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Fate of Dispersants Associated with the Deepwater Horizon Oil Spill

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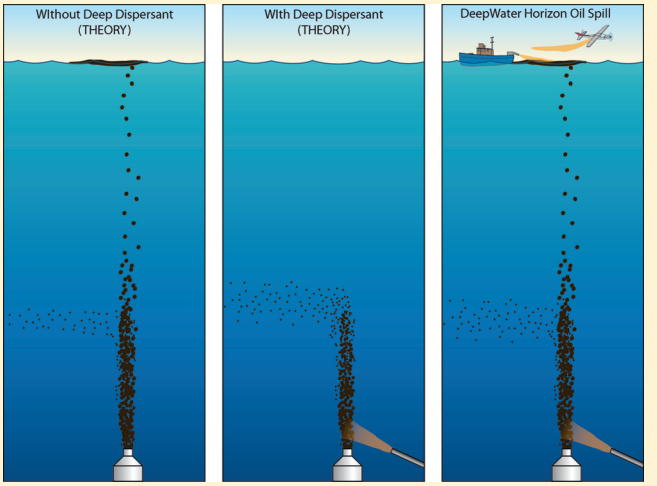
Supporting Information

ABSTRACT: Response actions to the Deepwater Horizon oil spill included the injection of ~771,000 gallons (2,900,000 L) of chemical dispersant into the flow of oil near the seafloor. Prior to this incident, no deepwater applications of dispersant had been conducted, and thus no data exist on the environmental fate of dispersants in deepwater. We used ultrahigh resolution mass spectrometry and liquid chromatography with tandem mass spectrometry (LC/MS/MS) to identify and quantify one key ingredient of the dispersant, the anionic surfactant DOSS (dioctyl sodium sulfosuccinate), in the Gulf of Mexico deepwater during active flow and again after flow had ceased. Here we show that DOSS was sequestered in deepwater hydrocarbon plumes at 1000−1200 m water depth and did not intermingle with surface dispersant applications. Further, its concentration distribution was consistent with conservative transport and dilution at depth and it persisted up to 300 km from the well, 64 days after deepwater dispersant applications ceased. We conclude that DOSS was selectively associated with the oil and gas phases in the deepwater plume, yet underwent negligible, or slow, rates of biodegradation in the affected waters. These results provide important constraints on accurate modeling of the deepwater plume and critical geochemical contexts for future toxicological studies.



INTRODUCTION

Approximately 2.1 million gallons of dispersant were applied to the surface (1.4 M gallons) and wellhead (0.77 M gallons) during the Deepwater Horizon oil spill between May 15 and July 12, 2010.[1] In both modes, dispersant was added to lower the interfacial tension between oil and water and thereby reduce the size of oil droplets formed by wave action (surface) or by ejection of oil and gas out of the wellhead (deepwater). On the seawater surface, application of dispersants can inhibit the formation of large emulsions or slicks that can coat and harm sensitive coastal environments. Following the addition of a dispersant, oil mixes below the seawater surface and can be degraded or dissolved into the water column.[2] Many investigations have been conducted on the use of dispersants on surface oil spills, and they have cautiously concluded that dispersants are successful in mitigating coastal impacts, when applied under the appropriate conditions.[2] No large-scale applications of dispersants in deep water had been attempted prior to the Deepwater Horizon oil spill, and thus no data exist on the fate of dispersant components released in the deep subsurface.

Dispersants are a mixture of surfactants and hydrocarbon-based solvents. Two dispersants were used extensively in the Deepwater Horizon oil spill: Corexit 9527 (surface applications only) and Corexit 9500A (both surface and wellhead). The anionic surfactant, dioctyl sodium sulfosuccinate (DOSS), is a component of both Corexit formulations and is used here as a tracer of the polar components of Corexit 9527 and 9500A in seawater. Other molecules should be studied in future investigations to assess the fate of the nonpolar surfactants and solvents of the two Corexit formulations (see recent U.S. government report[3]). At depth, Corexit 9500A was applied by a jet placed into the oil and gas flow ejected from the wellhead. Due to variability in well operations, the jet was not always applying Corexit nor was it always inserted into the oil and gas flow. However, when the Corexit jet and the oil and gas flow were colocated, Corexit was

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Table 1. All Data from May/June 2010 Samples[a]

