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Mechanistic investigation into sunlight-facilitated photodegradation of pyrene in seawater with oil dispersants

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ABSTRACT

This study investigated the effects of 3 model oil dispersants (Corexit EC9500A, Corexit EC9527A and SPC 1000) on photodegradation of pyrene under simulated sunlight. Both Corexit dispersants enhanced photodegradation of pyrene, while SPC1000 slightly inhibited the reaction. Span 80 and Tween 85 were the key ingredients causing the effects, though the underlying mechanisms differed. Span 80 enriches pyrene in the upper layer of water column, whereas Tween 85 induces a photosensitization process. Two reactive oxygen species, $^1\text{O}_2$ and $\text{O}_2^{\bullet-}$, were found responsible for pyrene photodegradation, though the presence of EC9500A suppressed the $^1\text{O}_2$ pathway. In terms of photodegradation products, EC9500A enhanced generation of polyaromatic intermediates, i.e., phenaleno[1,9-cd][1,2]dioxine, 1-hydroxypyrene, and 1,8-pyrenequinone, but did not alter the classical photodegradation pathway. The Corexit dispersants were more prone to photochemical decomposition, with multiple by-products detected. The information aids in our understanding of the effects of dispersants on photochemical weathering of oil compositions.

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1. Introduction

Oil dispersants are a mixture of surfactants and solvents, which can break up oil slicks into fine droplets by lowering the surface tension, thereby accelerating dispersion of oil into the water column, enhancing dissolution of oil components, and improving oil biodegradability (Gong et al., 2014a). Since the 1950s, oil dispersants have been increasingly used as a critical response measure to mitigate oil spill impacts in the marine environment (Cai et al., 2016; Ramachandran et al., 2004). During the 2010 Deepwater Horizon (DwH) oil spill, approximately 5.4 million barrels of oil were released from the Macondo well at a depth of 1500 m, of which 4.6 million barrels entered the Gulf (Gong et al., 2014b; Griffiths, 2012). As an emergency measure, approximately 2.1 million gallons of oil dispersants (i.e., Corexit EC9527A and Corexit EC9500A) were applied on the sea surface (1.4 M gallons) and wellhead (0.77 M gallons) (Kujawinski et al., 2011; Zhao et al., 2016). Corexit EC9527A was applied at the surface, while Corexit EC9500A was applied both in the surface and at the wellhead (Kujawinski et al., 2011).

One of the major concerns with the unprecedented application of oil dispersants during the DwH oil spill has been the potential adverse impacts on the marine organisms and human health, which remains an intensive research subject (Hemmer et al., 2011). In addition, as

dispersants may undergo various biotic and abiotic transformations, the resulting by-products have been feared to cause complex effects in the ecosystem (Barron, 2012). Yet, information on the transformation and environmental fate of dispersants remains limited.

Spilled oil in the environment undergoes various physico-chemical and biological weathering processes, including adsorption, biodegradation, dispersion, dissolution, emulsification, evaporation, and photodegradation (Fu et al., 2014; Gong et al., 2015; Plata et al., 2008). Photodegradation is known to be a major abiotic process affecting petroleum weathering with significant implications in the redox cycling, transport, and degradation of oil components (Nicodem et al., 2001; Zafriou et al., 1984). The large quantities of applied oil dispersants may have great impacts on the photodegradation of oil due to the strong chemical and physical interactions between the dispersant and oil components. Unfortunately, there has been little information on the effects of oil dispersants as well as the action mechanisms on photodegradation of oil components under solar irradiation.

Typically, the main components in oil are hydrocarbons including alkanes and aromatics (e.g., polycyclic aromatic hydrocarbons, PAHs) (Liu et al., 2012). Compared with alkanes, PAHs often pose greater ecological threat due to their higher toxicity, mutagenicity, carcinogenicity, and persistence (Nam et al., 2008). The Macondo oil during the DwH oil spill contained approximately 3.9% PAHs by weight, and the incident gushed approximately 2.1×10^4 tons of PAHs into the environment, which can pose both short- and long-term impacts on the Gulf of

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Mexico ecosystems (Liu et al., 2012; Reddy et al., 2012). Therefore, it is critical to evaluate weathering rate and extent of PAHs in the Gulf environment to guide the long-term risk assessment and remediation/restoration efforts.

Our previous study has indicated Corexit EC9500A could enhance the photodegradation of a prototype PAH (pyrene) in seawater under UVC (254 nm) irradiation, and several environmental factors (e.g., ionic strength, temperature, and humic substances) may affect the photodegradation process (Gong et al., 2015). However, the effect of oil dispersants on photodegradation of dispersed oil components under sunlight has not been explored (Note: natural sunlight reaching the earth surface contains almost no UVC (<280 nm)). Moreover, given the complexity of dispersant compositions, the effects of individual dispersant components on the photodegradation as well as the underlying physical and chemical mechanisms are yet to be revealed. Furthermore, information on the photochemical decomposition of oil dispersants in the marine environment has been limited.

The overarching goal of this study was to gauge the effects of model oil dispersants on photochemical degradation of representative PAHs under sunlight. Using pyrene as the prototype PAH and Corexit EC9500A, Corexit EC9527A and Dispersit SPC 1000 (hereafter referred to as EC9500A, EC9527A and SPC1000) as model dispersants, this work aimed to: 1) determine the rate and extent of photodegradation of pyrene in Gulf coast seawater under simulated solar irradiation in the presence of different types and concentrations of oil dispersants; 2) elucidate the underlying action mechanisms of key individual dispersant components on the photodegradation effectiveness; 3) identify the key reactive oxygen species (ROS), the photodegradation pathway, and intermediate products; and 4) examine photochemical weathering rate of oil dispersants and the degradation by-products derived from dispersant components under solar irradiation. The acquired information will aid in our understanding of dispersant effects on the photochemical weathering of oil and environmental fate of applied oil dispersants in the Gulf of Mexico ecosystem.

