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Stability of dioctyl sulfosuccinate (DOSS) towards hydrolysis and photodegradation under simulated solar conditions

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HIGHLIGHTS

- First study to report photolysis of DOSS
- Photolysis of DOSS reported in environmentally relevant light sources in salt water
- First study to report abiotic transformation products of DOSS

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ABSTRACT

Dioctyl sulfosuccinate (DOSS) is one of the main components of Corexit® EC9500A, a chemical dispersant formulation used at the surface and at depth during the response to the Deepwater Horizon incident. Despite being a high volume use chemical, data on its environmental stability are scarce. Hydrolysis and photodegradation of DOSS in both pure water and seawater were reported in the present study. DOSS photodegraded much faster under ultraviolet light source (254 nm, with half-life in hours) compared to relevant environmental light sources i.e., 350 nm and solar simulator (with half-lives in days). LC/MS–MS analysis of hydrolysis and photo-irradiated samples showed the presence of a common degradation product. MS/MS fragmentation of that product indicated a substitution of an octyl group by a hydroxyl group with a corresponding formula of $C_{12}H_{21}O_7S$, which was confirmed by HRMS detection (Q-TOF, m/z 309.1017, +1.29 ppm).

1. Introduction

Corexit® EC9500A and Corexit® EC9527A are two chemical dispersants used in the remediation efforts of oil spills. Corexit® EC9500A was heavily used in the Deepwater Horizon (DWH) oil spill (USG, 2010) whereas Corexit® EC9527A was the main dispersant used in the Alaska North Slope oil spill remediation in 2006 (Fingas, 2008). Based on the published studies that are available, Corexit® formulations have low to moderate toxicity to most aquatic species (George-Ares and Clark, 2000; Hemmer et al., 2010; Judson et al., 2010). One of the surfactants used in both Corexit formulations is dioctyl sulfosuccinate sodium salt (DOSS, CAS number 577-11-7, Fig. 1). DOSS is a high production volume chemical in the U.S. (USEPA, 2013) and is also used as an emulsifying and wetting agent in formulations of laxatives, cosmetics, detergents, pesticides and other consumer products (NCBI, 2013). Corexit® EC9500A and Corexit® EC9527A have been shown to contain 21 ± 2% and 22 ± 5% of DOSS, respectively (Ramirez et al., 2013). Besides the DOSS introduced to the Gulf of Mexico (GOM) as point source during the response to the DWH incident, GOM waters also receive DOSS through diffuse non-point sources such as riverine and estuarine discharges (Hayworth and Clement, 2012).

Studies of DOSS biodegradation in seawater seem contradictory. Garcia et al. (2009) have shown that DOSS is susceptible to biodegradation in both aerobic and anaerobic conditions in fresh waters. A more recent study by Campo et al. (2013) found that DOSS was biodegraded by 98% in 8 and ~38 days in cultures from surface and deep Gulf of Mexico waters (at 25 °C and 5 °C, respectively). However, Kujawinski et al. (2011) reported that DOSS was detected 300 km from the well 64 days after the Corexit application has ceased at concentrations reaching up to 2.1 μg/L, and the article results suggest that this compound is not biodegradable and any decrease in the concentration could be attributed only to dilution effects. In light of these contradictory findings, it is important to monitor DOSS and its degradation products in the environment as the released dispersed oil moves and transforms. Stability of

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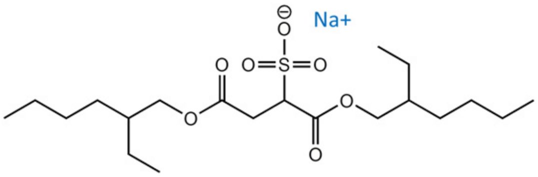

Fig. 1. Structure of DOSS.

DOSS towards photolysis and hydrolysis has not been studied before and is the main objective of this work. Photostability of DOSS was studied using UV light (254 and 350 nm) and in simulated solar radiation. The photolysis was studied in natural seawater and in pure water simultaneously to assess the importance of indirect versus direct photolysis processes.

2. Materials and methods

2.1. Chemicals

Neat DOSS sodium salt was purchased from Acros Organics (Geel, Belgium). Certified DOSS and DOSS-$^{13}C_4$ standards were purchased from Cambridge Isotopes Laboratories (Andover, Massachusetts, USA). Stock and working solutions of standards were prepared in acetonitrile. Optima LC/MS grade formic acid, acetonitrile and water were purchased from Fisher Scientific (Fairlawn, New Jersey, USA). Sodium hydroxide and sulfuric acid (certified A.C.S. grade) and ammonium hydroxide (trace metal grade) were also purchased from Fisher Scientific. Artificial seawater was prepared using the commercially available Instant Ocean® sea salt to 3.5% w/v.