	sample	lat (deg N)	lon (deg W)	depth (m)	distance to well (km)	DOSS (μg/L)	CDOM (mg/m^3)	methane (nM)
R/V *F. G. Walton Smith*	CAST 15; bottle 5	28.72322	88.48130	1140	9.3	0.42		
May/June 2010	CAST 41; bottle 12	28.68240	88.56958	800	19	0.35 (*)		
	CAST 41; bottle 8	28.68240	88.56958	1140	19	5.7 (*)		
	CAST 52; bottle 8	28.72025	88.39782	1160	2.1	11.7 (*)		
	CAST 52; bottle 3	28.72025	88.39782	1300	2.1	BD		
	CAST 59; bottle 6	28.73278	88.38322	1170	0.58	0.51		
	CAST 85; bottle 12	28.72557	88.38178	100	1.4	0.01		
	CAST 85; bottle 7	28.72557	88.38178	1140	1.4	6.0		
R/V *Cape Hatteras*	CAST 07; bottle 23	28.73017	88.37950	10	1.2	8.4 (*)	1.92	13
June 2010	CAST 07; bottle 9	28.73017	88.37950	870	1.2	4.3 (*)	2.38	30
	CAST 07; bottle 6	28.73017	88.37950	911	1.2	0.77 (*)	2.36	4600
	CAST 07; bottle 4	28.73017	88.37950	1000	1.2	BD	2.40	87
	CAST 08; bottle 7	28.70350	88.42117	1025	4.9	0.08	2.51	2800
	CAST 10; bottle 20	28.75083	88.36550	1044	2.5	0.07	2.62	
	CAST 10; bottle 11	28.75083	88.36550	1108	2.5	5.3	6.35	98,000
	CAST 10; bottle 5	28.75083	88.36550	1136	2.5	1.9	4.02	127,000
	CAST 12; bottle 5	28.76917	88.36433	1080	3.8	9.7	3.93	183,000
	CAST 13; bottle 4	28.78900	88.36550	1095	6.2	5.4	4.79	137,000
	CAST 13; bottle 2	28.78900	88.36550	1300	6.2	BD	2.48	27
	CAST 15; bottle 11	28.80533	88.44850	1120	9.9	1.5	3.49	48,000
	CAST 18; bottle 17	28.67367	88.31117	470	10	BD	1.97	
	CAST 18; bottle 4	28.67367	88.31117	1100	10	1.4	2.59	17,000
	CAST 21; bottle 9	28.72183	88.27267	810	11	BD	2.46	6400
	CAST 33; bottle 23	28.78467	88.39667	10	5.6	BD	1.22	7
	CAST 33; bottle 3	28.78467	88.39667	1110	5.6	2.0	3.11	25,000

[a] DOSS = dioctyl sodium sulfosuccinate; CDOM = chromophoric dissolved organic matter; BD = below detection. Blank spaces indicate measurements not conducted or variable results. (*) indicates that the DOSS concentrations were derived from the original DCM extracts according to Figure S1.

presumably mixed evenly into the oil as it ascended the water column. On the sea surface, dispersants were applied aerially and by small vessels. Corexit was applied to the ocean surface according to oil and weather conditions, likely resulting in spatial and temporal heterogeneity in Corexit surface water concentrations.

Here we examined DOSS concentrations in water column samples collected from the Gulf of Mexico during and after active flow of oil and gas from the Deepwater Horizon wellhead. We compared DOSS concentrations to tracers of oil and gas in the deepwater in order to assess the ability of this molecule to act as a tracer of oil released during this incident. In addition, we compared our observations to theoretical DOSS concentrations (calculated from release data and environmental parameters) to infer the impact of biodegradation and other loss processes on DOSS in the marine environment.

EXPERIMENTAL SECTION

We collected water samples throughout the water column on three research cruises in the Gulf of Mexico in May, June, and September 2010 (Tables 1 and 2). In June (R/V *Cape Hatteras*), the ocean surface was sprayed with a 1:1 solution of Dawn if surface oil was present during deployment and recovery. Between deployments, Niskin bottles were washed with freshwater and then treated with the Dawn solution if contamination was a concern. In September (NOAA Ship *Pisces*), no contamination was evident on the sea surface, and Niskin bottles were not cleaned between deployments. Water was transferred from Niskin bottles directly into clean Teflon or combusted glass bottles. Bottles were rinsed three times with sample water, filled, and stored frozen until extraction. All organic solvents were Optima grade or better (Fisher Scientific, MA). All glassware was combusted at 450 °C for at least 4 h or solvent-rinsed sequentially with methanol, acetone, methylene chloride, and hexane.

Extractions. We extracted our samples two ways. In the first round, we extracted three fractions for each sample in order to selectively analyze different polarity components of oil and dispersants. During sample analysis, we determined that DOSS could be removed by solid-phase extraction alone, and thus we used that technique as our sole method in the second round of samples.

In the first round, we extracted 500 mL of seawater three times with 100 mL of methylene chloride to remove the basic and neutral components of the oil and dispersants. We then acidified the aqueous layer to pH 3 with concentrated hydrochloric acid (Trace Metal grade, Fisher Scientific) and re-extracted three times with methylene chloride[4] to remove the acidic components. Methylene chloride extracts were combined after each round of three extractions and dried with combusted anhydrous sodium sulfate. Solvent was removed by rotary evaporation, and samples were reconstituted in methylene chloride, transferred to an amber vial, dried under a gentle stream of ultrahigh purity nitrogen, and stored frozen until analysis. To remove any remaining water-soluble components of oil and dispersants, the aqueous layer was then extracted with a solid phase resin made of modified styrene divinyl benzene polymer (PPL), according to published protocols.[5]

