Marine Snow Sedimented Oil Released During the Deepwater Horizon Spill

By Uta Passow and Kai Ziervogel

Example of a funnel-shaped, time-series sediment trap, with a 0.5 m² collection area.

Photo credit: V. Asper
INTRODUCTION

The sedimentation of oil compounds in association with marine snow, and the accumulation of oil compounds and marine particles on the seafloor after the Deepwater Horizon (DWH) oil spill in April 2010, were unexpected. Most unaccompanied oil compounds float, and prior to the DWH spill, sedimentation of oil was assumed to be dominated by chemical and physical interactions between oil and minerals. For instance, sinking of heavy residues of weathered surface oil mousse was recorded during the 1979 IXTOC spill in the Gulf of Mexico (Patton et al., 1981). When oil encounters mineral particles, small (usually <50 µm) oil-mineral aggregations (OMAs), which sink rapidly, may form (Muschenheim and Lee, 2002; Khelifa and Hill, 2006). During the DWH spill, some oil reached the seafloor in the immediate vicinity of the wellhead via direct fallout in association with drilling mud or as heavy burn residues, but research into the fate of the spilled oil revealed that the majority of the deposits settled via marine oil snow (MOS).

In contrast to oil mousse and OMAs, MOS formation is mainly driven by the interaction of planktonic organisms and their organic exudates (mucus) with oil. Marine snow (Table 1) becomes MOS when interacting with oil. Most MOS therefore forms under conditions similar to formation of non-oily marine snow, except for the mucus-rich microbial MOS that forms as a response to oil (Table 1).

Evidence of MOS formation and sedimentation following the DWH spill came from underwater camera observations, data from sediment traps (Yan et al., 2016), and observations of deposits at the seafloor (Chanton et al., 2014; Valentine et al., 2014; Brooks et al., 2015; Romero et al., 2015). The flocculent nature of these deposits, and their patchiness and large spatial extent, are all consistent with their sedimentation via MOS. The combination of processes leading to the formation, sinking, and modification of MOS, and the deposition and alteration of this material at the seafloor, are called MOSSFA (see Table 1; Daly et al., 2016).

FORMATION OF MARINE OIL SNOW

Marine oil snow forms through a variety of biologically mediated processes in which planktonic organisms actively or inadvertently repackage particles and oil into rapidly sinking marine snow. Controlled laboratory experiments simulating MOS formation and sinking under different environmental conditions have elucidated some of the mechanisms driving MOSSFA (Figure 1a). Oil may be integrated into marine snow during its formation or as it sinks through an oil plume. Sinking velocities of MOS can reach hundreds of meters per day, which is similar to other types of marine snow.

ABSTRACT. During and after the Deepwater Horizon (DWH) spill in the northern Gulf of Mexico, a massive amount of oil compounds and marine particles, termed floc, accumulated on the seafloor. It is now well established that sedimentation of oil following the DWH spill occurred largely in association with marine oil snow (MOS), a term that became accepted as describing marine snow that incorporates oil. A significant amount of the spilled oil made its way to the seafloor as MOS, appreciably affecting the distribution of oil within the ocean. This article summarizes current knowledge of the different types of MOS that sank, and the underlying processes that led to MOS formation as well as to the sedimentation and deposition of oil on the seafloor during and after the DWH spill.
(Passow et al., 2012). However, experiments show that freshly produced microbial MOS was positively buoyant for hours to days, which could delay its sinking (Passow et al., 2012; Fu et al., 2014; Passow, 2014). Specific formation mechanisms and sedimentation rates of MOS during the DWH spill varied greatly, both spatially and temporally, and the relative importance of the different types of MOS for the sedimentation of oil remains to be determined.

**Detrital MOS**

The first pulse of oil sedimentation, which formed loose floc layers on the seafloor directly below oil slicks (NRDA, 2015), was likely dominated by detrital MOS of dead planktonic organisms. Detrital MOS formation and sinking was not documented in detail; nevertheless, it was estimated that 40 to 70 trillion planktonic organisms (excluding bacteria and viruses) as well as a large number of zooplankton eggs perished in the upper 20 m of the ocean upon direct contact with spilled oil. Cell death is known to result in the formation of detrital aggregates, suggesting that detrital MOS caused the first massive sedimentation events.

