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Formation of rapidly-sinking, oil-associated marine snow

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ABSTRACT

Significant amounts of oil accumulated at the sea surface and in a subsurface plume during the Deepwater Horizon (DwH) spill in the Gulf of Mexico (GoM) in 2010. A substantial fraction of this oil was removed from the marine environment by mechanical recovery or burning, or it reached shorelines, whereas another fraction remained within the marine environment, where it dispersed (chemically or naturally), emulsified or sedimented. After the DwH accident the sedimentation of hydrocarbons to the seafloor via rapidly sinking, oil-associated marine snow has become a focus of attention, and it has been hypothesized that marine snow formation significantly impacted the distribution of the oil from the DwH spill.

Here, roller table experiments are presented that investigated the conditions inducing the formation of oil-associated marine snow, focusing especially on the effects of oil type, photochemical aging of oil, and the presence of phytoplankton or dispersant. Large, mucus-rich marine snow, termed microbial marine snow, formed in treatments incubated with the oil that had accumulated at the sea surface. This bacteria-mediated formation of up to cm-sized marine snow in the absence of particles $>1\ \mu m$, represents a unique formation pathway different from that of the physical coagulation of particles. Microbial marine snow, albeit smaller, also formed in the presence of crude oil that had been aged for ≥ 3 weeks in sunlight, but no particles formed in the presence of unaltered crude. The dispersant Corexit 9500A (Corexit:oil ratio = 1:100) impeded the formation of microbial marine snow, requiring a re-evaluation of the benefits and detriments of Corexit 9500A as a mediating measure. Phytoplankton aggregates also incorporated fossil carbon, providing an alternate pathway for the formation of oil-associated marine snow. The ubiquitous formation and rapid sedimentation of oil-rich marine snow can explain the high accumulation rate of flocculent material at the seafloor and on corals observed after the DwH spill. These results may raise awareness that oil spill response and assessment need to include sedimentation of hydrocarbons via marine snow as a significant distribution mechanism and may guide future modeling efforts and budget calculations.

1. Introduction

The Macondo blowout associated with the Deepwater Horizon (DwH) drilling platform was the largest marine oil spill in history and the first large spill located in the deep (>1000 m) ocean (Farrington, 2013). Between the start of the release on 20 April 2010 and the final capping on 15 July, an estimated 780,000 m^3 of crude oil and methane mixture was released from the well head at about 1500 m depth. With a density lower than that of seawater, the hydrocarbon mixture rose toward the surface. Due to dilution and dispersion, some of the rising hydrocarbons split off and formed a subsurface plume, whereas about half of the liquid hydrocarbons reached the sea surface, where a thick layer of oil formed (Atlas and Hazen, 2011; Diercks et al., 2010; Zhou et al., 2013).

Despite the initial buoyancy of the material, a substantial fraction of the hydrocarbons returned to the seafloor, where oil spill contaminated material accumulated in the months after the spill, impacting benthic organisms and leaving a clearly marked footprint of the DwH spill (Montagna et al., 2013; White et al., 2012). The processes which caused the redistribution of oil to the seafloor are currently not well understood; however, the rapid transport of particles from the sea surface to the deep ocean is a common global process that is frequently mediated by marine snow, which are rapidly sinking composite particles >0.5 mm (Alldredge and Silver, 1988; Armstrong et al., 2009; Asper et al., 1992; Diercks and Asper, 1997; Pilskaln et al., 1998). Additionally, it is known that oil may be transported to depths via oil–mineral aggregates (called OMAs or SPM–oil aggregates; Khelifa et al., 2005; Niu et al., 2011). Tar-like residues from weathered oil may also sink directly.

After the Ixtoc spill of 1979 the formation of pancakes and flakes were described as stages in the weathering cycle of floating

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petroleum residues (Patton et al., 1981). These pancakes and flakes, which formed on a timescale of months, were products of the aging oil at the sea surface, similar to pelagic tar (Patton et al., 1981). Such aged oil residues may eventually reach the seafloor.

Oil–mineral aggregates are usually $<50\,\mu m$ (Omotoso et al., 2002; Stoffyn-Egli and Lee, 2002), much smaller than marine snow, but may, depending on clay content and wave action, contribute appreciably towards moving oil residues to the sea floor (Khelifa et al., 2005; Niu et al., 2011), because of the high excess density of minerals. The wide continental shelf of the Northern GoM receives inorganic particles from continental rivers, run-off and coastal erosion and the mid-depth intermediate nephloid layers may extend far past the shelf edge (Dickson and McCave, 1986). Such subsurface mineral plumes, must have offered ample opportunity for the formation and sinking of OMAs after the DwH spill.

