



Petroleum films exposed to sunlight produce hydroxyl radical



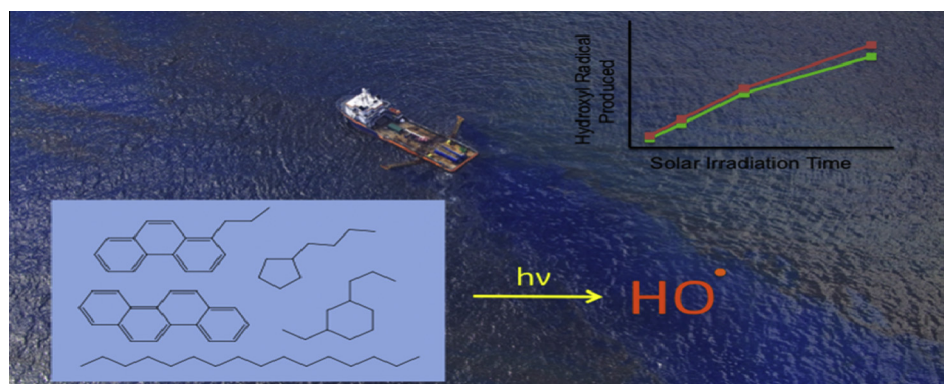
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HIGHLIGHTS

- Sunlight exposed oil films produced substantial amounts of hydroxyl radical.
- $\sim 4 \times 10^{-7}$ moles OH were produced in 24 h from sunlight irradiated 100 mg oil films.
- $[\text{OH}] = 1.2\text{--}2.4 \times 10^{-16}$ M in water under 100 mg irradiated oil films.
- TiO_2 nanoparticles changed the formation rate of hydroxyl radical.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 11 July 2013

Received in revised form 27 November 2013

Accepted 4 December 2013

Available online 7 January 2014

Keywords:

Petroleum
Crude oil
Oil spill
Hydroxyl radical
Photochemistry
Reactive transient

ABSTRACT

Sunlight exposed oil films on seawater or pure water produced substantial amounts of hydroxyl radical as a result of irradiation. Oil was collected from the surface of the Gulf of Mexico following the Deepwater Horizon spill and exposed to simulated sunlight in thin films over water. Photochemical production of hydroxyl radical was measured with benzoic acid as a selective chemical probe in the aqueous layer. Total hydroxyl radical formation was studied using high benzoic acid concentrations and varying exposure time. The total amount of hydroxyl radical produced in 24 h irradiations of thin oil films over Gulf of Mexico water and pure water were 3.7×10^{-7} and 4.2×10^{-7} moles respectively. Steady state concentrations of hydroxyl radical were measured using a competition kinetics approach. Hydroxyl radical concentrations of 1.2×10^{-16} to 2.4×10^{-16} M were observed for seawater and pure water under oil films. Titanium dioxide (TiO_2) nanomaterials were added to the system in an effort to determine if the photocatalyst would enhance oil photodegradation. The addition of TiO_2 nanoparticles dramatically changed the observed formation rate of hydroxyl radical in the systems with NP water at pH 3, showing increased formation rate in many cases. With photocatalyst, the steady state concentration of radical decreased, predominantly due to an increase in the hydroxyl radical scavenging rate with oxide present. This study illustrates that oil is a strong and important source of hydroxyl radical when exposed to sunlight. The fate of oil and other dissolved species following oil spills will be heavily dependent on the formation and fate of hydroxyl radical.

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1. Introduction

Photochemical transformation of intact crude oil has been studied to a limited extent over the last 40 years. In 1975, Hansen reported on the photodegradation of thin films of crude oil fractions on sea water (Hansen, 1975). Photochemical degradation

Abbreviations: BA, benzoic acid; NT, nanotube; *p*-HBA, *p*-hydroxybenzoic acid; GW, Gulf of Mexico water; NP, nanopure water.

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of PAHs in thin films of spilled oil on rocks were investigated (Plata et al., 2008). There have been numerous published studies regarding photoproducts produced in natural water from the photolysis of dissolved organic matter (DOM), which consists predominantly of dead plant material (Page et al., 2011). When DOM is exposed to sunlight, a number of reactive transients are formed, including hydroxyl radical (Zhou and Mopper, 1990), singlet oxygen (Zepp et al., 1981b; Zepp et al., 1985; Haag and Hoigné, 1986; Lindsey and Tarr, 2000a; Takeda et al., 2004; Page et al., 2010; 2013), superoxide (Petasne and Zika, 1987), organic radicals (Kieber and Blough, 1990; Zafiriou et al., 1990; Faust, 1999) and organic triplets (Zepp et al., 1981a). Methods for quantitating these transients have been reported (Zepp et al., 1981b; Haag and Hoigné, 1985; Zepp et al., 1985; Haag and Hoigné, 1986; Faust and Hoigne, 1987; Petasne and Zika, 1987; Kieber and Blough, 1990; Zafiriou et al., 1990; Zhou and Mopper, 1990). Since the composition of DOM varies with its environment (Klapper et al., 2002), differences in the transients and their functions have been observed (Page et al., 2010). Zhou and Mopper measured the production rates and steady state concentrations of photochemically produced hydroxyl radicals in coastal and open ocean waters and freshwaters (Zhou and Mopper, 1990). Vaughan and Blough measured OH production rates in the photolysis of fulvic acid solutions in natural water in the presence and absence of dioxygen (Vaughan and Blough, 1998). There have been many studies done with selective probes to detect the formation of reactive transients (Zepp et al., 1981b; Haag and Hoigné, 1985; Zepp et al., 1985; Haag and Hoigné, 1986; Faust and Hoigne, 1987; Petasne and Zika, 1987; Kieber and Blough, 1990; Zafiriou et al., 1990). Oil and natural organic matter likely have common origins (dead plant matter) but have different structures and compositions. Despite these differences, they may share similar functional groups and likely have some common mechanisms for photochemical formation of reactive transients. This study focused on the photochemical production of reactive transients that form when sunlight reacts with thin oil films over water. The role of these photochemical transients formed in the presence of thin oil films on water has not been fully explored. Furthermore, the subsequent chemical and biological processes that occur in the aqueous layer when sunlight reacts with oil are poorly understood. In order to better understand these effects when oil is spilled in an aquatic system, the formation and scavenging of hydroxyl radical was studied in oil on water systems under solar irradiation. Hydroxyl radicals have been previously implicated in the degradation of organic pollutants (Page et al., 2010, 2011), photo-Fenton chemistry (Lindsey and Tarr, 2000b; Page et al., 2010, 2011; Zepp et al., 1992) and the chemistry of natural organic compounds in aqueous environments (Zhou and Mopper, 1990). Consequently, hydroxyl radical is an important oxidant in the environment (Karadag et al., 2009; Grebel et al., 2010; Marin et al., 2011; Wenk et al., 2011; Page et al., 2013). In this study, the total amount of hydroxyl radical formation and the steady state concentrations were determined employing similar methods previously reported by Zhou and Mopper (Zhou and Mopper, 1990).

