



## Photochemical degradation of Corexit components in ocean water



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### HIGHLIGHTS

- Corexit was utilized during the Deepwater Horizon oil spill as a dispersant.
- We examined the photochemical fate of several Corexit components.
- Direct photolysis was less efficient than overall degradation in ocean waters.
- Hydroxyl radical rate constants for five Corexit components were determined.
- Hydroxyl radical in ocean waters was the major contributor to overall degradation.

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### ABSTRACT

Due to the large quantities of dispersants used during the Deepwater Horizon spill in 2010, there were immediate concerns with regards to the fate and transport of the mixture in ocean waters. Direct and sensitized photolysis experiments were carried out for two compounds chosen as surrogates for the Corexit mixture (9500 and 9527) that were applied to surface waters during the oil spill in the Gulf of Mexico. The results showed that direct photolysis did not contribute significantly to the overall degradation (max ~30%), therefore the focus shifted to sensitized photolysis, specifically the degradation stemming from the reaction rate with hydroxyl radical (HO<sup>•</sup>). The direct photochemical degradation rates for two of the compounds, dioctyl sulfosuccinate (DOSS) and dipropylene glycol butyl ether (DGBE) were measured as  $4.29 \times 10^{-6} \text{ s}^{-1}$  and  $5.95 \times 10^{-6} \text{ s}^{-1}$ , respectively; whereas the overall degradation rate in ocean water was  $1.56 \times 10^{-5} \text{ s}^{-1}$  and  $2.23 \times 10^{-5} \text{ s}^{-1}$ . The formation rates and apparent quantum yields for HO<sup>•</sup> formation were determined for six ocean water samples. The values ranged from  $1.81 \times 10^{-5}$  near shore to  $0.061 \times 10^{-5}$  for the open ocean. These degradation rates suggest the possibility for photolysis to play a role in the overall fate of Corexit.

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### 1. Introduction

In response to the Deepwater Horizon oil spill, approximately 1.1 million gallons of dispersants (Corexit 9500A and 9527) were applied to the ocean's surface from May 15th to July 12th, 2010 (Whitehouse, 2013). Dispersants are designed to break up oil

slicks, form manageable oil globules, and spread the oil/dispersant micelles throughout the water column. This process has been shown to protect the shoreline ecosystem and enhance oil biodegradation through the increased oil surface area (Research Council of the National Academies et al., 2005; Campo et al., 2013; Prince et al., 2013). The two Corexit mixtures are composed of numerous, both solvents and non-polar surfactants including petroleum distillates, propylene glycol, 2-butoxyethanol, Tween 80, Tween 85, Span 80, sodium 1,4-bis(2-ethylhexoxy)-1,3-dioxobutane-2-sulfonate, and dipropylene glycol butyl ether (in this work we have abbreviated dioctyl sulfosuccinate as DOSS and dipropylene glycol butyl ether as DGBE). The presence of these compounds was of concern due to the unprecedented quantities used and because of the potential toxicity of Corexit mixtures in an array of microbes (reduction in viability, DNA damage, and mutagenicity), crustaceans (George-Ares and Clark, 2000), sea grass and coral

*Abbreviations:* DOSS, dioctyl sodium sulfosuccinate; DGBE, dipropylene glycol butyl ether; RIs, reactive intermediates; HO<sup>•</sup>, hydroxyl radical; <sup>1</sup>O<sub>2</sub>, singlet oxygen; DOM, dissolved organic matter; <sup>3</sup>DOM\*, triplet excited dissolved organic matter; X<sup>•</sup>, X<sub>2</sub><sup>•-</sup>, halide radicals; S<sub>R</sub>, spectral slope ratio; SUVA<sub>254</sub>, specific ultraviolet absorbance at 254 nm; ε, molar absorptivity; k<sub>d</sub>, direct photolysis degradation rate; Φ<sup>q</sup>, apparent quantum yield; DOC, dissolved organic carbon; P<sub>HO<sup>•</sup></sub>, hydroxyl radical formation rate; k<sub>HO<sup>•</sup></sub>, hydroxyl radical rate constant; [RIs]<sub>ss</sub>, steady state concentration of reactive intermediate; [C], concentration of contaminant; k<sub>overall</sub>, overall degradation rate; MOSS, 2-ethylhexoxy-1,4-dioxobutane-2-sulfonate.

