate (SDSS) and solvents as a mixture of di(propylene glycol) butyl ether (DPnB), propylene glycol, and hydro-treated light distillates (petroleum) (Cai et al., 2016; Place et al., 2010; Scelfo and Tjeerdema, 1991).

Ozonation of organic contaminants can be affected by surfactants, and the effect depends on the type of the surfactants (anionic, nonionic and cationic). Pryor and Wu (1992) reported that the ozonation of methyl oleate was increased by 1.2 times when an anionic surfactant, sodium dodecyl sulfate (SDS), was increased from 0.02 M to 0.5 M. Chiu et al. (2007) observed that the presence of a nonionic surfactant Brij 30 decreased the gas–liquid mass transfer rates of both naphthalene and ozone, resulting in reduced removal efficiency of naphthalene. Chu et al. (2006) reported that ozonation of atrazine was enhanced by 17% by adding a nonionic surfactant, Brij 35, and the researchers stated that the surfactant played dual roles in the ozonation of atrazine: 1) it increased dissolution of ozone, and 2) it served as a radical booster and hydrogen source. Therefore, oil dispersants may also affect oil ozonation. Gong and Zhao (2017) observed that the presence of 18 and 180 mg/L of Corexit EC9500A inhibited the ozonation rate of phenanthrene by 32%–80%, and that for pyrene by 51%–85%, due to competition for the reactive ozone and free radicals. They also reported that in the presence of 18 mg/L of the dispersant, the pyrene degradation rate decreased with increasing solution pH and temperature. However, information has been lacking on the effects of oil dispersants on the ozonation of petroleum hydrocarbons (e.g. TPHs, *n*-alkanes and PAHs). Moreover, the influences of ozone concentration, pH, DOM and salinity on ozonation of petroleum hydrocarbons in the presence of oil dispersants have not yet been explored.

The overall goal of this study was to investigate the ozonation rate and extent of dispersed oil in dispersant-oil-seawater systems that are exposed to relatively high surface-level atmospheric ozone, and understand the roles of a model dispersant (Corexit EC9500A) in the

ozonation process. The specific objectives were to: 1) determine the ozonation rate and extent of various key petroleum components (TPHs, *n*-alkanes and PAHs) under simulated surface-level atmospheric ozone, 2) investigate effect of Corexit EC9500A on the ozone oxidation; and 3) elucidate the ozonation mechanisms. The findings will improve our understanding of the role of atmospheric ozone in the weathering of spilled oil.

2. Materials and methods

2.1. Materials

All chemicals used in this study were of analytical grade or higher unless indicated otherwise. Methanol was purchased from Alfa Aesar (Ward Hill, MA, USA). Chromatographic hexane, dichloromethane (DCM), NaOH and NaCl were obtained from Fisher Scientific (Fair lawn, NJ, USA). HCl was acquired from BDH Aristar (West Chester, PA, USA). 4-chlorobenzoic acid (pCBA) was procured from Acros Organics (Morris Plains, NJ, USA). A standard leonardite humic acid (LHA, IHSS 1S104H, 64% as total organic carbon (TOC)) was purchased from the International Humic Substances Society. The following standard reagents were purchased from Supelco (Bellefonte, PA, USA): a standard of *n*-alkanes mixtures (C9–C40), a standard for the 16 USEPA listed PAHs (Table S1 in Supplementary Materials (SM)), two internal standards (5 α -androstane for *n*-alkanes and fluorene-d₁₀ for PAHs), and a surrogate standard of naphthalene-d₈, acenaphthene-d₁₀, phenanthrene-d₁₀, and benzo(a)pyrene-d₁₂. Corexit EC9500A was obtained by courtesy of Nalco Company (Naperville, IL, USA). Table S2 in SM gives the formulations of Corexit EC9500A.

Seawater was collected from the top 30 cm of the water column from Grand Bay, AL, USA (N30.37926/W88.30684). Before use, the sample was first passed through 0.45 μ m membrane filters to remove suspended solids, and then sterilized at 121 °C for 35 min via autoclaving. Salient properties of the seawater sample are: pH = 8.1, DOM = 2.2 mg/L as TOC, salinity = 2 wt%, Cl⁻ = 18.55 g/L, NO₃⁻ = 2.55 g/L, SO₄²⁻ = 4.25 g/L, and ionic strength (IS) = 0.7 M.

A surrogate LSC oil was obtained through courtesy of BP (Houston, TX, USA). According to the supplier, the physical, chemical and toxicological properties of the surrogate oil are analogous to those of the Macondo Well crude oil of Mississippi Canyon Block 252. Before use, the crude oil was artificially weathered according to the evaporation method by Sorial et al. (2004). Briefly, 1.0 L of the crude oil was purged in the dark through a glass tube from the bottom of a flask at a constant air flowrate of \sim 2 L/min to remove the lighter compounds. After 10 days of the weathering process, the oil mass diminished from 807.1 to 608.5 g (by 24.6 wt%), and the density increased from 0.807 to 0.834 g/cm³. This procedure simulates the loss of the volatile oil compounds at sea surface shortly following an oil spill (Li et al., 2009).

2.2. Experimental set-up

Fig. 1 displays the schematic of the ozonation experiment set-up. The experiments were carried out in a glass cylinder batch reactor (H \times D = 5 cm \times 8 cm) with a thin quartz cover. The two ports connected with Teflon tubes were for gas flow and the other two ports sealed by ground glass joints were used for sample collection. Ozone was generated from medical grade oxygen 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. The gas (O₂ + O₃) flow rate into the reactor was 4 mL/min controlled by an Aalborg mass flow controller (Model GFC17, Orangeburg, New York, USA). The inlet ozone-laden gas was gently passed through the surface of the reaction solution. The inlet gas-phase ozone concentration was kept at 86 ppbv, which was analyzed by a M106-L Ozone Monitor (2B Technologies, Inc., Boulder, CO, USA) through measuring the UV absorbance at 254 nm. In the outlet gas-phase, the excess ozone was

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