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How the dispersant Corexit impacts the formation of sinking marine oil snow

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ABSTRACT

The vertical transport of sinking marine oil snow (MOS) and oil-sediment aggregations (OSA) during the Deepwater Horizon (DwH) spill contributed appreciably to the unexpected, and exceptional accumulation of oil on the seafloor. However, the role of the dispersant Corexit in mediating oil-sedimentation is still controversial. Here we demonstrate that the formation of diatom MOS is enhanced by chemically undispersed oil, but inhibited by Corexit-dispersed oil. Nevertheless, the sedimentation rate of oil may at times be enhanced by Corexit application, because of an elevated oil content per aggregate when Corexit is used. A conceptual framework explains the seemingly contradictory effects of Corexit application on the sedimentation of oil and marine particles. The redistribution of oil has central ecological implications, and future decisions on mediating measures or damage assessment will have to take the formation of sinking, oil-laden, marine snow into account.

1. Introduction

Research triggered by the DwH spill identified the accumulation of oil on the seafloor as a significant, and hitherto unaccounted, sink (Brooks et al., 2015; Daly et al., 2016; Larson et al., 2013). Using hopanes or radiocarbon measurements as tracers, the amount of oil reaching the sediment during and after the DwH spill has been estimated to be up to 14% (Chanton et al., 2014; Romero et al., 2015; Valentine et al., 2014). These estimates which are based on accumulation rates of oil on the seafloor, are considered lower limits. Organic matter once at the seafloor is not preserved, but rather bioturbated, consumed and degraded, except if the sedimentation event is so intense that the benthic community is smothered (Passow and Hetland, 2016). The reasons for the large and unexpected sedimentation event are still under investigation, and especially the effect of the application of the dispersant Corexit, which was used during the accident (John et al., 2016; Kujawinski et al., 2011) is still discussed controversially. During DwH the dispersant Corexit 9500A was used at a target dispersant to oil ratio (DOR) of 1:20, however, application and effective surfactant concentrations varied widely (Gray et al., 2014; White et al., 2014).

Different types of marine snow scavenged oil from the DwH spill, transporting it to depths (Passow, 2014; Passow and Ziervogel, 2016; Passow et al., 2012). Specifically, diatom aggregates contributed significantly to the sedimentation of oil (Yan et al., 2016). Marine snow is defined as organic-rich, porous composite particles > 0.5 mm, with rapid sedimentation rates largely driven by their large size. MOS, i.e., marine snow that has oil associated with it, may form via a variety of biological mechanisms, including the coagulation of diatoms or microbial exudate production (Passow, 2014). The presence of particulate exudates termed transparent exopolymer particles (TEP), is essential for the formation of all marine snow, including MOS, because TEP provide the glue and the matrix of marine snow (Alldredge et al., 1993). In contrast, OSA, that are variously described as oil-mineral-aggregates (OMA) or oil-particle-aggregates (OPA) or SPM-Oil aggregates (Fu et al., 2014; Khelifa et al., 2008a; Khelifa et al., 2008b; Khelifa and Hill, 2006; Niu et al., 2011; Zhao et al., 2016) form due to direct coagulation of suspended sediments and oil droplets, with exudates playing a minor role (Gong et al., 2014; Khelifa et al., 2005; Omotoso et al., 2002; Stoffyn-Egli and Lee, 2002). Compared to MOS, OSA are small (20–200 μm) and reach high sinking velocities (> 80 m/d) primarily because of the high excess density of their mineral component (Gong et al., 2014).

Here we present experimental results investigating the hypothesis that the addition of Corexit to oil-contaminated water reduced aggregate formation by diatoms, while increasing the incorporation of oil into the aggregates that did form. A total of five roller tank experiments were conducted to investigate the direct impacts of chemically undispersed or chemically (Corexit)-dispersed oil on the aggregation of

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Table 1a
Treatments of experiments 1 and 2.

Treatment name	Exp. 1: *Chaetoceros* sp. exponential phase	Exp. 2: *Chaetoceros* sp. stationary phase
Control	1.16 L *Chaetoceros*	1.16 L *Chaetoceros*
OIL (chemically undispersed oil)	1.16 L *Chaetoceros* + 1 mL Macondo oil	1.16 L *Chaetoceros* + 1 mL Macondo oil
Oil + Cor-10 (10 μL Corexit added)	1.16 L *Chaetoceros* + 1 mL Macondo oil + 10 μL Corexit	Not conducted
Oil + Cor-30 (30 μL Corexit added)	1.16 L *Chaetoceros* + 1 mL Macondo oil + 10 μL Corexit	1.16 L *Chaetoceros* + 1 mL Macondo oil + 30 μL Corexit

diatoms. Treatments with either diatom cultures and crude oil or with natural oil contaminated seawater with or without added diatoms, were compared to the respective treatments where Corexit was also added.

2. Methods

2.1. General experimental approach and set-up

Roller tanks mimic the sinking of aggregates through largely turbulent-free, off-shore environment (Ploug et al., 2010). The general set-up was the same in all five experiments. Replicate acrylic roller tanks of 1.16 L volume were filled bubble-free with diatom cultures and/or oil-contaminated natural seawater (Tables 1a and 1b). Macondo oil was added to oil treatments which contained no oil-contaminated seawater. Corexit treatments additionally contained Corexit 9500A at target DORs of 1:20 or 1:33. All experiments were incubated in the dark, at 20 °C at an rpm of 2.4 (experiments 1 & 2) or at 15 °C at an rpm of 1.4 (experiments 3, 4 & 5). Once aggregates ≥ 1 mm formed, they were isolated from the surrounding seawater, which contained unaggregated cells and aggregates < 1 mm, and both fractions were analyzed separately to investigate the partitioning of particulate organic carbon (POC), cells, and oil between rapidly sinking MOS, and unaggregated material that sinks at speeds compared to degradation rates.