2.2. Salt water

Salt water was taken from the shore at Bill Baggs State Park at Key Biscayne, Florida, USA, using a solvent-rinsed amber glass bottle. Salt water characteristics are shown in Table 1. Salt waters (SW) were filtered (0.2-μm) and stored in the dark at <4 °C until the experimental solutions were prepared, typically within a month.

2.3. Light sources employed in the study

Photodegradation experiments were conducted using Rayonet UV photochemical reactors (Southern New England Ultraviolet Co., Branford, CT) and a SunTest XLS Tabletop Xenon Exposure System (ATLAS Material Testing Technology LLC, Chicago, Illinois, USA). The photochemical reactor was operated with 16-mercury vapor lamps (UV 254 nm) or black light phosphor bulbs (UV 350 nm). UV 254 nm radiation is included in the present study to identify the photolysis products.

UV 350 nm is comparable to the range of the UVA region (315 nm–400 nm) of sunlight and hence commonly used to predict the photodegradation of organic compounds in the environment (Lam et al., 2003; Radjenovic et al., 2009; Sturini et al., 2009). In the environment, the environmental fate of organic compounds depends on its ability to undergo photolysis under sunlight (Jasper and Sedlak, 2013; Zeng and Arnold, 2013). However, the abundance of natural sunlight depends on many factors such as latitude (Li et al., 2002), depth of the photic zone and overcast conditions. For this reason, the results of the experiments conducted with natural sunlight may pose a challenge in comparing them. To overcome that, experiments were conducted with a SunTest, which is a surrogate of natural sunlight. The SunTest XLS produces a continuum of wavelengths from 300 nm to 800 nm by using a xenon lamp. The wavelength distribution and the intensity of the xenon lamp are very similar to those of natural sunlight (Diepens and Gijsman, 2007).

Table 1
Characteristics of salt water used in the experiment.

Parameter	Salt water
pH	7.9
Dissolved organic carbon (mg-C/L)	1.37
Electrical conductivity (μS/cm)	88,000
Salinity (ppt)	36

2.4. Sample irradiation

Standard solutions of DOSS (100 μg/L) were prepared in reverse osmosis deionized water (RODW) and SW. The photolysis experiments were performed once with internal replicates. Three 30-mL quartz tubes (Southern New England Ultraviolet Co., Branford, CT) were used for experiments in the photochemical reactor. The first tube was filled with 30 mL of RODW (blank) and the second and third were filled with solutions of DOSS in RODW, irradiating one of them while the other one was wrapped with aluminum foil (dark control). The same procedure was repeated using SW. All the tubes were placed on a merry-go-round to ensure uniform irradiation in the photochemical reactor chamber. For SunTest experiments, DOSS solutions were placed in three UV transparent *Nasco* WHIRL-PAK 2 oz bags and then the bags were floated in a water bath with circulating water during exposure to keep the solution at a constant temperature (25 °C). At regular intervals 1000 μL of the test solution was collected into a 2-mL LC amber vial containing 484 μL of acetonitrile, fortified with DOSS-$^{13}C_4$ (15.8 μL, 1.9 mg/L) and subsequently analyzed by LC–MS/MS.

2.5. Hydrolysis experiments

The test solution of standard DOSS (80 μL, 1.5 mg/L) in RODW was transferred to two vials each containing 5 mL of 0.01 M sulfuric acid and 0.01 M sodium hydroxide, respectively. Control solutions (no acid or base added) were prepared by spiking standard DOSS (80 μL, 1.5 mg/L) into 5 mL of RODW. The same procedure was repeated with artificial seawater. After 24 h reaction time, the pH was neutralized with formic acid or ammonium hydroxide. Then, 1000 μL of test solution was placed in a 2 mL amber vial containing 484 μL of acetonitrile, fortified with DOSS-$^{13}C_4$ (15.8 μL, 1.9 mg/L) and subsequently analyzed by LC–MS/MS.

2.6. Liquid chromatography

Liquid chromatography analysis was performed according to a previously published methodology by the same authors (Ramirez et al., 2013). HPLC separation was performed using an Accela quaternary pump equipped with a HTC-PAL autosampler system (Thermo Scientific, USA). Liquid chromatography was carried out using a Hypersil Gold

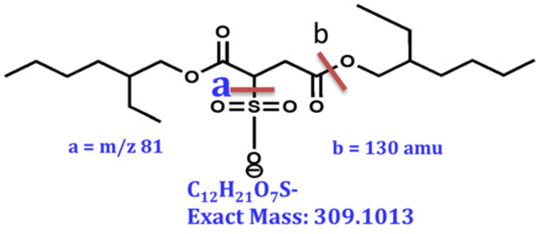

Fig. 2. Structure of degradation product DP1. Fragments a and b, masses monitored for the neutral loss experiments.