1   # Fate of Dispersants Associated with the Deepwater Horizon Oil Spill

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21 **ABSTRACT**

22 Response actions to the Deepwater Horizon oil spill included the injection of ~771,000 gallons

23 (2,900,000 L) of chemical dispersant into the flow of oil near the seafloor. Prior to this incident,

24 no deepwater applications of dispersant had been conducted and thus no data exists on the

25 environmental fate of dispersants in deepwater. We used ultrahigh resolution mass

26 spectrometry and liquid chromatography with tandem mass spectrometry (LC/MS/MS) to

27 identify and quantify one key ingredient of the dispersant, the anionic surfactant DOSS (dioctyl

28 sodium sulfosuccinate), in the Gulf of Mexico deepwater during active flow and again after

29 flow had ceased. Here we show that DOSS was sequestered in deepwater hydrocarbon plumes

30 at 1000-1200m water depth and did not intermingle with surface dispersant applications.

31 Further, its concentration distribution was consistent with conservative transport and dilution

32 at depth and it persisted up to 300 km from the well, 64 days after deepwater dispersant

33 applications ceased. We conclude that DOSS was selectively associated with the oil and gas

34 phases in the deepwater plume, yet underwent negligible, or slow, rates of biodegradation in

35 the affected waters. These results provide important constraints on accurate modeling of the

36 deepwater plume and critical geochemical contexts for future toxicological studies.

37

39 **INTRODUCTION**

40 Approximately 2.1 million gallons of dispersant were applied to the surface (1.4 M gallons) and

41 wellhead (0.77 M gallons) during the Deepwater Horizon oil spill between May 15 and July 12

42 2010 [1]. In both modes, dispersant was added to lower the interfacial tension between oil and

43 water and thereby reduce the size of oil droplets formed by wave action (surface) or by ejection

44 of oil and gas out of the wellhead (deepwater). On the seawater surface, application of

45 dispersants can inhibit the formation of large emulsions or slicks that can coat and harm

46 sensitive coastal environments. Following the addition of a dispersant, oil mixes below the

47 seawater surface and can be degraded or dissolved into the water column [2]. Many

48 investigations have been conducted on the use of dispersants on surface oil spills and they have

49 cautiously concluded that dispersants are successful in mitigating coastal impacts, when

50 applied under the appropriate conditions [2]. No large-scale applications of dispersants in deep

51 water had been attempted prior to the Deepwater Horizon oil spill and thus no data exists on

52 the fate of dispersant components released in the deep subsurface.

53 Dispersants are a mixture of surfactants and hydrocarbon-based solvents. Two dispersants were

54 used extensively in the Deepwater Horizon oil spill: Corexit 9527 (surface applications only)

55 and Corexit 9500A (both surface and wellhead). The anionic surfactant, dioctyl sodium

56 sulfosuccinate (DOSS), is a component of both Corexit formulations and is used here as a tracer

57 of the polar components of Corexit 9527 and 9500 in seawater. Other molecules should be

58 studied in future investigations to assess the fate of the non-polar surfactants and solvents of

59 the two Corexit formulations (see recent US government report [3]). At depth, Corexit 9500A

60 was applied by a jet placed into the oil and gas flow ejected from the wellhead. Due to

61 variability in well operations, the jet was not always applying Corexit nor was it always

62 inserted into the oil and gas flow. However, when the Corexit jet and the oil and gas flow were

63 co-located, Corexit was presumably mixed evenly into the oil as it ascended the water column.

64 On the sea surface, dispersants were applied aerially and by small vessels. Corexit was applied

65   to the ocean surface according to oil and weather conditions, likely resulting in spatial and

66   temporal heterogeneity in Corexit surface water concentrations.

67   Here we examined DOSS concentrations in water column samples collected from the Gulf of

68   Mexico during and after active flow of oil and gas from the Deepwater Horizon oil spill. We

69   compared DOSS concentrations to tracers of oil and gas in the deepwater in order to assess the

70   ability of this molecule to act as a tracer of oil released during this incident. In addition, we

71   compared our observations to theoretical DOSS concentrations (calculated from release data

72   and environmental parameters) to infer the impact of biodegradation and other loss processes

73   on DOSS in the marine environment.

74   **EXPERIMENTAL**

75   We collected water samples throughout the water column on three research cruises in the Gulf

76   of Mexico in May, June and September 2010 (Tables 1 and 2). In June (R/V *Cape Hatteras*), the

77   ocean surface was sprayed with a 1:1 solution of Dawn™ if surface oil was present during

78   deployment and recovery. Between deployments, Niskin bottles were washed with freshwater

79   and then treated with the Dawn solution if contamination was a concern. In September (NOAA

80   Ship *Pisces*), no contamination was evident on the sea surface and Niskin bottles were not

81   cleaned between deployments. Water was transferred from Niskin bottles directly into clean

82   Teflon or combusted glass bottles. Bottles were rinsed three times with sample water, filled, and

83   stored frozen until extraction. All organic solvents were Optima grade or better (Fisher

84   Scientific, MA). All glassware was combusted at 450°C for at least 4 hours, or solvent-rinsed

85   sequentially with methanol, acetone, methylene chloride and hexane.

86   *Extractions*

87   We extracted our samples two ways. In the first round, we extracted three fractions for each

88   sample in order to selectively analyze different polarity components of oil and dispersants.

89   During sample analysis, we determined that DOSS could be removed by solid-phase extraction

90   alone and thus we used that technique as our sole method in the second round of samples.

91 In the first round, we extracted 500 mL seawater three times with 100 mL of methylene chloride

92 to remove the basic and neutral components of the oil and dispersants. We then acidified the

93 aqueous layer to pH 3 with concentrated hydrochloric acid (Trace Metal Grade, Fisher

94 Scientific) and re-extracted three times with methylene chloride [4] to remove the acidic

95 components. Methylene chloride extracts were combined after each round of three extractions

96 and dried with combusted anhydrous sodium sulfate. Solvent was removed by rotary

97 evaporation and samples were reconstituted in methylene chloride, transferred to an amber

98 vial, dried under a gentle stream of ultrahigh purity nitrogen and stored frozen until analysis.

99 To remove any remaining water-soluble components of oil and dispersants, the aqueous layer

100 was then extracted with a solid phase resin made of modified styrene divinyl benzene polymer

101 (PPL), according to published protocols [5]. In parallel, we also extracted 400 mL of the samples

102 with only the PPL resin. Extracts from both resin treatments were eluted with 1 mL methanol

103 and stored in a combusted amber glass vial at -20°C until analysis. We then rinsed the original

104 sample bottle with methanol. All bottle rinses were dried down under N_2 gas and were

105 reconstituted in 50/50 acetonitrile/water prior to analysis. At the end of our protocol, we had

106 four extracts per sample: (1) DCM extract #1, (2) DCM extract #2, (3) PPL extract of DCM

107 aqueous layer, and (4) PPL extract of initial water sample.

108 Samples in extraction Round 1 were analyzed at the first opportunity, but some extracts were

109 stored >20 days in the freezer. For Round 1 samples, the reported DOSS concentration is the

110 sum of concentrations in the DCM extract #1, the PPL extract of the DCM aqueous layer and the

111 bottle rinse (where available). No DOSS was ever found in DCM extract #2 and so it was not

112 included in the final concentration. Prolonged storage proved to be detrimental to DOSS

113 quantification through excessive losses to vial walls (identified from decreases in DOSS

114 concentrations between repeat analyses; see below). Thus, we re-extracted all available samples

115 with the PPL resin only. For these Round 2 samples, the reported DOSS concentration is the

116 sum of concentrations in the PPL extract and the bottle rinse. DOSS concentrations in samples

117 that could not be re-extracted were estimated from a relationship derived between old (Round

118 1) and new (Round 2) extracts of the same sample (Figure S1). A Model II regression with a

119   reduced axis [6] was used to estimate these relationships, using Matlab code written by E.

120   Peltzer (MBARI; http://www.mbari.org/staff/etp3/regress.htm). Model II regressions are used

121   for correlations between two variables that both contain inherent error. The relationship

122   between the original DCM extracts and the PPL re-extracts was used to correct original DCM

123   extracts from the R/V *F. G. Walton Smith* cruise, conducted in May 2010. Concentrations

124   estimated by this method are denoted with a (*) in Table 1.

125   Samples collected in September (NOAA Ship *Pisces*) were extracted with PPL resin only and

126   analyzed immediately. Here, we also added $^{13}C_4$-labeled DOSS as a recovery standard prior to

127   extraction. These samples were analyzed within 3-4 days of extraction to minimize losses

128   associated with storage.