2. Materials and methods

2.1. Materials

Seawater samples were collected from the top 30 cm of the water column at Grand Bay, AL, USA (30°37'45" N, 88°18'25" W) in October 2012, and stored in a 4 °C refrigerator. Before use, the seawater was passed through 0.22 µm membrane filters to remove suspended solids and bacteria. Detailed physicochemical properties of the seawater have been described elsewhere (Fu et al., 2014).

All chemicals used in this study were of analytical or higher grade, and used as received. Pyrene, 1,4-benzoquinone, *tert*-butanol, and methanol were purchased from Alfa Aesar (Ward Hill, MA, USA). Sodium azide (NaN₃), NaOH, and NaCl were obtained from Fisher Scientific (Fair lawn, NJ, USA). Acetonitrile (HPLC grade) was purchased from EMD Millipore Corporation (Billerica, MA, USA). EC9500A and EC9527A were acquired through the courtesy of Nalco Company (Naperville, IL, USA). SPC1000 was procured from Polychemical Corporation (Chestnut Ridge, NY, USA). Individual compositions of the Corexit dispersants including propylene glycol (PG), 2-butoxyethanol (BE), sodium dioctyl sulfosuccinate (SDSS), Span 80, Tween 80, Tween 85, di(propylene glycol) butyl ether (DBE), and kerosene were obtained from either Sigma-Aldrich (St. Louis, MO, USA) or Fisher Scientific (Fair lawn, NJ, USA).

2.2. Experimental apparatuses

Simulated sunlight was generated using a 94041A solar simulator equipped with a 6279NS 450 W xenon-ozone free short arc lamp and an air mass 1.5 global filter to block the infrared in the visible zone (Newport Corporation, Irvine, CA) (Fig. S1a, Supporting information

(SI)). The optical path area was 10 × 10 cm, and the light intensity reached the reactor was 100 mW/cm², which was measured by using a 1916-R power meter with an 818-UV/dB photodetector (Newport Corporation, Irvine, CA). Table S1 (SI) gives the irradiance distribution of the solar simulator output. For comparison, a 4 W UV lamp (254 nm) was employed to determine the effect of UVC (<280 nm), which was excluded in the simulated sunlight. The UVC irradiation intensity reaching the reactor was 0.7 mW/cm². A cylindrical quartz tank reactor with a Pyrex pillar (80 × 75 mm) was fabricated as the photoreactor (Fig. S1b, SI). A water cooling system was attached to keep the reactor temperature constant. A quartz disc cover (4 × 0.08 in.) was used, which allowed vertical injection of simulated sunlight. A retaining clip and an obturating ring were used to seal the reactor during the photodegradation experiment. Duplicate samples were taken from sampling ports located on the opposite sides.

2.3. Experimental procedure

A stock solution of pyrene (0.3 g/L) was prepared in methanol, which was shaken overnight to assure complete dissolution. Then, a 300 mL pyrene solution (60 µg/L) was prepared by diluting the stock solution in 300 mL seawater, of which 250 mL was used for batch photodegradation kinetic tests. Before each test, the lamp was warmed up for ~30 min. The photodegradation was initiated by exposing the pyrene solution to sunlight or UV light under the aforementioned conditions, during which the reactor remained sealed and the solution was gently stirred (300 rpm) with a 1-inch magnetic bar. At predetermined times, samples were taken for determination of pyrene concentration (1 mL) or analysis of degradation products (10 mL). To investigate the effects of dissolved oxygen (DO), DO-free seawater was obtained by purging the seawater using pure nitrogen for 30 min, and then used in the experiments. To evaluate the effects of dispersants, individual dispersant components, and radical scavengers, the photodegradation tests were carried out in the presence of known concentrations of the chemicals. Control tests were conducted without light irradiation. Each experiment was conducted in duplicate and at 22 ± 1 °C.

To investigate the effects of dispersant components on the vertical distribution of pyrene in the water column, a 250 mL pyrene solution (60 µg/L) containing various individual dispersant components was stirred in the sealed reactor for 30 min without light irradiation, and then, samples (1 mL each) were taken from different water depths and analyzed for pyrene concentrations.

2.4. Analytical methods

UV spectra (200–400 nm) of various solutions were obtained using an HP 8453 UV–Vis spectrophotometer with a 1 × 1 cm quartz cell (Agilent Technologies, Santa Clara, CA, USA). Fluorescence measurements were conducted on a LS55 luminescence spectrometer (Perkin Elmer, Waltham, MA, USA), using a 10 mm path length quartz cuvette. The excitation wavelength was set at 335 nm and the emission spectra were recorded in the wavelength range of 350–550 nm at 1 nm increments. The slit width for both excitation and emission was fixed at 0.4 nm, and the scanning time was kept at 0.8 s per scan. Surface tension of dispersant solutions was measured on a 70,535 series DuNouy Tensiometer (CSC Scientific, Fairfax, VA, USA).

Pyrene concentration was determined using an HP 1100 HPLC system (Agilent Technologies, Santa Clara, CA, USA) equipped with a UV detector and a Zorbax SB-C18 column (150 × 468 mm). The mobile phase consisted of 70% acetonitrile, 30% water, and 0.1% phosphoric acid. The injection volume was 100 µL, and the mobile phase flow rate was 1.0 mL/min. The UV detection wavelength was 240 nm, and the method afforded a detection limit of 2.5 µg/L.

Photodegradation products were analyzed using an HP7890A/HP5975C GC–MS system (Agilent Technologies, Santa Clara, CA, USA).

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