The observations of unusually abundant, uncommonly large (mm to cm – sized), and fast sinking marine snow in the vicinity of the oil layer at the sea surface three to four weeks after the spill, in May 2010 (Passow et al., 2012), suggests that the formation of marine snow also contributed appreciably to the transport of oil contaminated material to the seafloor (Dell'Amore, 2010). In the absence of oil, marine snow is known to form either by zooplankton activity or due to coagulation of particles (Alldredge and Silver, 1988). Coagulation theory describes the formation of aggregates via collision and attachment of individual particles like cells, feces and detritus. Aggregation rates thus depend, among other things, on particle size, concentration and stickiness (Burd and Jackson, 2009; Jackson, 2005; Jackson and Burd, 1998). Because of their transient nature, events forming large quantities of marine snow are difficult to document in situ. Moreover, marine snow formation had never been recorded in association with spilled oil; as a result, important details of the marine snow formation event observed after the DwH spill were not documented.

Here, results of six controlled laboratory experiments that explore the formation of marine snow in association with oil are described. The experiments demonstrate specifically how the formation of oil-associated marine snow was influenced by oil type, photochemical aging of oil, the presence of Corexit and the presence of diatoms.

2. Methods

2.1. Experimental set up

The general aim of these laboratory experiments, which were conducted between 2011 and 2013, was to investigate the conditions resulting in the formation of different types of oil-associated marine snow (Table 1). Experiments 1, 2, 5 and 6 were conducted in one liter, rotating cylindrical Plexiglas tanks, which are the standard to mimic natural marine snow formation (Ploug and Passow, 2007; Shanks and Edmondson, 1989). One liter glass and quartz bottles were used in experiments 3 and 4 to allow aging in natural sunlight prior to the incubation on rolling tables. When rolling tanks are entirely filled and bubble free, they provide a turbulence-free environment (Ploug et al., 2010). Turbulent conditions were achieved by filling the tanks only partially or by using bottles (Jackson, 1994). A turbulent environment was provided in all experiments, except in experiment 1 were both turbulent and non-turbulent treatments were compared, and in experiment 6, because more quiescent conditions promote aggregation of diatoms. Tanks or bottles were rotated at 1.5–2.5 rotations per minute; at this speed sinking or floating marine snow never collided with container walls.

Each experiment consisted of 9–10 treatments filled with seawater to which, depending on treatment, oil, dispersant, and/ or phytoplankton was added. All experiments were conducted at 14 °C in walk-in environmental chambers with 12:12 h. light:dark cycles ($<30\,\mu mol\,m^{-2}\,s^{-1}$), except one treatment of experiment 1 where the impact of complete darkness was tested and except all treatments with diatoms, which were kept dark to avoid growth. Light conditions had no visible impact on marine snow formation in the absence of diatoms (experiment 1); thus dark treatments were not further pursued. The formation of marine snow was observed over periods ranging from 8 to 66 d, at the end of which any resulting marine snow was analyzed for dry weight, $PO^{13}C$, and content of transparent exopolymer particles (TEP).

2.2. Seawater

Seawater for experiments 1–4 was collected from above a natural seep off Santa Barbara, California (34.22.481 N, 119.51.197 W) and from above a natural seep in the GoM (GC600: 27°21.311′N, 90°33.196′W) for experiment 5. Seawater from both sites contained no visible oil slicks, but presumably bacterial communities habituated to episodic appearance of low levels of oil were present. Seawater was usually GFF-filtered before use, allowing the presence of the natural bacterial population, but removing particles $>1\,\mu m$. In experiment 1, microbial control treatments were conducted with $0.2\,\mu m$ pre-filtered or artificial seawater (Kester et al., 1967). Raw (unfiltered) seawater was used in another treatment in experiment 1, but concentrations of natural particles $>1\,\mu m$ were low. No significant differences in marine snow number, size and characteristics was observed between these different seawater treatments, indicating that aggregation of particles was not important for the formation of marine snow in experiment 1. Thus the different seawater treatments are all reported as replicates to the GFF-filtered treatments. Diatom cultures were

Table 1
Experiments 1–6 investigated the formation of oil containing marine snow: in experiment 1 both turbulent and non-turbulent treatments were run in parallel. Experiments testing aggregation of diatoms (5 & 6) were run without turbulence; all others (2–4) were conducted with turbulence. Different types of oils (see Table 2) were tested in all experiments, except in experiments 3 and 4 where Macondo crude oil was photo-oxidized for varying amounts of time. Treatments with the dispersant Corexit were present in experiments 1–4. Treatments with diatoms were present in experiments 5 and 6.

Main factors investigated **Microbial marine snow formation in the absence of particles $>1\,\mu m$**	Exp. #	Oil types used
Impact of turbulence	1	Spill oil
Impact of oil type	1, 2, 5, 6	Spill oil; LA-oil; Mac.-oil, CS oil
Impact of photo-oxidation of oil		Mac.-oil
for 1.5 and 3 weeks	3	
for 6 and 12 weeks	4	
Impact of Corexit		Spill oil; LA-oil; Mac.-oil
Low conc.: (10 μL Cor.: 1 mL oil)	2, 3, 4	
High conc.: (1 mL Cor.: 1 mL oil)	1	
Incorporation of oil into phytoplankton aggregates		
Impact of oil type & diatom species	5, 6	Spill oil; Mac.-oil; CS oil

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