129   *Chromatography and Mass Spectrometry*

130   All extracts were analyzed with liquid chromatography coupled to a linear ion-trap mass

131   spectrometer (LTQ XL, Thermo Scientific). Extracts were amended with 60 pg μL^{-1} (ppb) of

132   universally-labeled ^{2}H-DOSS as an injection standard to correct for matrix effects. 25 μL of

133   sample was injected onto a 2.1 x 150 mm, 3 μm Atlantis T3 column (Waters Corp., Milford MA)

134   and the injection loop was washed extensively with 2 mL of 60/40 acetonitrile/ isopropanol to

135   reduce sample carry-over. The solvent flow rate was 300 μL min^{-1} and the gradient program

136   was: 50% solvent A hold for 2 min (during which the column eluent was diverted to waste);

137   followed by a 3-min gradient to 100% solvent B; hold at 100% B for 4 min; equilibrate at 50% A

138   for 5 min. Solvent A was 95/5 water/acetonitrile with 4 mM ammonium acetate and solvent B

139   was 95/5 acetonitrile/water with 4 mM ammonium acetate. The autosampler and column

140   temperatures were held at 15 °C and 35 °C, respectively. The column eluent was infused into

141   the LTQ-MS under negative electrospray ionization mode. Instrument optimization (tuning)

142   was done by infusing a mixture of DOSS and ^{2}H-labeled DOSS standards. The optimized mass

143   spectrometer settings are as follows: sheath gas (N_2) flow rate 35 (arbitrary units), spray voltage

144   4 kV, capillary temperature 270 °C, capillary voltage –69 V, tube lens voltage –112 V. Detection

145   of DOSS was based on the observation of a peak at *m*/*z* 421 at a retention time of 6 min with the

146   concomitant observation of MS/MS fragments at *m*/*z* 227 and 291, generated by collision

147   induced dissociation (CID) with helium gas. Quantification of DOSS was conducted with the

148   extracted ion chromatogram for *m*/z 421, via a 7-point standard curve and normalization for the

149   injection standard. The lowest concentration measured in our method is 0.003 μg L^{-1}, assuming

150   a concentration factor of 400 during extraction. The detection limit could be lowered further if

151   the extracted sample volume was increased. We confirmed our low concentrations by analyzing

152   two large-volume (~7L) samples collected in October 2010 (cast 283, cast 284, Table 2). A

153   representative LC/MS spectrum is provided in Figure S2. Due to the variability in sample

154   storage time period between collection and extraction, we used the ^{13}C-DOSS to confirm that no

155   large losses occurred during extraction but did not use it to correct our DOSS concentrations.

156   Selected samples were also examined with ultrahigh resolution mass spectrometry. In these

157   cases, aliquots of sample were infused into the electrospray ionization (ESI) interface of a 7T

158   LTQ-Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer (LTQ FT-Ultra,

159   Thermo Scientific, MA). Samples were analyzed in negative electrospray ionization mode at

160   400,000 resolving power (defined at *m*/z 400). Approximately 200 scans (i.e., transients) were

161   collected per sample. The transients were summed, processed and Fourier-transformed

162   according to previously published protocols [7]. The mass spectrometer was calibrated weekly

163   with an external standard (CalMix, Thermo Scientific) and individual summed spectra were re-

164   calibrated internally according to a series of ions differing by –CH$_2$ groups [8]. This method was

165   used to characterize field samples and 1 mg mL^{-1} aqueous solutions of Corexit 9500A and 9527.

166   CID fragmentation of putative DOSS peaks (*m*/z 421.2263) in Corexit standards and field

167   samples was conducted in the ion-trap with normalized collision energy of 19%. Representative

168   MS/MS spectra are provided in Figure S3.

169   *Percent recovery experiments*

170   We conducted three percent recovery experiments to assess our ability to recover DOSS from

171   seawater samples. We tested the recoveries of 1(twice) and 10 μg L^{-1} DOSS from seawater; no oil

172   was added to this matrix. The critical micelle concentration (CMC) of DOSS is approximately

173   177 mg L^{-1} (estimated from data in Chatterjee et al. [9], see Supplementary Information); thus

174   none of our experiments should contain micelles. In general, we could recover 30-40% of added

175   DOSS in the aqueous phase with an additional 40% recovered from the bottle rinse. Thus up to

176   half of the DOSS added in our control experiments adhered to the Teflon bottle walls. We

177   conclude that the bottle rinse is an essential part of quantification of DOSS, particularly if

178   samples are refrigerated where wall absorption can continue during storage. The surface-

179   activity of this compound was evident in the fact that samples, or extracts, could not be stored

180   in liquid form (aqueous or organic) for longer than a week without significant ($\geq$50%) loss to the

181   container walls. Dilute Corexit solutions (<10 mg mL^{-1}) also showed this loss behavior. All

182   DOSS standard solutions must be remade from the solid form every week. As a result, we

183   caution against the use of our extraction protocol on filtered samples due to the likely

184   adsorptive loss of DOSS to filter pores. In our first round of extractions, we lost considerable

185   DOSS to the vial walls during storage between extraction and analysis. We recommend that

186   samples requiring storage be stored dry in the freezer and then reconstituted within a day or

187   two of the anticipated analysis.

188   **RESULTS AND DISCUSSION**

189   We first detected DOSS in field samples as a peak at m/z 421.2265 (calculated exact mass of

190   negative ion is 421.2263 amu) in FT-MS spectra of PPL extracts of the DCM-extracted aqueous

191   layer (Figure S3A). We confirmed the identity of DOSS in two ways. First, we observed peaks

192   consistent with three isotopomers of DOSS (calculated exact masses: $^{13}C_1$-DOSS = 422.2296 amu,

193    $^{34}S_1$-DOSS = 423.2221 amu, and $^{13}C_2$-DOSS = 423.2330 amu), at the same relative intensities as in

194   Corexit 9527. Second, we compared MS/MS spectra of the m/z 421 peak in Corexit 9500A with

195   the same peak in our field samples (Figure S3B). In both instances, characteristic fragment ions

196   were observed at m/z 227 and 291. We did not observe the fragment ion associated with loss of

197   the sulfo- group (m/z 81) due to the lower mass limit of collision-induced dissociation in the ion-

198   trap mass spectrometer. Comparison to an internal database of mass spectra including northern

199   Atlantic Ocean [10] and mid-Pacific Ocean waters failed to yield a matching molecule. This

200   database does not contain data from the Gulf of Mexico prior to the oil spill. Nevertheless, the

201   absence of this molecule in many of our Gulf samples excludes the possibility of pervasive

202   DOSS contamination of the Gulf of Mexico from pre-spill anthropogenic activity and/or the

203   Mississippi River. We conclude that DOSS is specific to samples collected from this oil spill.

204   We first assessed DOSS concentrations during oil flow near the wellhead in May/June 2010.

205   Here, DOSS concentrations ranged between 0 (non-detectable) and 12 µg L^{-1}. These

206   concentrations are substantially lower than the critical micelle concentration of DOSS, implying

207   that all the DOSS was fully dissolved in the water phase. We analyzed many fewer samples

208   from the surface ocean than from the deepwater. As a result, we are not able to constrain

209   surface DOSS concentrations to a great extent. Nevertheless, only one sample from the near-

210   surface (CH, Cast 7, 10m; Figure 1) had an appreciable DOSS concentration, which we attribute

211   to surface dispersant application in close proximity (1.2 km) to the wellhead, or to aberrant

212   behavior associated with an errant injection at the wellhead (see below). We attribute the lack

213   of DOSS in the other two surface (<100 m) samples to (a) longer distances from the well head,

214   (b) lack of a recent surface application and/or (c) lack of vertical mixing below the first few

215   meters of the sea surface. The bulk of elevated DOSS concentrations occurred in waters between

216   1000 and 1200 m depth (Figure 1, Table 1). These elevated concentrations coincided with the

217   depth horizon of increased fluorescence signals [11] and of increased methane concentrations,

218   measured by *in situ* mass spectrometry [12] and by on-shipboard analysis [11]. This depth

219   horizon has been referred to as the deepwater plume of hydrocarbons and gas emanating from

220   this oil spill. It likely represents an intrusion of fluid and fine oil droplets that detrained from

221   the buoyant oil and gas jet above the Deepwater Horizon oil spill and traveled laterally as a

222   result of density stratification and currents in the deep Gulf of Mexico [13, 14].

223   Dispersant was applied at the sea-surface and at the wellhead (1500 m) during the oil spill.

224   DOSS was present in both Corexit 9527 and Corexit 9500A, at 17% and 10% by weight,

225   respectively, based on our LC/MS method. Nonetheless, our data suggest that the two

226   applications did not substantially intermingle throughout the water column. Instead, the

227   deepwater application appears to have been restricted to the depth horizons where previous

228   investigators found significant oil signatures [11, 12]. Recent data from the Operational Science

229   Advisory Team (OSAT) at the Unified Area Command indicate that another component of the

230   dispersant, the solvent dipropylene glycol n-butyl ether, DPnB, was also enhanced in this depth

231   horizon [3]. This suggests that the dispersant traveled into this 1000-1200m depth horizon and

232   was not transported further towards the surface. This is consistent with the intended role of the

233   dispersant to form very small liquid oil droplets that are retained in deep water, although

234   dissolution with subsequent vertical transport as well as partitioning with other phases such as

235   gas or hydrate cannot be fully excluded.