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Table 2. Data from September 2010 (NOAA Ship *Pisces*)[a]

sample	lat (deg N)	lon (deg W)	distance from well (km)	depth (m)	DOSS (μg/L)	fluorescence (mg/m^3)
CAST 193; bottle 22	27.17980	90.59212	277	900	BD	1.76
CAST 193; bottle 15	27.17980	90.59212	277	1100	BD	2.05
CAST 193; bottle 10	27.17980	90.59212	277	1150	BD	1.80
CAST 193; bottle 1	27.17980	90.59212	277	1400	0.003	1.97
CAST 198; bottle 11	26.70938	90.62685	315	1150	0.003	1.96
CAST 200; bottle 14	26.53471	90.58365	327	970	BD	1.92
CAST 200; bottle 5	26.53471	90.58365	327	1150	BD	1.89
CAST 209; bottle 12	27.32558	91.26098	323	1200	BD	1.88
CAST 209; bottle 6	27.32558	91.26098	323	1300	BD	1.89
CAST 211; bottle 17	27.19940	91.84156	380	1040	BD	1.84
CAST 213; bottle 13	27.06779	91.97551	398	1000	BD	1.98
CAST 214; bottle 15	26.93886	91.77283	388	1000	BD	1.93
CAST 222; bottle 13	27.09103	90.57789	283	1165	0.006	2.10
CAST 228; bottle 10	27.41416	89.88178	208	1025	BD	1.99
CAST 230; bottle 15	27.52755	89.64140	182	1050	0.068	2.00
CAST 233; bottle 20	27.75458	89.26696	139	1030	0.059	1.88
CAST 239; bottle 13	28.39784	88.61225	44	1150	0.030	
CAST 240; bottle 7	28.51041	88.52982	29	1300	BD	
CAST 240; bottle 15	28.51041	88.52982	29	1150	BD	
CAST 283; bottle 13 (LV)	28.61500	88.51300	18	1155	0.022	
CAST 284; bottle 4 (LV)	28.76018	88.36576	49	1240	0.021	

[a] The same abbreviations as Table S1; LV = large-volume (~7 L) samples. Fluorescence signal was measured here by AquaTracka. Methane data were not available for these samples.

In parallel, we also extracted 400 mL of the samples with only the PPL resin. Extracts from both resin treatments were eluted with 1 mL of methanol and stored in a combusted amber glass vial at −20 °C until analysis. We then rinsed the original sample bottle with methanol. All bottle rinses were dried down under N_2 gas and were reconstituted in 50/50 acetonitrile/water prior to analysis. At the end of our protocol, we had four extracts per sample: (1) DCM extract #1, (2) DCM extract #2, (3) PPL extract of DCM aqueous layer, and (4) PPL extract of initial water sample.

Samples in extraction Round 1 were analyzed at the first opportunity, but some extracts were stored >20 days in the freezer. For Round 1 samples, the reported DOSS concentration is the sum of concentrations in the DCM extract #1, the PPL extract of the DCM aqueous layer, and the bottle rinse (where available). No DOSS was ever found in DCM extract #2 and so it was not included in the final concentration. Prolonged storage proved to be detrimental to DOSS quantification through excessive losses to vial walls (identified from decreases in DOSS concentrations between repeat analyses; see below). Thus, we re-extracted all available samples with the PPL resin only. For these Round 2 samples, the reported DOSS concentration is the sum of concentrations in the PPL extract and the bottle rinse. DOSS concentrations in samples that could not be re-extracted were estimated from a relationship derived between old (Round 1) and new (Round 2) extracts of the same sample (Figure S1). A Model II regression with a reduced axis[6] was used to estimate these relationships, using Matlab code written by E. Peltzer (MBARI; http://www.mbari.org/staff/etp3/regress.htm). Model II regressions are used for correlations between two variables that both contain inherent error. The relationship between the original DCM extracts and the PPL re-extracts was used to correct original DCM extracts from the R/V *F. G. Walton Smith* cruise, conducted in May 2010. Concentrations estimated by this method are denoted with a (*) in Table 1.

Samples collected in September (NOAA Ship *Pisces*) were extracted with PPL resin only and analyzed immediately. Here, we also added $^{13}C_4$-labeled DOSS as a recovery standard prior to extraction. These samples were analyzed within 3−4 days of extraction to minimize losses associated with storage.

Chromatography and Mass Spectrometry. All extracts were analyzed with liquid chromatography coupled to a linear ion-trap mass spectrometer (LTQ XL, Thermo Scientific). Extracts were amended with 60 pg μL^{-1} (ppb) of universally labeled ^{2}H-DOSS as an injection standard to correct for matrix effects. Twenty-five μL of sample was injected onto a 2.1 × 150 mm, 3 μm Atlantis T3 column (Waters Corp., Milford MA), and the injection loop was washed extensively with 2 mL of 60/40 acetonitrile/isopropanol to reduce sample carry-over. The solvent flow rate was 300 μL min^{-1}, and the gradient program was as follows: 50% solvent A hold for 2 min (during which the column eluent was diverted to waste); followed by a 3-min gradient to 100% solvent B; hold at 100% B for 4 min; equilibrate at 50% A for 5 min. Solvent A was 95/5 water/acetonitrile with 4 mM ammonium acetate and solvent B was 95/5 acetonitrile/water with 4 mM ammonium acetate. The autosampler and column temperatures were held at 15 and 35 °C, respectively. The column eluent was infused into the LTQ-MS under negative electrospray ionization mode. Instrument optimization (tuning) was done by infusing a mixture of DOSS and ^{2}H-labeled DOSS standards. The optimized mass spectrometer settings are as follows: sheath gas (N_2) flow rate 35 (arbitrary units), spray voltage 4 kV, capillary temperature 270 °C, capillary voltage −69 V, tube lens voltage −112 V. Detection of DOSS was based on the observation of a peak at m/z 421 at a retention time of 6 min with the concomitant observation of MS/MS fragments at m/z 227

and 291, generated by collision induced dissociation (CID) with helium gas. Quantification of DOSS was conducted with the extracted ion chromatogram for m/z 421, via a 7-point standard curve and normalization for the injection standard. The lowest concentration measured in our method is 0.003 μg L^{-1}, assuming a concentration factor of 400 during extraction. The detection limit could be lowered further if the extracted sample volume was increased. We confirmed our low concentrations by analyzing two large-volume (~7 L) samples collected in October 2010 (cast 283, cast 284, Table 2). A representative LC/MS spectrum is provided in Figure S2. Due to the variability in sample storage time period between collection and extraction, we used the ^{13}C-DOSS to confirm that no large losses occurred during extraction but did not use it to correct our DOSS concentrations.