This study investigated photochemical formation of hydroxyl radical from crude oil collected from the deepwater horizon oil spill that occurred on April 10, 2010. Photochemical production of hydroxyl radical was investigated for oil films on seawater and pure water matrices. Furthermore, this study investigated the effect of photocatalysts on hydroxyl radical formation during solar irradiation. Photocatalysts are a potential method of speeding decomposition of spilled oil, which was our motivation for investigating photocatalyst amended oil. In addition to accelerating overall degradation rates, photocatalysts can change the reaction mechanisms and the products formed. We have evidence that changes in photoproduct identity occurs upon addition of a

photocatalyst (see Fig. S-3 in Supporting Information), although the details are not yet understood. Changes in oil composition and production of photoproducts can exert important influences on oil fate, toxicity, and bioavailability. Changes in toxicity have been observed upon irradiation of oil with simulated sunlight (King et al., 2014). The fundamental knowledge (hydroxyl radical formation rate, scavenging rate, and steady state concentration) generated by this study may translate into better technologies and better protocols for minimizing the negative impacts of an oil spill in an aquatic system. Titanium dioxide is a low cost, readily abundant, low toxicity material that has potential to enhance oil degradation. Results will help identify low cost, effective remediation strategies in order to better mitigate the harmful effects of an oil spill.

2. Experimental

2.1. Materials

Pure water was obtained by purification of distilled water with a Barnstead nanopure UV water treatment system (NP water). Gulf of Mexico water (GW) was obtained from the Mississippi Sound and filtered first through 0.45 μm membrane filters then 0.2 μm membrane filters (Gelman Sciences 90 mm Supor-450 and Supor-200, respectively) and stored in the dark at 4 °C. The gulf water had a pH of 7.9 and a salinity of 23 ppt. Surface oil was collected on May 24, 2010 directly from the surface of the Gulf of Mexico (latitude 28.801 and longitude -89.119) about 50 miles NW of the Deepwater Horizon site. This oil had risen to the surface through 1500 m of Gulf water and remained on the surface prior to collection. Therefore, water soluble and volatile compounds had been removed from the surface oil prior to collection. Samples were stored in the dark at 4 °C. Benzoic acid (BA, 99.5%), 4-hydroxybenzoic acid (*p*-HBA, 99 + %), 2-hydroxybenzoic acid (salicylic acid) ACS grade, 99 + %, 3-hydroxybenzoic acid (99%), and P25 titanium dioxide (99.5%), 1-propanol (PrOH) (99.9%), and 2,4-dinitrophenylhydrazine (DNPH) (70%) were purchased from Aldrich. Stearic acid was obtained from JT Baker. Dimethyl sulfoxide (DMSO) (certified ACS), acetonitrile (ACN), trifluoroacetic acid (TFA), both HPLC grade, were obtained from Fisher. Propionaldehyde (98%) was purchased from Fluka. All reagents were used as received.

2.2. Instrumentation

For photochemical studies, an Atlas CPS+ solar simulator was used at an intensity equivalent to approximately 1.3 times that of solar noon (AM 1.5). The optical spectrum of the irradiation source in the solar simulator used in our studies was similar to the optical spectrum of the sun, with a slightly higher intensity. To standardize our instrument, a Hamamatsu S1718 solar cell (calibrated at the National Renewable Energy Laboratory) was used to measure the intensity of light in the simulator. From the measured intensity, it was discovered that the output of our solar simulator set at its maximum output (765 W/cm², 300–800 nm only) was equivalent to 1.26 times the intensity of full sunlight (1000 W/m² full spectrum AM 1.5). Based on solar irradiance data from the National Solar Radiation Database (NREL, 2013) at latitude 28.85, longitude -88.35 (the nearest location to our sampling site), the average daily amount of direct and diffuse solar radiation received on a horizontal surface at this location in 2009 was 4972 W h/m². Our solar simulator produced about 1260 W/m². Dividing this irradiance into the average daily insolation yields a value of 3.95 h, representing the amount of time in our solar simulator equivalent to an average day of insolation at this location.

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