236   One cast (R/V *Cape Hatteras* Cast 07, Figure 1) consistently shows different behavior than the

237   other casts during May and June. In particular, DOSS is not associated with peaks in florescence

238   or methane concentration, but instead occurs at higher concentrations at shallower depths. We

239   attribute this unique profile to a possible errant injection of dispersant, away from the primary

240   flow of gas and oil from the wellhead. In that case, simple dissolution of DOSS and other

241   dispersant components during ascent would govern the DOSS profile, rather than association

242   with the hydrocarbon flow. Given the unique nature of this profile, we have excluded these

243   data from our interpretations below but we include the data in figures for reference.

244   To assess the extent to which DOSS was trapped in deep water, we compared the observed

245   DOSS concentrations to the concurrent methane concentration in samples from June 2010

246   (Figure 2A). We chose methane because it was effectively dissolved in the water column [15]

247   and did not travel appreciably to the surface [11], because the flux can be estimated [11, 16], and

248   because it was not markedly affected by degradation at this point in the spill [11]. The DOSS

249   and methane concentrations are correlated (Model II regression; R^2 = 0.80; n = 11; Figure 2A),

250   suggesting that these two compounds were released concurrently in these waters. By scaling

251   the DOSS to methane ratio by the methane flux rate from the well head (~1.1×10^8 mol d^{-1} [16] −

252   1.5×10^8 mol d^{-1} [11]), we calculate a DOSS release rate of 5200-7100 kg day^{-1}. Given the highly

253   approximate assumptions involved, this range is remarkably close to the average reported

254   release rate (4800 kg day^{-1}; range 1300-8100 kg day^{-1}, see below). Since most methane was

255   trapped at depth [11], these calculations indicate that DOSS released at the wellhead became

256   trapped in the deepwater hydrocarbon and gas plume.

257   The nearly 1:1 correlation between DOSS and methane as well as the consistency between their

258   release rates indicates that DOSS was not biodegraded or otherwise lost in the vicinity of the

259   well head during conditions of active flow, as methane was shown to act conservatively under

260   these conditions [11]. DOSS concentration also correlated with CDOM values (Model II

261   regression; R^2 = 0.49, n = 14; Figure 2B), with dilution being the most obvious factor driving

262   covariance in all three parameters. Our interpretation of these observations is that neither

263   DOSS nor methane was substantially affected by biodegradation close to the wellhead and

264   instead was transported conservatively by deep water currents.

265   To evaluate our hypothesis of conservative transport, we compared our observed DOSS

266   concentrations with those expected from recorded Corexit applications. Based on our analysis

267   of DOSS in Corexit 9500A, we calculate that the average DOSS application was 4800 kg per day,

268   given a Corexit 9500A daily application of approximately 12,500 gallons (see Supplementary

269   Information). In the deep ocean, this means that over 290,000 kg of DOSS were released to

270   surrounding waters over the spill period. In order to estimate an expected DOSS concentration

271   in our samples, we hypothesized a theoretical water parcel within which Corexit might have

272   been fully mixed with oil (details in Supplementary Information). The average DOSS

273   concentration in this parcel after one hour of DOSS application at the average rate would be 7

274   μg L^{-1}. The total volume of Corexit 9500A applied each day varied widely (3,400 – 21,100

275   gallons), so the expected concentrations of DOSS in subsurface water likely vary between 2 and

276   12 μg L^{-1}. This calculation does not consider higher frequency variability and it assumes that all

277   the DOSS (and dispersant) moved into our defined plume. However, even with these

278   assumptions, measured concentrations (range: 0.4 – 12 μg L^{-1}) are remarkably similar to the

279   expected concentrations, suggesting that the dispersant was moving conservatively into the

280   plume near the wellhead and was not appreciably degraded or lost during active flow.

281   After flow of oil from the well ceased in July, we measured DOSS concentrations in samples

282   near- and far-field from the Deepwater Horizon oil spill site (September samples). We found

283   that DOSS concentrations had markedly decreased at all sampled sites and DOSS was

284   undetectable in the plume samples located furthest from the spill site (Figure 3). We estimated

285   the loss of DOSS due to latitudinal turbulent mixing (perpendicular to the center line of the

286   plume), using the approach outlined in Schwarzenbach *et al.* [17] (see Supplementary

287   Information). If we assume that the initial concentration of DOSS at the wellhead was 7 µg L^{-1}

288   and that it would take 45 days for a water parcel to travel 300 km (at an average current velocity

289   of 7.8 cm s^{-1} [12]), then the concentration after this time and distance should be approximately

290   0.04 µg L^{-1}. For 500 km distance (74 days), we find that the expected concentration is 0.01 µg L^{-1}.

291   With the anticipated variability in DOSS application rate, concentrations at this distance could

292   range between 0.001 and 0.02 µg L^{-1}. These values are within an order of magnitude of our

293   current detection limit of 0.003 µg L^{-1}. However, closer to the well head, turbulent mixing would

294   not have diluted the DOSS to such an extent and indeed, we calculated expected concentrations

295   of 0.08 µg L^{-1} in the 100 km range (range: 0.005 – 0.14 µg L^{-1}) and 1.2 µg L^{-1} in the 10 km range

296   (range: 0.07 – 2.1 µg L^{-1}). In comparison, our DOSS concentrations in September ranged from 0

297   (undetectable) to 0.07 µg L^{-1}, approximately 2-3 orders of magnitude lower than in May and

298   June. These data are within the anticipated range of DOSS concentrations after conservative

299   transport and highlight the persistence of DOSS in the deep water column, up to 64 days and

300   300 km after the dispersant applications ceased on July 12, 2010.

301   It is possible that biodegradation or sedimentation is also contributing to the decrease of DOSS

302   concentration in these water masses. However, observed concentrations are similar to those

303   predicted for a given distance and so we conclude that the primary process acting to alter DOSS

304   concentration is dilution. Previous studies in freshwater environments have given conflicting

305   results for biodegradation of DOSS in aqueous solution [18, 19]. Given the variability in DOSS

306   release rates at the wellhead, biodegradation rates would have to exceed the dilution rate by

307   ~10X in order for the impact of biodegradation to be observed in our data sets. Since our data

308   fall within 10X of the expected concentrations, our results do not support a significant

309   component of biodegradation in DOSS fate in the Gulf of Mexico. We cannot test our hypothesis

310   further because there are no conservative oil, gas or dispersant molecules identified at this time

311   (to our knowledge) with which we can normalize our DOSS concentrations. Methane, as used

312   above, is biologically available to methanotrophs in these waters and the elapsed time is

313   sufficient for methane oxidation to have occurred [16]. Fluorescent signals are increasingly

314   difficult to distinguish from the background as oil degrades and its bulk fluorescent properties

315   change. In addition, these signals measure a bulk property rather than individual molecules and

316   mask many molecular-level changes that may be occurring during transport. Work is underway

317   in our laboratories to assess the composition (and concentration) of petroleum components

318   remaining in these samples after > 2 months of biodegradation [20].

319   Based on our observations, we cannot assess whether the dispersant application was successful

320   in reducing the oil droplet size or in increasing the sequestration of oil in deep water. However,

321   we can conclude that DOSS, and presumably the other Corexit components, became

322   sequestered in deep plumes. Two or more possibilities may explain these observations. In one

323   scenario, DOSS dissolved into the water during ascent and detrained at approximately 1100 m

324   through partitioning with methane, water, gas hydrate or other compounds. In this case, if the

325   DOSS dissolved completely or partitioned with natural gas, it may suggest that the dispersant

326   was rendered unavailable to the oil and thus ineffective in dispersing the liquid oil. In a second

327   scenario, Corexit was associated with small liquid oil droplets that were sequestered in this

328   plume [21]. If the DOSS was deposited in these small oil droplets, it may suggest that the

329   chemical dispersion was highly effective. We have rejected the hypothesis that DOSS was

330   associated with large oil droplets since their higher buoyancy would be expected to force them

331   to travel to the surface [21], presumably releasing dispersant en route [2]. This effect is not

332   evident in our data (except perhaps in the case of Cast 07 from the R/V *Cape Hatteras*). Chemical

333   measurements of liquid oil components at different depths as well as modeling studies of

334   mixed-phase flow will be needed to distinguish between our two hypotheses for DOSS

335   sequestration in the deepwater plume.

336   Our calculations of dispersant concentrations near the wellhead (or in the deepwater plume)

337   indicate that deepwater, or pelagic, biota traveling through the deepwater plume likely

338   encountered 1-10 μg L^{-1} DOSS or 10-100 μg L^{-1} Corexit, between ~1 and 10 km from the actively-

339   flowing wellhead, with concentration decreasing with distance. The dispersant was applied at

340   an effective dispersant-to-oil ratio of 0.05%, based on published volume estimates for the spill

341 [22], but ratios were likely ~10X higher in the plume itself, based on volume estimates for the

342 southwestern plume [12]. Regardless, these concentrations and dispersant-to-oil ratios are lower

343 than those tested in published toxicology assays [2, 18, 23]. However, further tests are needed to

344 assess stress responses of pelagic biota to oil, gas, dispersant and associated mixtures. In

345 particular, our study has not assessed the fates or reactivities of the non-ionic surfactants and

346 the hydrocarbon solvents present in Corexit 9500A, each of which may have unique

347 toxicological impacts. In short, the application of this material in the deep ocean is new and

348 unprecedented and so merits further study of pelagic macro- and microbiota at

349 environmentally relevant Corexit concentrations and dispersant-to-oil ratios.