Selected samples were also examined with ultrahigh resolution mass spectrometry. In these cases, aliquots of sample were infused into the electrospray ionization (ESI) interface of a 7T LTQ-Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer (LTQ FT-Ultra, Thermo Scientific, MA). Samples were analyzed in negative electrospray ionization mode at 400,000 resolving power (defined at m/z 400). Approximately 200 scans (i.e., transients) were collected per sample. The transients were summed, processed and Fourier-transformed according to previously published protocols.[7] The mass spectrometer was calibrated weekly with an external standard (CalMix, Thermo Scientific), and individual summed spectra were recalibrated internally according to a series of ions differing by $-CH_2$ groups.[8] This method was used to characterize field samples and 1 mg mL^{-1} aqueous solutions of Corexit 9500A and 9527. CID fragmentation of putative DOSS peaks (m/z 421.2263) in Corexit standards and field samples was conducted in the ion-trap with normalized collision energy of 19%. Representative MS/MS spectra are provided in Figure S3.

Percent Recovery Experiments. We conducted three percent recovery experiments to assess our ability to recover DOSS from seawater samples. We tested the recoveries of 1(twice) and 10 μg L^{-1} DOSS from seawater; no oil was added to this matrix. The critical micelle concentration (CMC) of DOSS is approximately 177 mg L^{-1} (estimated from data in Chatterjee et al.,[9] see the Supporting Information); thus none of our experiments should contain micelles. In general, we could recover 30−40% of added DOSS in the aqueous phase with an additional 40% recovered from the bottle rinse. Thus up to half of the DOSS added in our control experiments adhered to the Teflon or glass bottle walls. We conclude that the bottle rinse is an essential part of quantification of DOSS, particularly if samples are refrigerated where wall absorption can continue during storage. The surface-activity of this compound was evident in the fact that samples, or extracts, could not be stored in liquid form (aqueous or organic) for longer than a week without significant (>50%) loss to the container walls. Dilute Corexit solutions (≤10 mg mL^{-1}) also showed this loss behavior. All DOSS standard solutions must be remade from the solid form every week. As a result, we caution against the use of our extraction protocol on filtered samples due to the likely adsorptive loss of DOSS to filter pores. In our first round of extractions, we lost considerable DOSS to the vial walls during storage between extraction and analysis. We recommend that samples requiring storage be stored dry in the freezer and then reconstituted within a day or two of the anticipated analysis.

RESULTS AND DISCUSSION

We first detected DOSS in field samples as a peak at m/z 421.2265 (calculated exact mass of negative ion is 421.2263 amu)

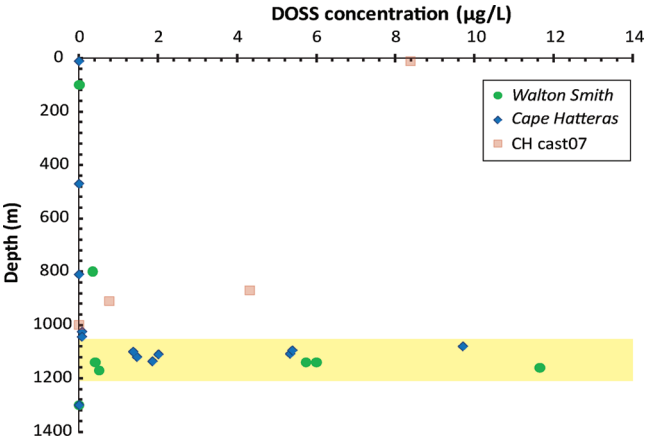

Figure 1. Composite depth profile of DOSS concentrations observed in May/June 2010 samples from R/V *F. G. Walton Smith* (May/June, green circles) and from R/V *Cape Hatteras* (June, blue diamonds). One cast from the R/V *Cape Hatteras* (CH cast 07) is highlighted in red squares to show that it is very different from all other casts. The yellow box denotes the region of high CDOM and high methane concentrations observed by other investigations.[11,12].

in FT-MS spectra of PPL extracts of the DCM-extracted aqueous layer (Figure S3A). We confirmed the identity of DOSS in two ways. First, we observed peaks consistent with three isotopomers of DOSS (calculated exact masses: $^{13}C_1$-DOSS = 422.2296 amu, $^{34}S_1$-DOSS = 423.2221 amu, and $^{13}C_2$-DOSS = 423.2330 amu), at the same relative intensities as in Corexit 9527. Second, we compared MS/MS spectra of the m/z 421 peak in Corexit 9500A with the same peak in our field samples (Figure S3B). In both instances, characteristic fragment ions were observed at m/z 227 and 291. We did not observe the fragment ion associated with loss of the sulfo-group (m/z 81) due to the lower mass limit of collision-induced dissociation in the ion-trap mass spectrometer. Comparison to an internal database of mass spectra including northern Atlantic Ocean [10] and mid-Pacific Ocean waters failed to yield a matching molecule. This database does not contain data from the Gulf of Mexico prior to the oil spill. Nevertheless, the absence of this molecule in many of our Gulf samples excludes the possibility of pervasive DOSS contamination of the Gulf of Mexico from pre-spill anthropogenic activity and/or the Mississippi River. We conclude that DOSS is specific to samples collected from this oil spill.