Experiments 1 and 2 were conducted with Macondo surrogate oil and *Chaetoceros* sp. (isolated Nov. 2014 at 38.70°N, 123.67°W), a common bloom-forming diatom species that aggregates well. Three types of treatments, each in duplicate, were compared: a control (media), an oil addition (OIL) and 1–2 oil plus Corexit addition with 10 μL or 30 μL Corexit added (Oil + Cor-10, Oil + Cor-30) (Table 1a). To prepare the OIL treatments, 1 mL of Macondo oil (Marlin Platform, Dorado source oil) was slowly added into the center of the turning tank, using a syringe inserted through the silicon stopper. Corexit 9500A (Clean Seas), either 10 μL or 30 μL, was added for the oil plus Corexit treatments (DOR: 1:33 or 1:10). Upon addition of source oil, oil droplets rose to the top, and especially in the absence of Corexit, a slick layer formed, which was not available for aggregation and was not sampled.

Experiments 3, 4 and 5 were conducted with oil-contaminated seawater (ConSW) collected by bucket from the sea surface (Bucket IDs: RS-37 and RS-085C) near Santa Barbara, CA (34°27 N, 120°03 W), 1.5 and 9 days after the Refugio pipeline spill. *Skeletonema grethae* (CCMP 775) was added to replicate treatments (Table 1b). The oil-contaminated seawater without and with *S. grethae* (in early stationary phase) were compared to the respective treatments where 50 μL Corexit per liter was also added. The oil-contaminated seawater was siphoned into roller tanks from below the bucket surface. Whereas an oil layer was clearly visible in the source samples 1.5 days after the spill, only traces of visible oil was present 9 days after the spill.

Table 1b
Treatments of experiments 3, 4 and 5.

Treatment	Exp. 3: ConSW from 5/21	Exp. 4: ConSW from 5/28	Exp. 5: ConSW from 5/28
ConSW	0.96 L ConSW 0.20 L *S. grethae*	1.16 L ConSW	0.96 L ConSW 0.20 L *S. grethae*
ConSW + Cor	0.96 L ConSW 0.20 L *S. grethae* 50 μL Corexit	1.16 L ConSW 50 μL Corexit	0.96 L ConSW 0.20 L *S. grethae* 50 μL Corexit

Oil-contaminated seawater (ConSW), collected after the Refugio oil spill. ConSW + Cor = ConSW and 50 μL Corexit per mesocosm.

The oil spilled at Refugio Beach 19 May 2015 was a heavy, pipeline oil, stemming from the Monterey Formation (Nelson et al., 2016). The Macondo oil, which is the surrogate oil for the DwH accident, is lighter than the Monterey oil (0.865 g mL^{-1} vs. 0.946 g mL^{-1}). Additionally, the Monterey oils are known for their high adhesiveness, Sockeye Sour, for example, has an adhesion factor of 98 after initial weathering (Tables 2–6 in (National Academies of Sciences, 2016)).

Diatom cultures were grown at 70 μmol $\text{m}^{-2}\,\text{s}^{-1}$ using modified F/2 media, with reduced macro-nutrients: nitrate: 58.9 μM, phosphate: 3.6 μM, and silicic acid: 53.5 μM, as final concentrations in the media.

2.2. Sampling

Aggregate appearance and numbers were monitored during all experiments. When aggregates had formed, all treatments were harvested, except in experiment 3 where a replicate tank of each treatment was incubated for 6 more days before analysis. As no change in aggregation and partitioning dynamics was observed between both sampling dates, they are presented as replicates. After careful removal of tanks from rolling tables, aggregates > 1 mm (visually discernable) were manually collected and analyzed separately (Passow, 2014). After all aggregates > 1 mm were removed the remainder of the material, termed surrounding seawater (SSW), was subsampled. Both fractions were analyzed for POC, cell abundance and TEP (transparent exopolymer particles), and samples from exp. 1 and 2, also for PO^{13}C. In experiments 1 and 2, oil concentrations and partitioning of oil between the aggregate and SSW phase was determined using POC and PO^{13}C data. In experiments 3, 4 and 5 a similar endmember calculation was not possible, because oil contaminated natural seawater was used. Relative oil concentration (estimated oil equivalence = EOE) was estimated from fluorescence in the surrounding seawater of experiments 3, 4 and 5.

2.3. Analysis

Duplicate filters (GF/F) prepared for POC analysis were measured in a CEC44OHA elemental analyzer (Control equipment). The PO^{13}C signature was determined on replicate filters using a Finnigan Delta Plus Advantage.

Diatom cells were counted (Olympus CX41) using a hemocytometer; at least 6 subsamples and 200 cells each were counted per sample. Counts were at times only conducted on 1 of the two replicate treatments.

TEP concentrations were determined in triplicate using the colorimetric method and are expressed in Gum Xanthan equivalents (GXeq.) (Passow and Alldredge, 1995). Corexit binds to the dye Alcian Blue used for TEP determinations, generating artificially high "TEP" values in the presence of Corexit. Results from methodological tests imply that the degree of this interference depends greatly on the presence of other substances, like oil or dissolved organic matter (DOM), to which Corexit appears to bind competitively. Thus TEP concentrations in the presence of Corexit couldn't be corrected for such artifacts, and TEP concentrations in treatments containing Corexit are not considered.

All biomass results (cell abundance, POC, TEP concentration) are normalized per tank to allow budgets and make aggregate and SSW fractions directly comparable.

EOE was determined using a Trilogy Turner Fluorometer with the crude oil module 7200-63, which measures at excitation wavelength of