362 **Supplementary Information Available**

363 We include the calculations referred to above as Supplementary Information. In addition, the SI

364 contains ancillary mass spectral data and dispersant application data for our study period (May

365 25, 2010 – June 21, 2010). This information is available free of charge via the Internet at

366 http://pubs.acs.org/.

TABLES

Table 1. All data from May/June 2010 samples. 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.

	Sample	Lat (deg N)	Lon (deg W)	Depth (m)	Distance to well (km)	DOSS (µg/L)	CDOM (mg/m³)	Methane (nM)
R/V F. G. Walton Smith May/June 2010	CAST 15; bottle 5	28.72322	88.48130	1140	9.3	0.42		
	CAST 41; bottle 12	28.68240	88.56958	800	19	0.35 (*)		
	CAST 41; bottle 8	"	"	1140	"	5.7 (*)		
	CAST 52; bottle 8	28.72025	88.39782	1160	2.1	11.7 (*)		
	CAST 52; bottle 3	"	"	1300	"	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	"	"	1140	"	6.0		
R/V Cape Hatteras June 2010	CAST 07; bottle 23	28.73017	88.37950	10	1.2	8.4 (*)	1.92	13
	CAST 07; bottle 9	"	"	870	"	4.3 (*)	2.38	30
	CAST 07; bottle 6	"	"	911	"	0.77 (*)	2.36	4600
	CAST 07; bottle 4	"	"	1000	"	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	"	"	1108	"	5.3	6.35	98,000
	CAST 10; bottle 5	"	"	1136	"	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	"	"	1300	"	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	"	"	1100	"	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	"	"	1110	"	2.0	3.11	25,000

Table 2. Data from September 2010 (NOAA Ship *Pisces*). Same abbreviations as Table S1; LV = large-volume (~7 L) samples. Fluorescence signal was measured here by AquaTracka™. Methane data was not available for these samples.

Sample	Lat (deg N)	Lon (deg W)	Distance from Well (km)	Depth (m)	DOSS (µg/L)	Fluorescence (mg/m³)
CAST 193; bottle 22	27.17980	90.59212	277	900	BD	1.76
CAST 193; bottle 15	"	"	"	1100	BD	2.05
CAST 193; bottle 10	"	"	"	1150	BD	1.80
CAST 193; bottle 1	"	"	"	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	"	"	"	1150	BD	1.89
CAST 209; bottle 12	27.32558	91.26098	323	1200	BD	1.88
CAST 209; bottle 6	"	"	"	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	"	"	"	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	

FIGURE CAPTIONS

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].

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: $[DOSS] = (2.2 \pm 0.5) [CDOM] - (5.0 \pm 1.8)$, $r^2 = 0.49$.

Figure 3. Map view of DOSS concentrations at plume depth (~1000 – 1200m) 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}. 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 sub-region represented by (A).

REFERENCES

1.   www.whitehouse.gov/blog/issues/Deepwater-BP-oil-spill.

2.   NRC, *Oil Spill Dispersants: Efficacy and Effects*. National Academy of Sciences: 2005.

3.   OperationalScienceAdvisoryTeam *Summary report for sub-sea and sub-surface oil and dispersant detection: Sampling and monitoring*; Unified Area Command: December 17, 2010.

4.   Stanford, L. A.; Kim, S.; Klein, G. C.; Smith, D. F.; Rodgers, R. P.; Marshall, A. G., Identification of water-soluble heavy crude oil organic-acids, bases and neutrals by electrospray ionization and field desorption ionization Fourier transform ion cyclotron resonance mass spectrometry. *Env. Sci. Tech.* **2007,** *41*, 2696-2702.

5.   Dittmar, T.; Koch, B.; Hertkorn, N.; Kattner, G., A simple and efficient method for the solid-phase extraction of dissolved organic matter (SPE-DOM) from seawater. *Limnol. Oceanogr. Meth.* **2008,** *6*, 230-235.

6.   Ricker, Linear regressions in fishery research. *J. Fish. Res. Board Can.* **1973,** *30*, 409-434.

7.   Kido Soule, M. C.; Longnecker, K.; Giovannoni, S. J.; Kujawinski, E. B., Impact of instrument and experimental parameters on the repeatability and reproducibility of peaks in ultrahigh resolution ESI FT-ICR mass spectra of natural organic matter. *Org. Geochem.* **2010,** *41*, 725-733.

8.   Stenson, A. C.; Marshall, A. G.; Cooper, W. T., Exact masses and chemical formulas of individual Suwannee River fulvic acids from ultrahigh resolution electrospray ionization Fourier transform ion cyclotron resonance mass spectra. *Anal. Chem.* **2003,** *75*, 1275-1284.

9.   Chatterjee, A.; Moulik, S. P.; Sanyal, S. K.; Mishra, B. K.; Puri, P. M., Thermodynamics of micelle formation of ionic surfactants: A critical assessment for sodium dodecyl sulfate, cetyl pyridinium chloride and dioctyl sulfosuccinate (Na salt) by microcalorimetric, conductometric, and tensiometric measurements. *J Phys Chem B* **2001,** *105*, 12823-12831.

10.   Kujawinski, E. B.; Longnecker, K.; Blough, N. V.; Del Vecchio, R.; Finlay, L.; Kitner, J. B.; Giovannoni, S. J., Identification of possible source markers in marine dissolved organic matter using ultrahigh resolution electrospray ionization Fourier-transform ion cyclotron resonance mass spectrometry. *Geochim. Cosmochim. Acta* **2009,** *73*, 4384-4399.

11.   Valentine, D. L.; Kessler, J. D.; Redmond, M. C.; Mendes, S. D.; Heintz, M. B.; Farwell, C.; Hu, L.; Kinnaman, F. S.; Yvon-Lewis, S.; Du, M.; Chan, E. W.; Garcia Tigreros, F.; Villanueva, C. J., Propane respiration jump-starts microbial response to a deep oil spill. *Science* **2010,** *330*, 208-211.

12.   Camilli, R.; Reddy, C. M.; Yoerger, D. R.; Van Mooy, B. A. S.; Jakuba, M. V.; Kinsey, J. C.; McIntyre, C. P.; Sylva, S. P.; Maloney, J. V., Tracking hydrocarbon plume transport and biodegradation at Deepwater Horizon. *Science* **2010,** *330*, 201-204.

13.   Socolofsky, S. A.; Adams, E. E., Multi-phase plumes in uniform and stratified crossflow *J Hydraul Res* **2002,** *40*, 661-672.

14.   Socolofsky, S. A.; Adams, E. E., Role of slip velocity in the behavior of stratified multiphase plumes. *J Hydraul Eng* **2005,** *131*, 273-282.

15.	Yvon-Lewis, S. A.; Hu, L.; Kessler, J. D., Methane flux to the atmosphere from the Deepwater Horizon oil disaster. *Geophys. Res. Lett.* **In press.**

16.	Kessler, J. D.; Valentine, D. L.; Redmond, M. C.; Du, M.; Chan, E. W.; Mendes, S. D.; Quiroz, E. W.; Villanueva, C. J.; Shusta, S. S.; Werra, L. M.; Yvon-Lewis, S.; Weber, T. C., A persistent oxygen anomaly reveals the fate of spilled methane in the deep Gulf of Mexico. *Science* **in press**.

17.	Schwarzenbach, R. P.; Gschwend, P. M.; Imboden, D. M., *Environmental Organic Chemistry*. John Wiley & Sons, Inc.: New York, NY, 1993; p 681.

18.	Garcia, M. T.; Campos, E.; Marsal, A.; Ribosa, I., Biodegradability and toxicity of sulphonate-based surfactants in aerobic and anaerobic aquatic environments. *Water Res.* **2009,** *43*, 295-302.

19.	Franzetti, A.; Di Gennaro, P.; Bevilacqua, A.; Papacchini, M.; Bestetti, G., Environmental features of two commercial surfactants widely used in soil remediation. *Chemosphere* **2006,** *62*, 1474-1480.

20.	Hazen, T. C.; Dubinsky, E. A.; DeSantis, T. Z.; Andersen, G. L.; Piceno, Y. M.; Singh, N.; Jansson, J. K.; Probst, A.; Borglin, S. E.; Fortney, J. L.; Stringfellow, W. T.; Bill, M.; Conrad, M. E.; Tom, L. M.; Chavarria, K. L.; Alusi, T. R.; Lamendella, R.; Joyner, D. C.; Spier, C.; Baelum, J.; Auer, M.; Zemla, M. L.; Chakraborty, R.; Sonnenthal, E. L.; D'Haeseleer, P.; Holman, H.-Y. N.; Osman, S.; Lu, Z.; Van Nostrand, J. D.; Deng, Y.; Zhou, J.; Mason, O. U., Deep-sea oil plume enriches indigenous oil-degrading bacteria. *Science* **2010,** *330*, (204-207).