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(Goodbody-Gringley et al., 2013), and complex species such as fish and ducks (George-Ares and Clark, 2000).

Natural processes can mitigate the presence of Corexit in ocean waters. Previously, the combination of biodegradability alongside hydrolysis was shown to be especially effective in the breakdown of one of the main components of Corexit, DOSS (Campo et al., 2013). DOSS is the most commonly studied chemical of the mixture and has been used as a tracer for Corexit (Kujawinski et al., 2011). The reported concentrations of DOSS appeared to significantly decrease as the samples moved away from the wellhead and many open ocean and deep-water samples were below detection limits (Kujawinski et al., 2011). Furthermore, the Operational Science Advisory Team collected over nine thousand samples in the five months following Corexit application and found that the four components (propylene glycol, 2-butoxyethanol, DOSS, and dipropylene glycol) they measured were never detected at levels exceeding EPA's aquatic life benchmarks (Team, 2010). However, there is still interest in understanding the role of natural abiotic processes in the degradation of the components of this mixture.

Photolytic processes, both direct and sensitized, can have a significant impact on the mitigation of organic compounds in seawater. Direct photolysis depends on the absorption of light by a compound that initiates a reaction and is limited by the amount of light screening of the aquatic system (Schwarzenbach et al., 2002). Sensitized photolysis of target compounds in seawater depends on the formation, and subsequent reactivity of reactive intermediates (RI), such as singlet oxygen ( $^1\text{O}_2$ ) (Blough and Zepp, 1995), hydroxyl radical ( $\text{HO}^\bullet$ ) (Vione et al., 2006), triplet excited dissolved organic matter ( $^3\text{DOM}^*$ ) (Canonica et al., 1995), and halide radicals ( $\text{X}^\bullet$ ,  $\text{X}_2^{\bullet-}$ ) (Grebel et al., 2012). Of these RIs,  $\text{HO}^\bullet$  is often the key to determining the degradation of contaminants, as it is a non-selective and highly reactive oxidant with reaction rate constants around  $10^8\text{--}10^9\text{ M}^{-1}\text{ s}^{-1}$  (Buxton et al., 1988).  $^3\text{DOM}^*$  is formed by the absorbance of specific chromophores, quinone-type compounds or aromatic ketones, and is a precursor for  $^1\text{O}_2$ , and halide radicals (Del Vecchio and Blough, 2004; al Housari et al., 2010). In marine systems,  $\text{HO}^\bullet$  is also formed through the photolysis of nitrate/nitrite and photo-Fenton processes (Blough and Zepp, 1995). Scavenging reactions of  $\text{HO}^\bullet$  can subsequently produce halide and carbonate radicals, which decrease the degradation rates for contaminants due to the increased selective reaction of these radicals (depending on contaminant structure) (Grebel et al., 2010). Within the pH ranges found in ocean waters, the inhibition of contaminant degradation follows the general trend of  $\text{Br}^- > \text{carbonates} > \text{Cl}^-$  with bromide potentially scavenging as much as 93% of the  $\text{HO}^\bullet$  formed (Mopper and Zhou, 1990).

Previous studies have examined the degradation of organic compounds in marine systems where several contaminants (ibuprofen, ketoprofen,  $17\alpha$ -ethinylestradiol (Matamoros et al., 2008)) have been shown to be photochemically degraded by the  $\text{HO}^\bullet$  produced from the DOM and nitrate present in the system. The scavenging reactions involving halides did not interfere with this degradation. However, with other compounds (triclosan (Aranami and Readman, 2007), carbofuran (Campbell et al., 2004), carbamazepine (Chiron et al., 2006)), there was increased degradation in salt water in comparison to freshwater, which was attributed to the formation of halide radicals. Halide radicals are more selective oxidants and tend to react with electron-rich chromophores to form chlorinated or brominated by-products (Grebel, 2011). For  $17\beta$ -estradiol there was an observed reduction in  $\text{HO}^\bullet$  induced photolysis in marine systems, which was attributed to the scavenging of  $\text{HO}^\bullet$  and to the effect of halides on photobleaching (Grebel et al., 2012). It was also found that photobleaching of DOM by halides destroyed the chromophores necessary to produce  $^3\text{DOM}^*$  and without this precursor the  $\text{HO}^\bullet$  induced degradation was decreased (Grebel et al., 2009).