**Microbial MOS**

Activities of hydrocarbon-degrading bacteria that flourished in surface waters within days to weeks after the onset of the DWH spill (Atlas and Hazen, 2011; Yang et al., 2014) stimulated the formation of microbial MOS (Passow et al., 2012; Ziervogel et al., 2012). Abundant large, centimeter-sized microbial MOS particles were observed at the margin of surface oil slicks in May 2010. Bacteria responded to the oil, or the oil-water emulsions, by producing large amounts of extracellular polymeric substances (EPSs), which formed the sticky matrix of microbial MOS (Passow et al., 2012; Passow, 2014; Ziervogel et al., 2012, 2014a). EPSs protect against toxins and also emulsify oil compounds, which increases their bioavailability (Gutierrez et al., 2013). EPS-rich microbial MOS has a mucus-like appearance (Figure 1c) and provides structure and substrate for microbial communities. Like biofilms, microbial MOS matrices harbor complex bacterial communities that interact with oil compounds and the emerging degradation products (McGenity et al., 2012; Joye et al., 2014). Experimentally formed microbial MOS revealed high levels of bacterial activities and oil degradation rates (Baelum et al., 2012; Arnosti et al., 2016). Microbial MOS thus contributes to degradation and sedimentation of oil compounds, and en route releases high levels of dissolved oil compounds into the surrounding water (Ziervogel et al. 2012).

Chemical oil dispersants, such as those used during the DWH oil spill (e.g., Corexit 9500; see John et al., 2016, in this issue), may affect the formation of microbial MOS. The presence of Corexit-dispersed oil inhibited or retarded the formation of MOS initially (Passow, 2014), but longer-term experiments suggest that after days to weeks, MOS appears to form (Fu et al., 2014). Possibly, Corexit disperses EPS, which impedes the formation of the marine snow matrix until Corexit is degraded. Corexit also affects the composition of the bacterial community (Kleindienst et al., 2015), with possible consequences for MOS formation.

**Phytoplankton MOS**

A large oil sedimentation event associated with phytoplankton was detected in August 2010 using sediment traps, suggesting that as soon as conditions allowed the formation of phytoplankton blooms, the resulting aggregates incorporated oil, forming sinking phytoplankton MOS (Yan et al., 2016). Laboratory experiments indicate that during and after the DWH spill, phytoplankton aggregates incorporated large amounts of oil (Passow, 2014). Diatom biomarkers in the floc layer that accumulated on the seafloor in DeSoto Canyon to the northeast of the sunken wellhead (Brooks et al., 2015; Mason et al., 2014) confirm that phytoplankton MOS was an important transport vehicle for oil from the DWH spill. Several diatom species have, in the past, been found to regularly co-occur with oil deposits (Kowalewska and Konat, 1997;...
Kowalewska, 1999; Lubecki and Kowalewska, 2010; Parsons et al., 2014), but reasons were not detailed. In fact, this co-occurrence not only suggests the importance of phytoplankton for the sedimentation of oil but also hints at a more complex relationship between diatoms and oil.

After the DWH spill, phytoplankton concentrations were significantly higher than historical averages (Hu et al., 2011), and elevated chlorophyll concentrations have been found associated with hydrocarbon spills or seeps (Ozhan et al., 2014; D’souza et al., 2016). Thus, the size or frequency of phytoplankton blooms, and their sedimentation, may have been elevated compared to non-spill years due to the DWH spill. Additionally, increased nutrient and clay concentrations due to freshwater input (Brooks et al., 2015), as well as resulting salinity gradients, which are known to enhance the formation of particles (Le Floch et al., 2002; Wetz et al., 2009), may have further enhanced the sedimentation potential. Increased sedimentation rates of diatoms could explain the exceptional deposition rate of material in the six months following the spill (Brooks et al., 2015).

**Zooplankton MOS**

During feeding, many zooplankton species effectively concentrate particles (and oil droplets) in their feeding structures, bodies, or fecal pellets. Discarded zooplankton feeding structures, like appendicularian houses, pteropod webs, or fecal pellets thus efficiently transport oil to the seafloor (Conover, 1971; Lee et al., 2012). It was estimated that daily sedimentation of fecal pellets from doliolids (Tunicata) alone could transport up to 200 µg oil m$^{-3}$ to depth (Lee et al., 2012). The importance of zooplankton-derived MOS for the downward flux of oil after the DWH spill remains, however, largely unexplored.