21.	Socolofsky, S. A.; Adams, E. E., Liquid volume fluxes in stratified multiphase plumes. *J Hydraul Eng* **2003,** *129*, 905-914.

22.	Crone, T. J.; Tolstoy, M., Magnitude of the 2010 Gulf of Mexico oil leak. *Science* **2010,** *330*, 634.

23.	Judson, R. S.; Martin, M. T.; Reif, D. M.; Houck, K. A.; Knudsen, T. B.; Rotroff, D. M.; Xia, M.; Sakamuru, S.; Huang, R.; Shinn, P.; Austin, C. P.; Kavlock, R. J.; Dix, D. J., Analysis of eight oil spill dispersants using rapid, in vitro tests for endocrine and other biological activity. *Env. Sci. Technol.* **2010,** *44*, 5979-5985.

Brief: Chemical dispersant applied at the wellhead during the Deepwater Horizon oil spill was sequestered with hydrocarbons in a deepwater plume and traveled conservatively into the far-field.
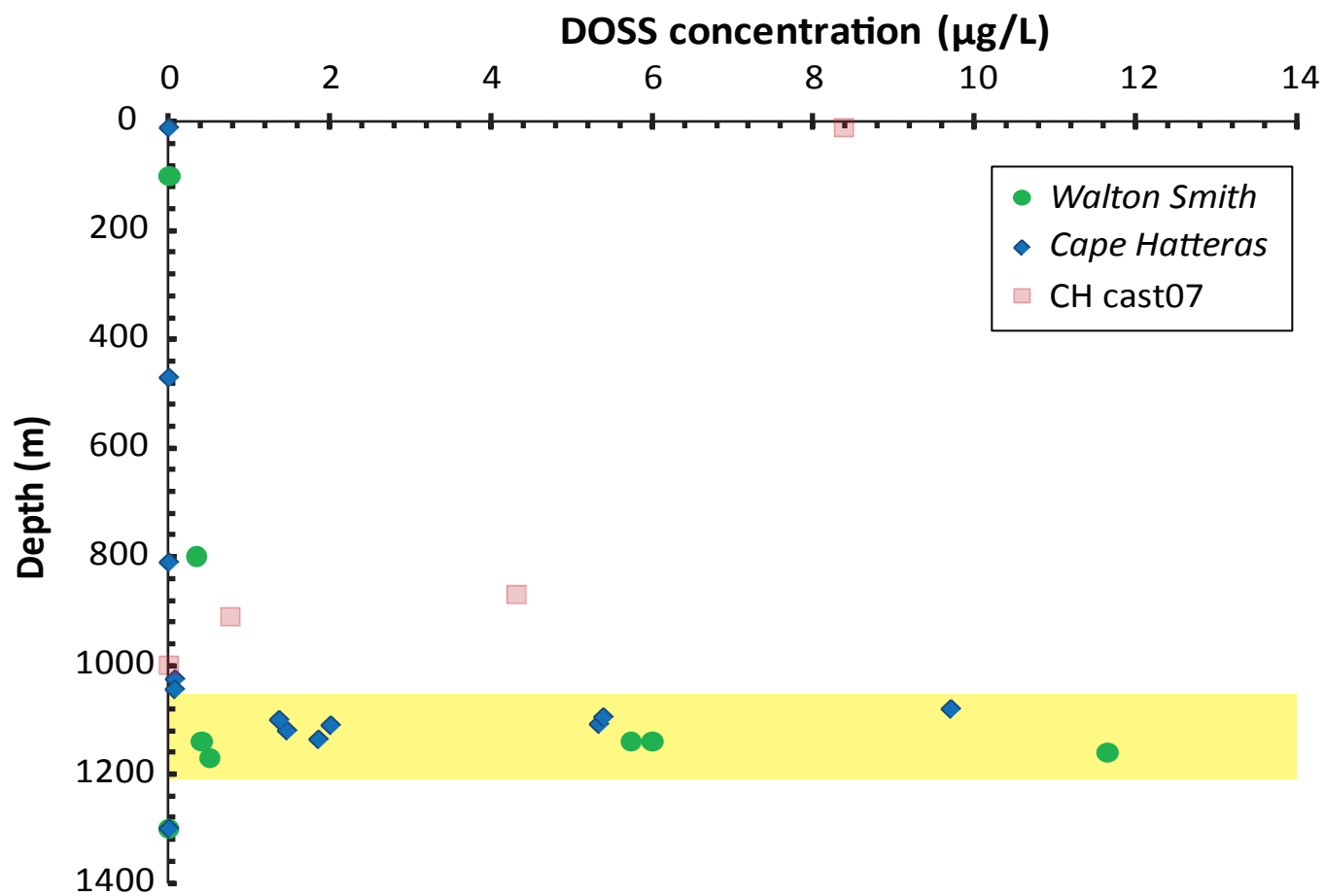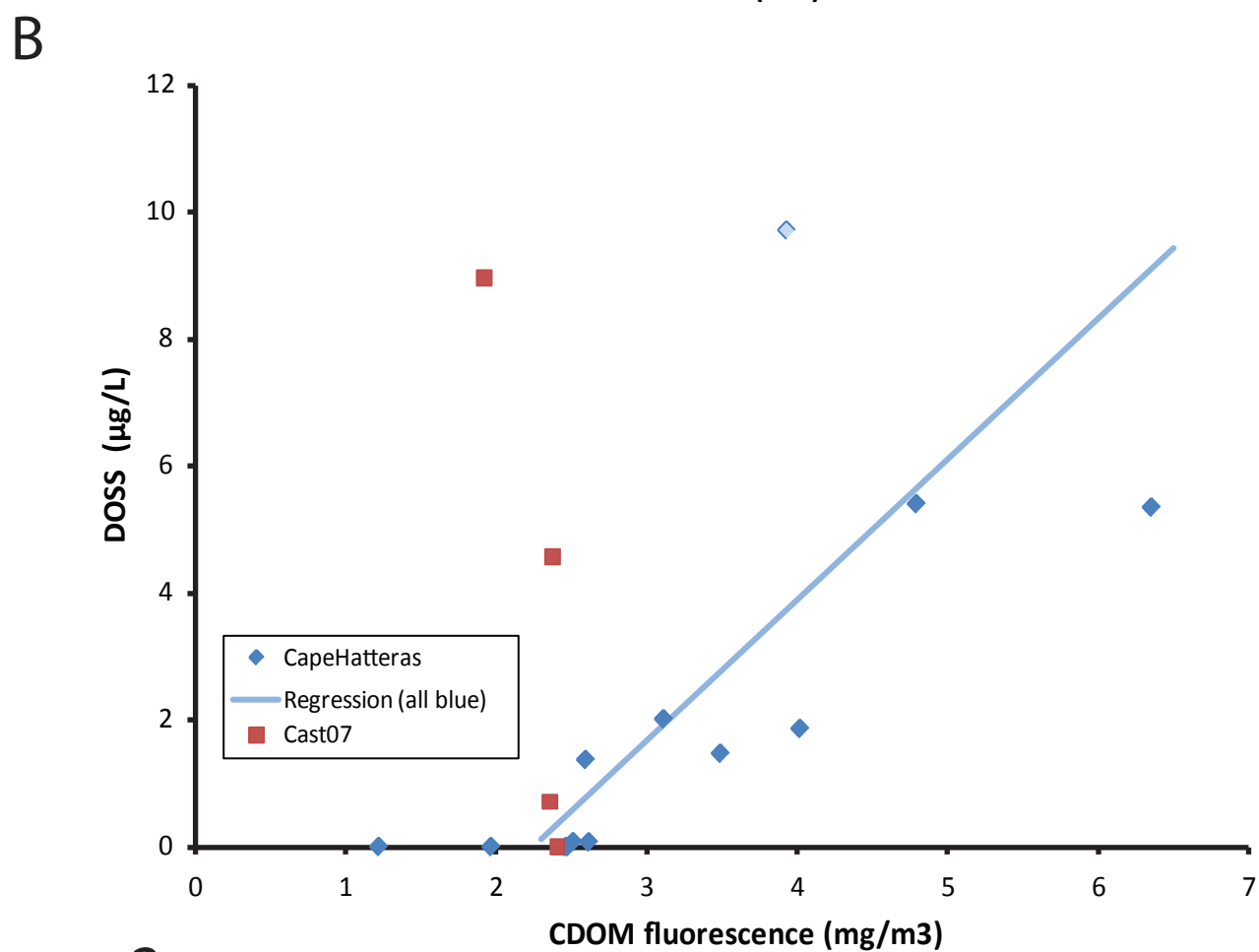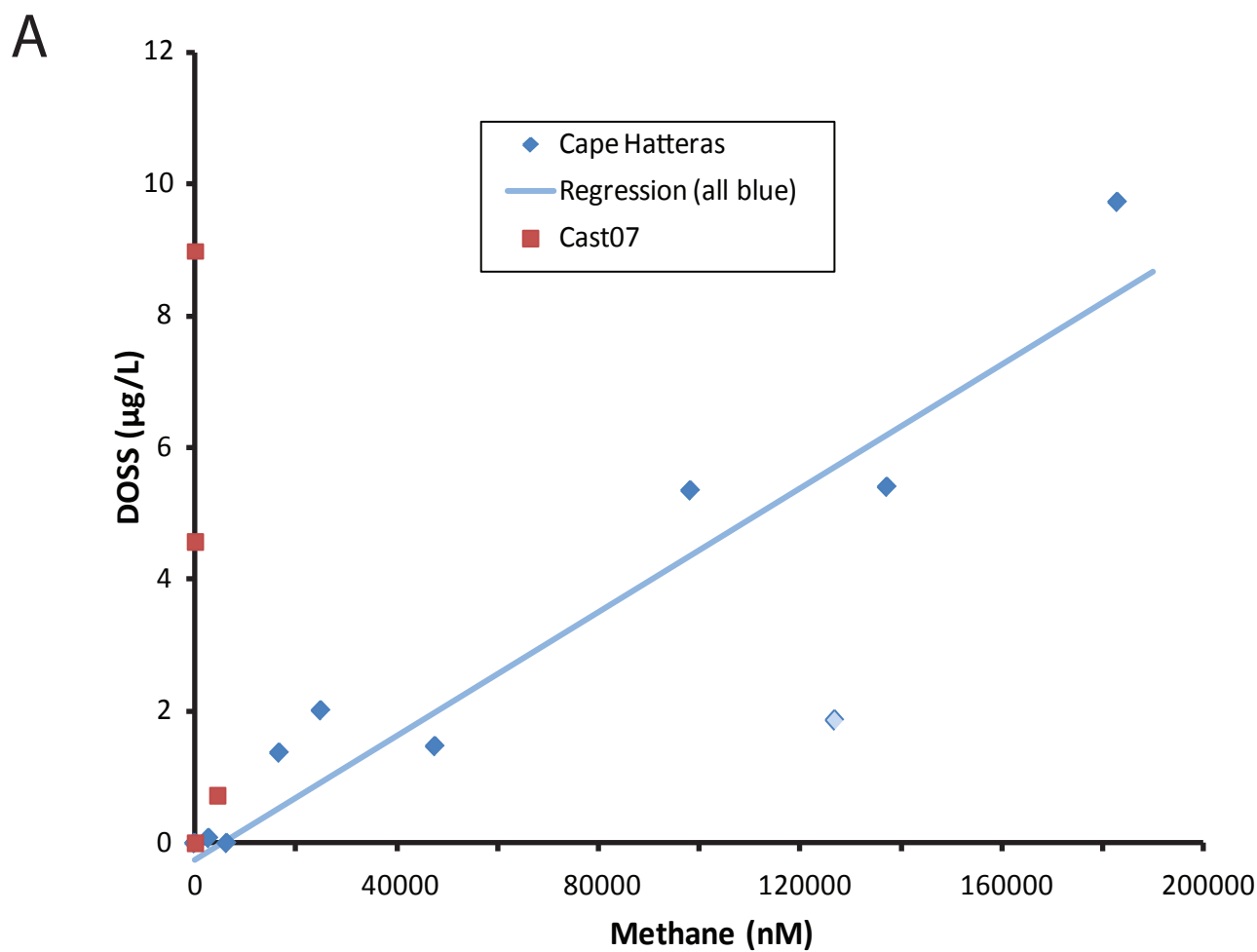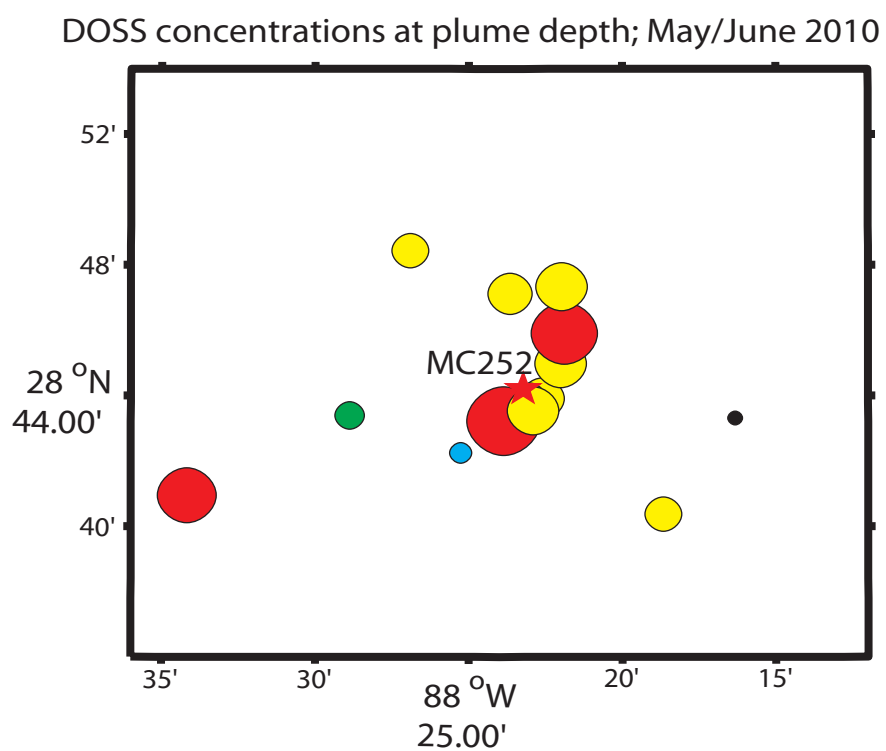
Figure 1.