We first assessed DOSS concentrations during oil flow near the wellhead in May/June 2010. Here, DOSS concentrations ranged between 0 (nondetectable) and 12 μg L^{-1}. These concentrations are substantially lower than the critical micelle concentration of DOSS, implying that all the DOSS was fully dissolved in the water phase. We analyzed many fewer samples from the surface ocean than from the deepwater. As a result, we are not able to constrain surface DOSS concentrations to a great extent. Nevertheless, only one sample from the near-surface (CH, Cast 7, 10 m; Figure 1) had an appreciable DOSS concentration, which we attribute to surface dispersant application in close proximity (1.2 km) to the wellhead, or to aberrant behavior associated with an errant injection at the wellhead (see below). We attribute the lack of DOSS in the other two surface (<100 m) samples to (a) longer distances from the well head, (b) lack of a recent surface application, and/or (c) lack of vertical mixing below the first few meters of the sea surface. The bulk of elevated DOSS concentrations occurred in waters between 1000 and 1200 m

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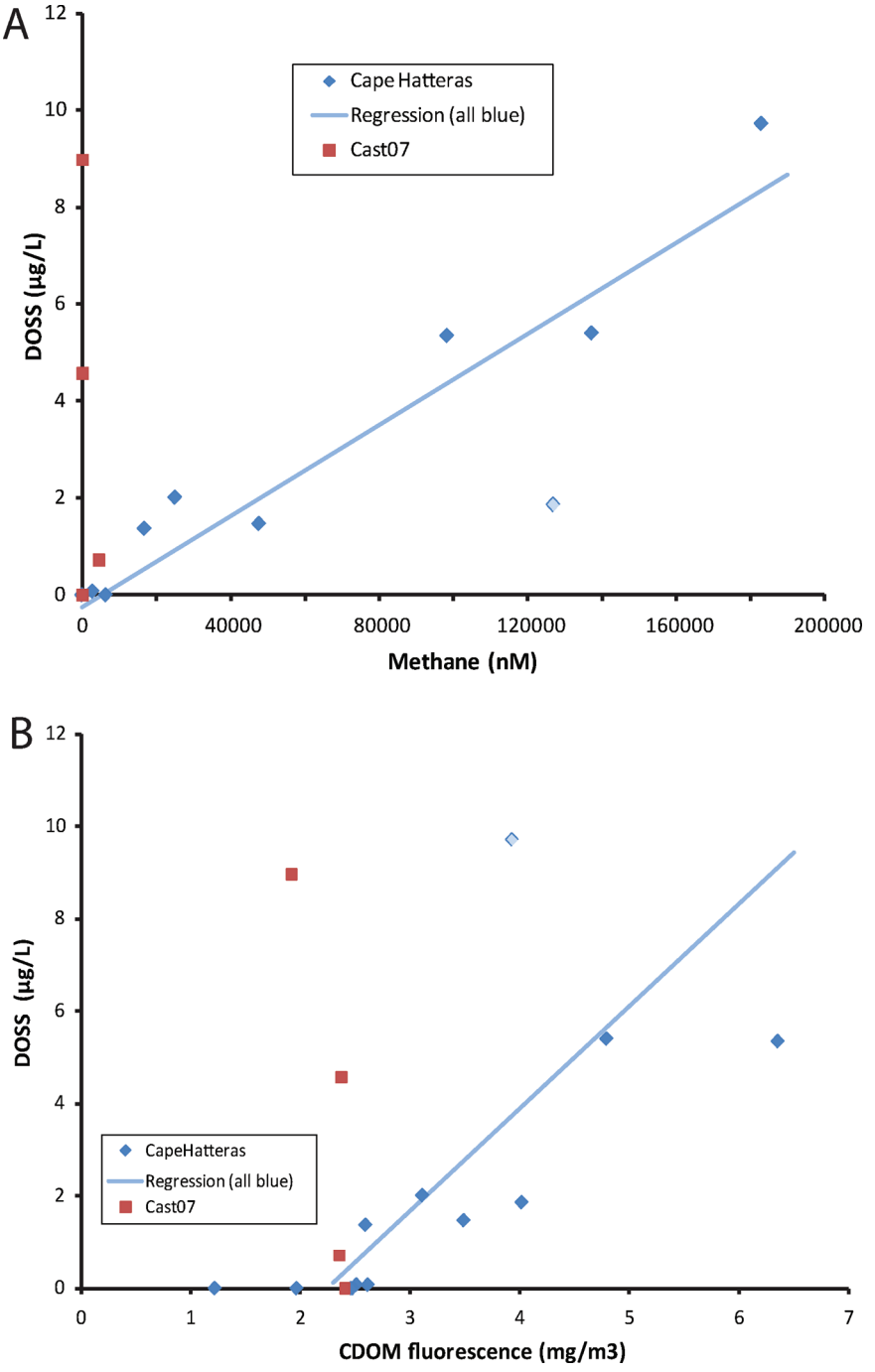