As DOM plays a critical role in the formation of RIs, its optical properties have been useful in predicting reactivity. Several parameters have been used successfully including E2:E3 ratio (absorbance at 254 nm to absorbance at 365 nm), spectral slope ratio ( $S_R$ ), and fluorescence quantum yield. The spectral slope ratio has been used to model the molecular weight, source, and the level of photobleaching of organic matter samples, but it has also been shown to correlate to the quantum yield of  $^1\text{O}_2$  (Helms et al., 2008; Peterson et al., 2012). The E2:E3 ratio also correlates with the quantum yields of  $^1\text{O}_2$  and the production of hydrogen peroxide (Dalrymple et al., 2010). The fluorescence quantum yield is a ratio of the absorbance of DOM to the fluorophores present in the sample and is correlated with the apparent quantum yield of  $\text{HO}^\bullet$  (Lee et al., 2013). However, these relationships have not been developed for ocean water systems.

The purpose of this study was to determine the potential for the degradation of Corexit through sensitized photolysis in ocean water samples. This potential for  $\text{HO}^\bullet$  sensitized photolysis was examined for five compounds in the Corexit mixture, including DOSS, DGBE, Tween 80, Tween 85 and Span 80 (structures shown in Table 1). This was accomplished by measuring their absolute  $\text{HO}^\bullet$  reaction rates in addition to the formation and quantum yield of  $\text{HO}^\bullet$  in six ocean water samples. The optical properties of the ocean water DOM were also monitored as a means of assessing the  $\text{HO}^\bullet$  formation. Further, the photolytic degradation of two Corexit compounds (DOSS and DGBE) was analyzed in detail by assessing the contribution of direct photolysis in addition to following the overall photolytic degradation in one ocean water sample.

## 2. Materials and methods

### 2.1. Materials

Corexit 9500 was obtained from Nalco Holding Company (IL, USA). Standards for the eight compounds found in Corexit were obtained from Sigma Aldrich (MO, USA). HPLC-grade acetonitrile, methanol, and deionized water were obtained from Fisher Scientific (PA, USA).

### 2.2. Ocean water sample collection and characterization

Six ocean water samples were obtained from the Gulf of Mexico. Samples were collected from Grand Isle, LA (shoreline sample) and from locations starting in Terrebonne Bay to Caminada Pass, off the coast of LA (Ocean water sites 1–5). Water quality data (dissolved organic carbon, bromide concentrations, and chloride concentrations) were measured. A Cary 100 UV Spectrophotometer (Agilent, USA) was used to take UV-Vis scans for each of the ocean water samples. The dissolved organic carbon (DOC) content was determined using a TOC- $V_{\text{SCH}}$  (Shimadzu Corp., Japan), which has a minimum detection limit of  $0.2\text{ mgC L}^{-1}$ . Specific ultraviolet absorbance at 254 nm ( $\text{SUVA}_{254}$ ) was calculated by normalizing the absorbance at 254 nm by the DOC content (Weishaar et al., 2003). The spectral slope ratio ( $S_R$ ) was calculated by determining the ration of  $S_1$  to  $S_2$ .  $S_1$  is the slope of the log-normal regression between  $A_{275}$  and  $A_{295}$  and  $S_2$  is the slope of the log-normal regression of  $A_{350}$  and  $A_{400}$  (Helms et al., 2008).

### 2.3. Analytical methods for degradation of DOSS and DGBE

Ion trap LC-MS methods were developed to detect DOSS and DGBE. An Agilent 1100 series HPLC (CA, USA) was used with a reverse phase XDB- $\text{C}_{18}$  column (Agilent, CA, USA) and it was connected to an Esquire (LC/MS/MS) ion trap mass spectrometer

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