Figure 2.

A

DOSS concentrations at plume depth; May/June 2010

B
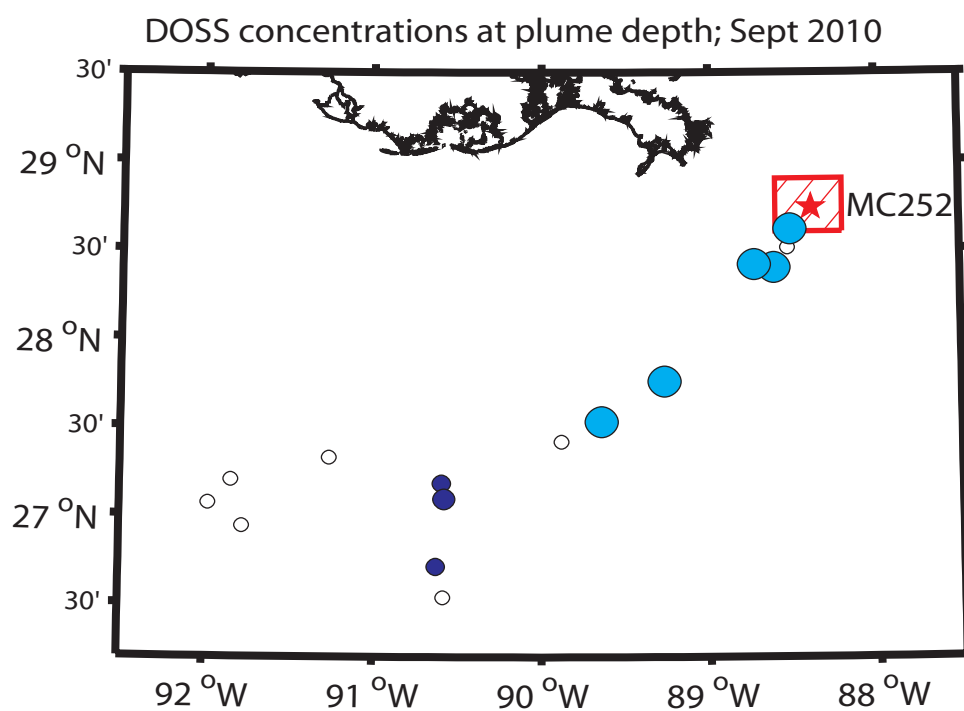
DOSS concentrations at plume depth; Sept 2010

Figure 3.

Supplementary Information

Fate of Dispersants Associated with the Deepwater Horizon Oil Spill

Elizabeth B. Kujawinski, Melissa C. Kido Soule, David L. Valentine, Angela K. Boysen, Krista Longnecker, Molly C. Redmond

8 pages of Supplementary Information with 4 figures and 0 tables

Calculations:

Calculation of critical micelle concentration

Chatterjee et al. [1] provide data for the critical micelle concentration (CMC) of DOSS under different salt conditions (Chatterjee et al., Table 5) at 293 K (20degC). We estimate the salinity of seawater to be 34 ppt or 34 mg mL^{-1} seawater. This is converted to molarity with the molecular weight of Na and Cl, to be 0.6 M Na$^+$. Using the Corrin-Harkins equation in Chatterjee et al. [1], we can estimate the critical micelle concentration under seawater salinity:

$$\log CMC = CONSTANT - f \log[counterion]$$

Using the data provided for [Na$^+$] = 0.005 (CMC = 2.03 mM, f = 0.35), we can calculate that the CONSTANT is -0.5. We can now insert the values for seawater salinity to get CMC = 0.38 mM or 178 mg L^{-1}.