Figure 2. (A) Correlation between methane and DOSS concentrations in samples from June 2010 (R/V *Cape Hatteras*). Samples from the CH07 cast are shown in red squares and were not included in regression analysis. A Model II regression line was calculated for all data (solid line) and its equation is $[DOSS] = ((4.7 \pm 0.7) \times 10^{-5})\,[CH_4] - (0.3 \pm 0.6)$, $r^2 = 0.80$. (B) Correlation between CDOM fluorescence and DOSS concentrations in the same samples. CH cast 07 samples were treated as in (A). A Model II regression line was calculated for all data (solid line) and its equation is $[DOSS] = (2.2 \pm 0.5)\,[CDOM] - (5.0 \pm 1.8)$, $r^2 = 0.49$.

depth (Figure 1, Table 1). These elevated concentrations coincided with the depth horizon of increased fluorescence signals[11] and of increased methane concentrations, measured by *in situ* mass spectrometry[12] and by on-shipboard analysis.[11] This depth horizon has been referred to as the deepwater plume of hydrocarbons and gas emanating from this oil spill. It likely represents an intrusion of fluid and fine oil droplets that detrained from the buoyant oil and gas jet above the Deepwater Horizon oil spill and traveled laterally as a result of density stratification and currents in the deep Gulf of Mexico.[13,14]

Dispersant was applied at the sea-surface and at the wellhead (1500 m) during the oil spill. DOSS was present in both Corexit 9527 and 9500A, at 17% and 10% by weight, respectively, based on our LC/MS method. Nonetheless, our data suggest that the two applications did not substantially intermingle throughout the water column. Instead, the deepwater application appears to

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have been restricted to the depth horizons where previous investigators found significant oil signatures.[11,12] Recent data from the Operational Science Advisory Team (OSAT) at the Unified Area Command indicate that another component of the dispersant, the solvent dipropylene glycol n-butyl ether, DPnB, was also enhanced in this depth horizon.[3] This suggests that the dispersant traveled into this 1000−1200 m depth horizon and was not transported further toward the surface. This is consistent with the intended role of the dispersant to form very small liquid oil droplets that are retained in deep water, although dissolution with subsequent vertical transport as well as partitioning with other phases such as gas or hydrate cannot be fully excluded.

One cast (R/V *Cape Hatteras* Cast 07, Figure 1) consistently shows different behavior than the other casts during May and June. In particular, DOSS is not associated with peaks in fluorescence or methane concentration but instead occurs at higher concentrations at shallower depths. We attribute this unique profile to a possible errant injection of dispersant, away from the primary flow of gas and oil from the wellhead. In that case, simple dissolution of DOSS and other dispersant components during ascent would govern the DOSS profile, rather than association with the hydrocarbon flow. Given the unique nature of this profile, we have excluded these data from our interpretations below, but we include the data in figures for reference.

To assess the extent to which DOSS was trapped in deep water, we compared the observed DOSS concentrations to the concurrent methane concentration in samples from June 2010 (Figure 2A). We chose methane because it was effectively dissolved in the water column[15] and did not travel appreciably to the surface,[11] because the flux can be estimated,[11,16] and because it was not markedly affected by degradation at this point in the spill.[11] The DOSS and methane concentrations are correlated (Model II regression; $R^2 = 0.80$; $n = 11$; Figure 2A), suggesting that these two compounds were released concurrently in these waters. By scaling the DOSS to methane ratio by the methane flux rate from the well head ($\sim 1.1 \times 10^8$ mol d^{-1} [16] $- 1.5 \times 10^8$ mol d^{-1} [11]), we calculate a DOSS release rate of 5200−7100 kg day^{-1}. Given the highly approximate assumptions involved, this range is remarkably close to the average reported release rate (4800 kg day^{-1}; range 1300−8100 kg day^{-1}, see below). Since most methane was trapped at depth,[11] these calculations indicate that DOSS released at the wellhead became trapped in the deepwater hydrocarbon and gas plume.

The nearly 1:1 correlation between DOSS and methane as well as the consistency between their release rates indicates that DOSS was not biodegraded or otherwise lost in the vicinity of the well head during conditions of active flow, as methane was shown to act conservatively under these conditions.[11] DOSS concentration also correlated with CDOM values (Model II regression; $R^2 = 0.49$, $n = 14$; Figure 2B), with dilution being the most obvious factor driving covariance in all three parameters. Our interpretation of these observations is that neither DOSS nor methane was substantially affected by biodegradation close to the wellhead and instead was transported conservatively by deep water currents.

To evaluate our hypothesis of conservative transport, we compared our observed DOSS concentrations with those expected from recorded Corexit applications. Based on our analysis of DOSS in Corexit 9500A, we calculate that the average DOSS application was 4800 kg per day, given a Corexit 9500A daily application of approximately 12,500 gallons (see the Supporting Information). In the deep ocean, this means that over 290,000 kg of DOSS were released to surrounding waters over the spill period. In order to estimate an expected DOSS concentration in our samples, we hypothesized a theoretical water parcel within which Corexit might have been fully mixed with oil (details in the Supporting Information). The average DOSS concentration in this parcel after one hour of DOSS application at the average rate would be 7 $\mu g\ L^{-1}$. The total volume of Corexit 9500A applied each day varied widely (3400−21,100 gallons), so the expected concentrations of DOSS in subsurface water likely vary between 2 and 12 $\mu g\ L^{-1}$. This calculation does not consider higher frequency variability, and it assumes that all the DOSS (and dispersant) moved into our defined plume. However, even with these assumptions, measured concentrations (range: 0.4−12 $\mu g\ L^{-1}$) are remarkably similar to the expected concentrations, suggesting that the dispersant was moving conservatively into the plume near the wellhead and was not appreciably degraded or lost during active flow.