**SEDIMENTATION AND DEPOSITION OF OIL**

MOSSFA events that carried spill contaminants to depth lasted for several months after the wellhead was capped (Yan et al., 2016), but a good spatiotemporal understanding of the different MOSSFA events is still missing. During transit from the surface to the seafloor, sinking marine snow is consumed, fragmented, and repackaged by zooplankton (Rivkin et al., 1996; Rueseler et al., 2007) and utilized and solubilized by bacteria (Kiørboe and Jackson, 2001; Iversen and Ploug, 2013). Additionally, marine snow collects particles (and oil) it encounters en route. Marine snow sedimentation events literally sweep the water column, efficiently removing suspended particles (Smetacek, 1985). Due
Deposition rates of Deepwater Horizon-related marine oil snow immediately after the oil spill were at least four times higher than in 2011 or 2012, and were significantly higher than average sediment deposition rates prior to the spill.

CONCLUSION
Although it has long been known that oil on the seafloor is often found in association with specific phytoplankton, the efficient downward transport of oil via phytoplankton or detrital MOS had not been appreciated before the intense research efforts by federal, industrial, and academic scientists following the DWH spill. Also new was discovery of the formation of microbial MOS in response to the oil. Understanding some of the mechanisms governing MOS formation and sedimentation raises questions regarding the spatiotemporal variability of its different pathways and their relative importance.

The location and size of DWH surface slicks changed daily due to the interactions of currents and wind. Any area contaminated with oil at the surface or at depth could potentially have had that oil transported to the seafloor if a sedimentation event coincided with the presence of the oil. Sedimentation events are mostly biologically driven and depend on the unexpected nature of the sedimentation of MOS and the spill, these processes were not well documented with respect to the DWH spill.

Deposition rates of DWH-related MOS immediately after the oil spill were at least four times higher than in 2011 or 2012, and were significantly higher than average sediment deposition rates prior to the spill (Brooks et al., 2015; Romero et al., 2015). Sinking MOS covered corals (White et al., 2012; Hsing et al., 2013) and formed a 0.5–1.2 cm thick loose floc layer on the seafloor. The observed changes in sediment structure suggest a shoaling of the oxygen penetration depths, indicative of several large sedimentation pulses during the four to six months’ period of elevated deposition (Brooks et al., 2015). The floc that accumulated on sediments was redistributed, resuspended, and processed, with the resulting spatial footprint of floc on the seafloor partially determined by topography. The fate of settled floc was a function of environmental parameters such as hydrodynamic forces, sediment characteristics (e.g., pore size), and temperature, as well as biological activity. The microbial degradation of oil components, for instance, increased after settling of MOS as indicated by changes in bacterial community composition (Kimes et al., 2013; Mason et al., 2014) and bacterial metabolic rates in the floc layers (Ziervogel et al., 2014b). Spatial differences in deep-sea sediments, for example, due to the impact of Mississippi River effluent, gave rise to a spatial mosaic of floc concentrations and characteristics. Moreover, loose floc was prone to resuspension by currents. Re-aggregation, elevated microbial activity, and lateral transport of the resuspended floc were a consequence (Ziervogel et al., 2015). Lateral redistribution during such events further enhances the high variability in floc thickness and quality.