Expected DOSS concentrations during well blowout

We measured the concentration of DOSS in Corexit 9500A and Corexit 9527 using our LC/MS method. For Corexit 9500A, DOSS is present at 99.0 mg/g Corexit, or 0.099 g DOSS per g Corexit 9500A. We can convert this value to find that Corexit 9500A is ~10% DOSS by weight. For Corexit 9527, DOSS is present at 170 mg/g Corexit. Using the same conversions, we find that Corexit 9527 is ~17% DOSS by weight. Using the measured densities of the two Corexit formulations, we can convert these values into mass DOSS per gallon Corexit. For 9500A, the measured density of the entire solution was 25.7 mg per 25 μL, so

$$\frac{DOSS}{Corexit9500A} = \left(\frac{25.7mg}{25\mu L}\right) * \left(\frac{1g}{1000mg}\right) * \left(\frac{10^6 \mu L}{1L}\right) * \left(\frac{3.7L}{gal}\right) * \left(\frac{0.099gDOSS}{gCorexit}\right) = 380\frac{gDOSS}{galCorexit}$$

We can perform the same calculation for Corexit 9527 (measured density = 28.5 mg / 25 μL) and we calculate that there are 717 g DOSS per gallon Corexit 9527.

For the remaining calculations, we focus solely on Corexit 9500A because that was the formulation used in the wellhead application. The range of daily wellhead applications was 3,400 – 21,100 gallons, with an average of 12,500 gallons (Figure S4). The average value during our study period (May 25 – June 19) was 12,400 gallons per day. Given the absence of hourly flow rate data, we assume that these applications were constant over the 24-hour period associated with a given day.

We start with the conceptual model of a water parcel that is small enough to be filled and well-mixed with Corexit 9500A in one hour. We assume a constant current velocity of 7.8 cm / s [2]. Over an hour, water would travel 279 m at this velocity. This sets the horizontal length dimension of our parcel. We assume the height of the parcel is 100m, estimated from the vertical

region of high DOSS concentrations (Manuscript Figure 1). The horizontal width was assumed to be 1 km, as measured by *in situ* mass spectrometry by Camilli *et al.*[2]. We assume that vertical transport of this parcel from the wellhead to ~1100m is short relative to horizontal advective transport. Thus, we assume that water rises to the plume depth instantaneously.

The volume of this water parcel is:

$$Vol = L * W * H = 279m * 1000m * 100m = 2.79 X 10^7 m^3 \left(\frac{100cm}{1m}\right)^3 \left(\frac{1ml}{1cm^3}\right)\left(\frac{1L}{1000mL}\right) = 2.79 X 10^{10} L$$

The hourly application of Corexit 9500A would be 12,400 gallons / 24 hr, or 517 gallons / hr. This corresponds to 196 kg DOSS per hour. This DOSS would be mixed throughout the water parcel outlined above and so the concentration of DOSS in this water parcel would be:

$$\frac{196kgDOSS}{2.79 X 10^{10} L}\left(\frac{10^9 \mu g}{1kg}\right) = 7 \frac{\mu g DOSS}{L}$$

Using this approach for the range of reported Corexit 9500A applications, we estimate that the range of expected concentrations is 1.9 – 12 µg/L.

Expected DOSS concentrations after turbulent mixing through horizontal advection

We approximated the expected dilution factor for DOSS during advective transport through the approach outlined in Schwarzenbach *et al.* [3] For this calculation, we assume latitudinal transport only, i.e., mixing perpendicular to the plume center line. We assume that vertical mixing and longitudinal mixing (along the plume center line) are negligible due to vertical density gradients and to the continuous addition of DOSS at the wellhead, respectively. The variance associated with turbulent mixing during transport should increase as a function of the apparent eddy diffusivity and time. Thus, we have the equation (9-48 from Schwarzenbach *et al.* [3]):

$$\sigma^2 = 2Et$$

where σ is the variance (units of length), E is the apparent diffusivity (length^2 per time) and t is time. Our furthest point in the September data set is 400 km away from the wellhead. We use 300 km as our reference point in this calculation because it is halfway between 100 and 1000 km on a log plot. Using the figure (9.10) presented in Schwarzenbach *et al.* [3], we estimate that E should be 10^7 cm^2 / sec. Using the current velocity of 7.8 cm / sec [2], we calculate that it would take 45 days for this water parcel to travel 300 km. Thus,

$$\sigma_t^2 = 2\left(10^7 \frac{cm^2}{s}\right) 45days \left(\frac{60s}{1\min}\right)\left(\frac{60\min}{1hr}\right)\left(\frac{24hr}{1day}\right)\left(\frac{1km}{10^5 cm}\right)^2 = 7800km^2$$

In the initial water parcel, the DOSS was spread over 1 km in diameter, so σ_0 = 1km / 2 or 0.5 km. Thus, σ_0^2 = (0.5km)^2 = 0.25 km^2 at the wellhead. After traveling 300 km, the concentration should decrease by the inverse of the increase in the variance, σ^2. In mathematical terms,

$$\frac{[DOSS]_t}{[DOSS]_0} = \frac{\sigma_0}{\sigma_t} = \frac{\sqrt{0.25km^2}}{\sqrt{7800km^2}} = 5.6X10^{-3} = \frac{[DOSS]_t}{[DOSS]_0} = \frac{x}{7\mu g/L}$$

$$x = 7\frac{\mu g}{L} * 5.6X10^{-3} = 0.04\frac{\mu g}{L}$$

We repeated this calculation for shorter travel lengths, 10 km and 100 km. For 10 km, the travel time would be 1.5 days and E was estimated to be 10^5 cm^2 / sec. We calculate σ^2 to be 2.6 km^2 and the new DOSS concentration to be 1.2 µg/L. For 100 km, the travel time would be 15 days and E was estimated to be 10^6 cm^2 / sec. Here, we calculate σ^2 to be 260 km^2 and the new DOSS concentration to be 0.08 µg/L. We calculated that our detection limit of 0.003 µg/L would be reached at 1500 km.

REFERENCES

1.   Chatterjee, A.; Moulik, S. P.; Sanyal, S. K.; Mishra, B. K.; Puri, P. M., Thermodynamics of micelle formation of ionic surfactants: A critical assessment for sodium dodecyl sulfate, cetyl pyridinium chloride and dioctyl sulfosuccinate (Na salt) by microcalorimetric, conductometric, and tensiometric measurements. *J Phys Chem B* **2001,** *105*, 12823-12831.

2.   Camilli, R.; Reddy, C. M.; Yoerger, D. R.; Van Mooy, B. A. S.; Jakuba, M. V.; Kinsey, J. C.; McIntyre, C. P.; Sylva, S. P.; Maloney, J. V., Tracking hydrocarbon plume transport and biodegradation at Deepwater Horizon. *Science* **2010,** *330*, 201-204.

3.   Schwarzenbach, R. P.; Gschwend, P. M.; Imboden, D. M., *Environmental Organic Chemistry*. John Wiley & Sons, Inc.: New York, NY, 1993; p 681.

4.   www.whitehouse.gov/blog/issues/Deepwater-BP-oil-spill.

FIGURES

Figure S1. Comparison of original and re-extracts of same samples. All re-extracts were generated by solid-phase extraction onto PPL resin. These data are compared to the concentrations of DOSS in the original PPL extracts (blue diamonds) and in the original DCM extracts (#1 only; red squares). One data-point in each comparison was rejected as an outlier (shown in pale colors). Model II regression lines are shown in dashed lines. The equations for these lines are:

(PPL) [old] = (0.056 $\pm$ 0.007) [new] + (20.3 $\pm$ 15.1), r^2 = 0.85

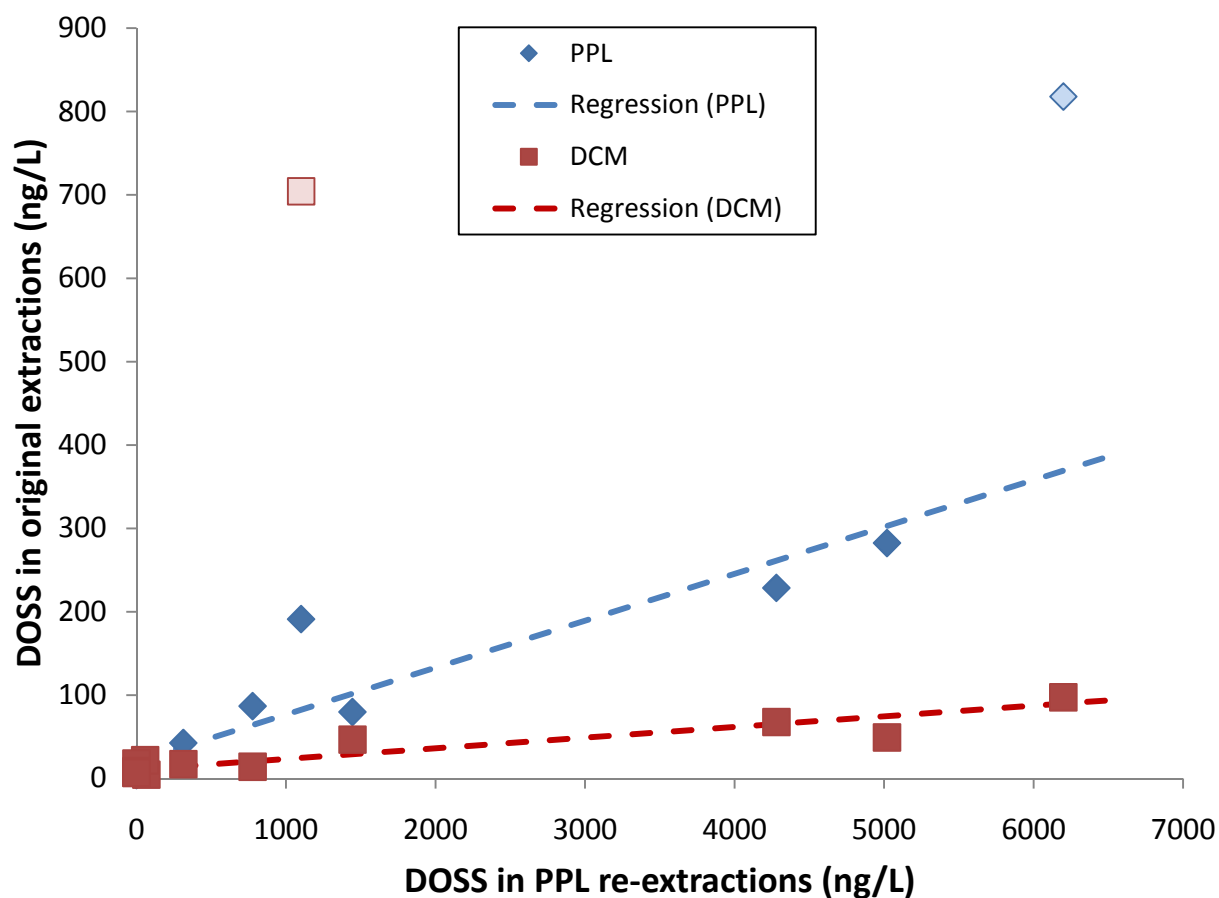(DCM) [old] = (0.013 $\pm$ 0.002) [new] + (10.5 $\pm$ 4.0), r^2 = 0.86

Figure S2. LC/MS spectrum of field sample (R/V *Cape Hatteras*, Cast 07, bottle 23, 10m). The top spectrum is the total ion chromatogram in the ion-trap mass spectrometer. The middle panel shows the extracted ion chromatogram for *m/z* 421. The retention time of the one peak (6.16 min) matches the retention time of DOSS in standards. The bottom panel shows the extracted ion chromatogram for the fragment ions at *m/z* 227 and 291.
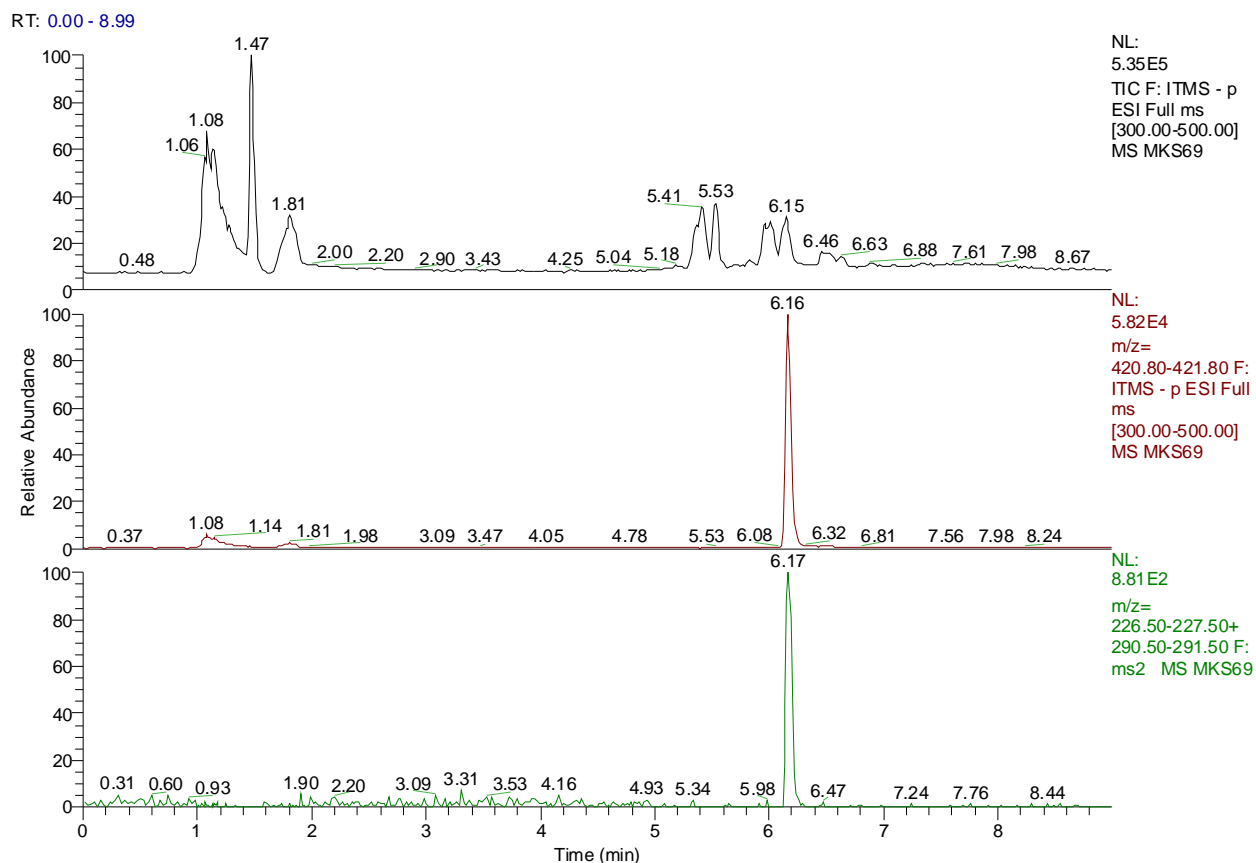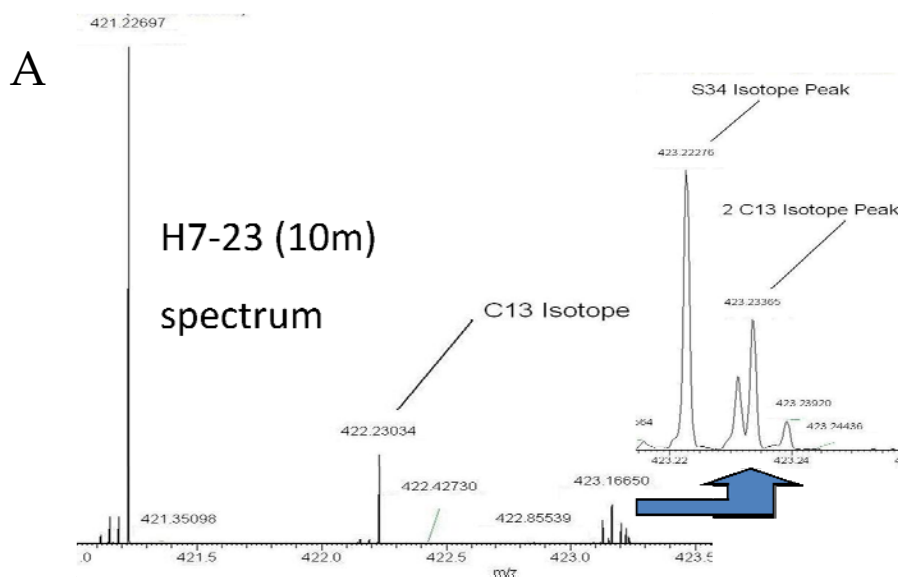
Figure S3. (A) Isotopomer identification in a field sample (same as in Figure S3). The spectrum here was acquired with negative ion mode ESI FT-ICR MS. Mass accuracy was <1 ppm after internal recalibration. (B) Fragmentation spectra of *m/z* 421.226x in Corexit 9527 and in a field sample. Fragments were generated with CID in the ion-trap and the masses of the fragments were measured in the FT-ICR MS.

A

421.22697

H7-23 (10m)

spectrum

C13 Isotope

S34 Isotope Peak

423.22276

2 C13 Isotope Peak

423.23365

422.23034

423.23920

x64

423.24436

423.22   423.24   4

422.42730

423.16650

421.35098

422.85539

.0   421.5   422.0   422.5   423.0   423.5

m/z

B

227

291

227   291

Figure S4. Dispersant applications for the month of our study period. Data was collated from press-releases and technical data within daily reports from the Deepwater Horizon Incident Joint Information Center [4].