After flow of oil from the well ceased in July, we measured DOSS concentrations in samples near- and far-field from the Deepwater Horizon oil spill site (September samples). We found that DOSS concentrations had markedly decreased at all sampled sites and DOSS was undetectable in the plume samples located furthest from the spill site (Figure 3). We estimated the loss of DOSS due to latitudinal turbulent mixing (perpendicular to the center line of the plume), using the approach outlined in Schwarzenbach et al. [17] (see the Supporting Information). If we assume that the initial concentration of DOSS at the wellhead was 7 $\mu g\ L^{-1}$ and that it would take 45 days for a water parcel to travel 300 km (at an average current velocity of 7.8 cm s^{-1} [12]), then the concentration after this time and distance should be approximately 0.04 $\mu g\ L^{-1}$. For 500 km distance (74 days), we find that the expected concentration is 0.01 $\mu g\ L^{-1}$. With the anticipated variability in DOSS application rate, concentrations at this distance could range between 0.001 and 0.02 $\mu g\ L^{-1}$. These values are within an order of magnitude of our current detection limit of 0.003 $\mu g\ L^{-1}$. However, closer to the well head, turbulent mixing would not have diluted the DOSS to such an extent, and indeed, we calculated expected concentrations of 0.08 $\mu g\ L^{-1}$ in the 100 km range (range: 0.005−0.14 $\mu g\ L^{-1}$) and 1.2 $\mu g\ L^{-1}$ in the 10 km range (range: 0.07−2.1 $\mu g\ L^{-1}$). In comparison, our DOSS concentrations in September ranged from 0 (undetectable) to 0.07 $\mu g\ L^{-1}$, approximately 2−3 orders of magnitude lower than in May and June. These data are within the anticipated range of DOSS concentrations after conservative transport and highlight the persistence of DOSS in the deep water column, up to 64 days and 300 km after the dispersant applications ceased on July 12, 2010.

It is possible that biodegradation or sedimentation is also contributing to the decrease of DOSS concentration in these water masses. However, observed concentrations are similar to those predicted for a given distance, and so we conclude that the primary process acting to alter DOSS concentration is dilution. Previous studies in freshwater environments have given conflicting results for biodegradation of DOSS in aqueous solution.[18,19] Given the variability in DOSS release rates at the wellhead, biodegradation rates would have to exceed the dilution rate by $\sim 10\times$ in order for the impact of biodegradation to be observed in our data sets. Since our data fall within $10\times$ of the expected concentrations, our results do not support a significant component of biodegradation in DOSS fate in the Gulf of Mexico. We cannot test our hypothesis further because there are no conservative oil, gas, or dispersant molecules identified at this time (to our knowledge) with which we can normalize our DOSS