Sedimentation rates of oil were estimated indirectly from material deposited at the seafloor using oil compounds (Valentine et al., 2014; Stout et al., 2015) or radioactive carbon signals (Chanton et al., 2014), or directly from sediment traps (see title page photo; Stout and German, 2015). It is estimated that at least 2%–15% of all the spilled oil reached the seafloor (Box 1), but the patchy distribution of deposited MOS and the complexity of MOSSFA processes (Daly et al., 2016) combined with the large spatial extent of this signal result in a significant uncertainty in this estimate. An estimated deposition of around 10% or even 15% of the spilled oil is almost certainly too low for several reasons. First, sediment sampling efforts focused on the vicinity of the spill site, covering an area of about 24,000 km² (Box 1), whereas the cumulative area of surface oil coverage was five times higher (112,115 km²). High deposition rates outside of the main sampling area, like in DeSoto Canyon, confirmed that MOS sedimentation occurred in an area greater than the vicinity of the spill site. Second, biotic and abiotic processes at the seafloor such as bioturbation, degradation, and lateral transport reduce the thickness of floc layers, thus skewing estimates of sedimentation rates based on deposition rates measured in sediment cores. This presumably was less of a problem in areas where deposition rates were extremely high, because thick floc layers resulted in the suffocation of benthic organisms and thus reduced bioturbation and loss. In contrast, moderate to small sedimentation events would leave a signal on the seafloor that lasts only days to weeks. Material collected in sediment traps is preserved, but the lack of good spatial sediment-trap coverage prevents significant spatial understanding of oil sedimentation rates during the DWH spill.
**Box 1. Consolidating Estimates of Petroleum Deposition onto the Seafloor**

**FIGURE B1.** The triangle marks the Deepwater Horizon well, and the yellow circles are coring sites in the DeSoto Canyon area. See Table B1 for footprint characteristics. The dotted footprint assumes sedimentation rates as measured with a shallow sediment trap in the Viosca Knoll region over the area in which at least 30 cumulative oiling days were observed. This increased the original deposition footprint (green, blue) appreciably. The composite map was produced by georeferencing published pdf format maps and digitizing into a common reference frame using GIS software. The composite map is projected in the Web Mercator projection with a WGS1984 Datum. Base map sources: ESRI, DeLorme, GEBCO, and NOAA NGDC.

**TABLE B1.** Deepwater Horizon footprint characteristics. See Figure B1 for locations of the dotted and solid color lines.

<table>
<thead>
<tr>
<th>Deposition or Sedimentation</th>
<th>Area km²</th>
<th>Fraction of spilled oil</th>
<th>Measured Quantity</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orange Footprint</td>
<td>NA</td>
<td>NA</td>
<td>Impact on benthic macro- and meiofauna</td>
<td>Montagna et al. (2013)</td>
</tr>
<tr>
<td>Blue Footprint</td>
<td>1,300</td>
<td>1%–9%*</td>
<td>Hopane in floc on sediment</td>
<td>Valentine et al. (2014)</td>
</tr>
<tr>
<td>Green Footprint</td>
<td>1,800</td>
<td>4%*</td>
<td>Hopane in floc on sediment</td>
<td>Stout et al. (2015)</td>
</tr>
<tr>
<td>Solid Black Footprint</td>
<td>24,000</td>
<td>3%–5%*</td>
<td>Radiocarbon in floc at sediment surface</td>
<td>Chanton et al. (2014)</td>
</tr>
<tr>
<td>Dotted Footprint =</td>
<td>7,600</td>
<td>Additional 1%–2%*</td>
<td>Flux rates of oil compounds</td>
<td>Stout et al. (2015)</td>
</tr>
<tr>
<td>Additional area of ≥ 30 oiling days</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DeSoto Canyon area</td>
<td>~2,000</td>
<td>Additional &lt;1%</td>
<td>Oil compounds in floc on sediment</td>
<td>Romero et al. (2015)</td>
</tr>
</tbody>
</table>

* These estimates are considered minimum values as they frequently do not include oil residue below the sediment surface, as the spatial extent of oil deposition is frequently truncated, and as deposition rates are small compared to sedimentation rates (also see text).

NA = not applicable.
organism dynamics. In a general sense, increased productivity results in increased sedimentation, but this relationship is not straightforward, and a swarm of salps, for instance, would lead to large settling rates. Coincidence of oil and a sedimentation pulse may thus be hard to predict. Additionally, it appears that the oil itself, as well as the char from in situ burning, promoted aggregation and sedimentation, increasing the probability of sedimentation events during the spill.

The formation and settling of MOS has far-reaching implications for the distribution pathways of oil and for benthic ecosystems. The post DWH research efforts emphasize the need for accurate quantification of sedimentation rates and processes during and after spills in order to improve future response efforts. Sediment traps and marine snow cameras should be an essential component of any future monitoring program after a spill.

REFERENCES


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