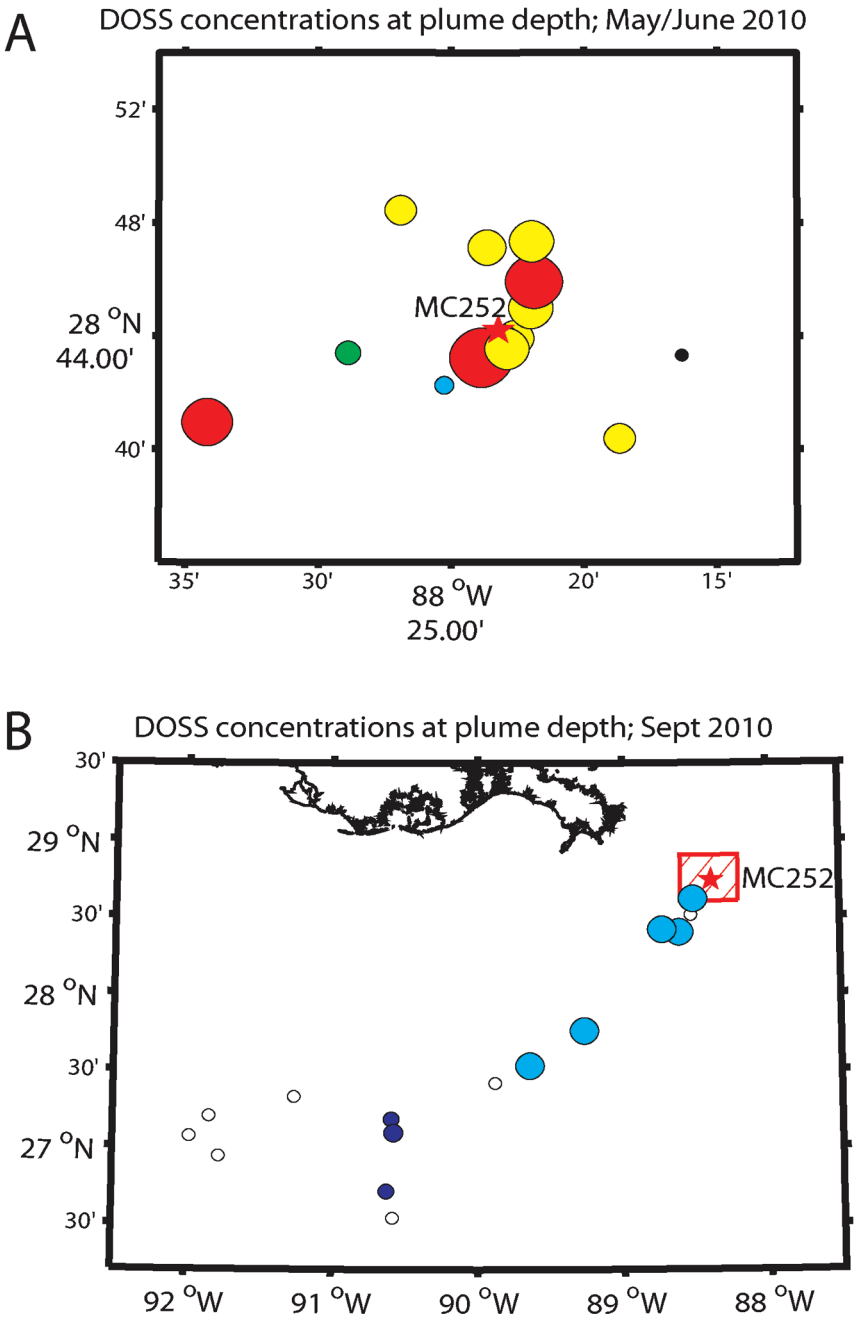

Figure 3. Map view of DOSS concentrations at plume depth (~1000−1200 m) in May/June (**A**) and in September (**B**) 2010. Color and size of dots indicate concentration magnitude in each plot. White = below detection; blue = <0.01 μg L^{-1}; cyan = 0.011−0.1 μg L^{-1}; green = 0.11−1.0 μg L^{-1}; yellow = 1.0−9.0 μg L^{-1}; red = >9.1 μg L^{-1}. Black indicates samples taken at this location but not in plume depth horizon. The Deepwater Horizon oil spill site (MC-252) is denoted with a red star in both plots. The red hatched box in (B) denotes the subregion represented by (A).

concentrations. Methane, as used above, is biologically available to methanotrophs in these waters, and the elapsed time is sufficient for methane oxidation to have occurred.[16] Fluorescent signals are increasingly difficult to distinguish from the background as oil degrades and its bulk fluorescent properties change. In addition, these signals measure a bulk property rather than individual molecules and mask many molecular-level changes that may be occurring during transport. Work is underway in our laboratories to assess the composition (and concentration) of petroleum components remaining in these samples after >2 months of biodegradation.[20]

Based on our observations, we cannot assess whether the dispersant application was successful in reducing the oil droplet size or in increasing the sequestration of oil in deep water. However, we can conclude that DOSS, and presumably the other Corexit components, became sequestered in deep plumes. Two or more possibilities may explain these observations. In one scenario, DOSS dissolved into the water during ascent and detrained at approximately 1100 m through partitioning with methane, water, gas hydrate, or other phases. In this case, if the DOSS dissolved completely or partitioned with natural gas, it

may suggest that the dispersant was rendered unavailable to the oil and thus ineffective in dispersing the liquid oil. In a second scenario, Corexit was associated with small liquid oil droplets that were sequestered in this plume.[21] If the DOSS was deposited in these small oil droplets, it may suggest that the chemical dispersion was highly effective. We have rejected the hypothesis that DOSS was associated with large oil droplets since their higher buoyancy would be expected to force them to travel to the surface,[21] presumably releasing dispersant en route.[2] This effect is not evident in our data (except perhaps in the case of Cast 07 from the R/V *Cape Hatteras*). Chemical measurements of liquid oil components at different depths as well as modeling studies of mixed-phase flow will be needed to distinguish between our two hypotheses for DOSS sequestration in the deepwater plume.

Our calculations of dispersant concentrations near the wellhead (or in the deepwater plume) indicate that deepwater, or pelagic, biota traveling through the deepwater plume likely encountered 1−10 μg L^{-1} DOSS or 10−100 μg L^{-1} Corexit, between ∼1 and 10 km from the actively flowing wellhead, with concentration decreasing with distance. The dispersant was applied at an effective dispersant-to-oil ratio of 0.05%, based on published volume estimates for the spill,[22] but ratios were likely ∼10× higher in the plume itself, based on volume estimates for the southwestern plume.[12] Regardless, these concentrations and dispersant-to-oil ratios are lower than those tested in published toxicology assays.[2,18,23] Nevertheless, further tests are needed to assess stress responses of pelagic biota to oil, gas, dispersant, and associated mixtures. In particular, our study has not assessed the fates or reactivities of the nonionic surfactants and the hydrocarbon solvents present in Corexit 9500A, each of which may have unique toxicological impacts. In short, the application of this material in the deep ocean is new and unprecedented and so merits further study of pelagic macro- and microbiota at environmentally relevant Corexit concentrations and dispersant-to-oil ratios.

■ ASSOCIATED CONTENT

Supporting Information. We include the calculations referred to above and ancillary mass spectral and dispersant application data for our study period (May 25, 2010−June 21, 2010). This material is available free of charge via the Internet at http://pubs.acs.org.

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