Changes in Sediment Redox Conditions Following the BP DWH Blowout Event

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Changes in sediment redox conditions following the BP DWH blowout event


Abstract

Following the blowout of the Macondo well, a pulse in sedimentation resulted in changes in sedimentary redox conditions. This is demonstrated by downcore and temporal changes in the concentration of redox sensitive metals: Mn, Re, and Cd. Sediment cores collected in the NE Gulf of Mexico (GoM) reveal increased sedimentation after the Deepwater Horizon (DWH) blowout. The formation of mucous-rich marine snow in surface waters and subsequent rapid deposition to underlying sediments is the likely cause. Respiration of this material resulted in decreased pore-water oxygen concentration and a shoaled redoxcline, resulting in two distinct Mn peaks in sediments following the event, one typically in the top 10 mm, with the other at 20–30 mm. Most cores near the wellhead reveal this non-steady state behavior for up to two years after the event. Associated with the Mn minimum between the two Mn peaks, a modest (15–30%) enrichment of Re consistent with reducing sediments typically exists. A three-year time series of three stations following the event reveal that sediment Re increased 3–4 times compared to the pre-impact baseline value for two years, indicating sediments are increasingly more reducing for two years. In the third year, Re concentration decreased, suggesting a return towards pre-impact conditions. In select sites where the density of benthic foraminifera was determined, an assemblage-wide decrease occurred coincident with reducing conditions as determined by redox sensitive metals, demonstrating the important consequences of changing redox conditions on benthic ecosystems. Determination of redox sensitive metals will continue to constrain the temporal evolution of reducing conditions, which will serve to document the long-term effects of the spill, and the possible return to pre-event conditions.

Keywords: Oil spill, Gulf of Mexico, Deepwater Horizon, Paleoredox, Trace metal, Rhenium, Manganese

1. Introduction

The uncontrolled release of oil following the blowout event on April 20, 2010 on the Deepwater Horizon drilling platform was unique in many respects. It was the largest offshore accident in the history of the U.S. petroleum industry with over 600 million L of oil (Atlas and Hazen, 2011) and 1.0–1.5 × 10^10 mol of natural gas (Valentine et al., 2010) released into the marine environment at a depth of 1544 m, accompanied by over 6.8 million L of dispersant (Kujawinski et al., 2011). This was the largest accidental release of petroleum and gas into the marine environment, at the deepest depth of 1544 m, accompanied by over 6.8 million L of dispersant (Valentine et al., 2010) released into the marine environment at a spill. The dispersant was added both at depth and at the surface.

The exact fate of the released oil is difficult to determine; best estimates are that 35–60% reached the surface, where it evaporated, was deposited on the coast, or was incorporated into flocculent material (Ryerson et al., 2012; Thibodeaux et al., 2011). Subsurface intrusions of natural gas and oil formed, at 1000–1300 m and at ~400 m (Joye et al., 2011). These estimates leave about one third of the total oil released unaccounted for.

During and following the event, a large amount of mucous-rich marine snow contaminated with oil formed in the surface waters (Passow et al., 2012). Several mechanisms have been proposed to explain the formation of the marine snow following the event, including coagulation of phytoplankton with oil droplets; coagulation of suspended matter with the oil droplets; and production of mucosoid material from the degraders of the oil, which grew and multiplied rapidly following the event (Passow et al., 2012). Increased microbial activity following the event has been well documented at the surface and in the water column (Edwards et al., 2011; Joye et al., 2014; Redmond and Valentine, 2011; Valentine

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et al., 2010; Ziervogel et al., 2012). The consequent microbial production of sticky transparent exopolymeric particles (TEP) enhances the aggregation process, as would the release of exopolymeric substances (EPS) by phytoplankton (Passow, 2000; Verduco and Santschi, 2010). Marine snow may have formed within the subsurface oil intrusions as well as at the surface (Passow, 2014; Passow et al., 2012; Ziervogel et al., 2012).

The large flocs of marine snow observed in the upper water column were the precursors of what is observed as a substantial sedimentation pulse (Schrope, 2013). While exact documentation of the sedimentation event remains challenging due to the rapid time scale, there is evidence in the benthic environment of increased sedimentation over an extensive area in the NE Gulf of Mexico (GoM) close to the wellhead following the spill (Montagna et al., 2013; White et al., 2012; Ziervogel et al., 2012). The swift transport of particles from the surface to the sediments is a well-established process with relatively large sinking particles (e.g. Alldredge and Silver, 1988; Asper et al., 1992). Consistent with this pulse, a visually distinctive, brown, fine-grained surface layer in the top 1–2 cm with dark brown or black bands is seen in the sediment cores affected by the blowout event.

A single mechanism for this increase in sedimentation has not been identified. The formation and aggregation of marine snow following the event, sinking rapidly to the bottom, is one likely scenario. Mucous-rich marine snow was observed following the spill (Passow et al., 2012), and in simulations of the spill (Passow, 2014), which is consistent with the rapid sedimentation to depth. Changes in the outflow of the Mississippi River is another feasible mechanism. The Mississippi River was diverted in an effort to protect sensitive coastlines, and with a modest increase in Mississippi River outflow (Blanchi et al., 2011), silicilastic input to the GoM may have increased. About 5% of the total oil released was burned (Ryerson et al., 2012); the pyrogenic remnant waste could be another contributor to the sedimentation pulse, albeit a minor one. Our hypothesis was that the pulse of organic rich material to the sea floor was associated with the marine snow event resulted in increased respiration of organic carbon in the sediments, which in turn resulted in decreased oxygen in sediment pore waters. We use changes in the relative concentration of redox sensitive elements, Mn, Re, and Cd, to constrain changes in the redox state of marine sediments following the blowout event.

1.1. Background: redox sensitive metals

Authigenic enrichment of redox sensitive metals occurs under reducing conditions since these metals undergo a change in redox state and either become less soluble, are adsorbed to surfaces, or form insoluble metal sulfides. These metals have been exploited in numerous studies to constrain paleoredox conditions (e.g. Crusius et al., 1996; Dean, 1989; Morford et al., 2001, 2012; Nameroff et al., 2002; Tribovillard et al., 2006). Bulk Mn is depleted, and Re, Cd, V, Mo, and U are all authigenically enriched under reducing conditions providing an excellent proxy for low oxygen and anoxic environments. In this study, we focus on Mn, Re and Cd. Several excellent review articles (Algeo and Rowe, 2012; Morford and Emerson, 1999; Tribovillard et al., 2006) describe these processes in detail; a summary of their geochemical behavior is provided below.

1.1.1. Manganese

The redox chemistry of manganese (Mn) in marine sediments has been studied extensively, in part due to the importance of Mn cycling across the redoxcline in reducing environments. Solid Mn (IV) oxides delivered from overlying seawater are readily reduced to dissolved Mn(II) when pore water oxygen is consumed. The soluble Mn(II) diffuses upward, and where pore water oxygen is present, is then oxidized to Mn(V) oxide completing the redox cycle of Mn in the sediment (e.g. Burdige and Gieskes, 1983; Froelich et al., 1979; Gobeil et al., 1997). A distinct peak in bulk Mn typically marks the top of the redoxcline. Recent findings of abundant porewater Mn (III) in hemipelagic sediments requires a revision of this classic redox model to include one electron transfer reactions for the Mn cycle (Madison et al., 2013). Dissolved Mn(III) intermediates are produced by oxidation of Mn(II) by dissolved oxygen as well as dissimilatory MnO2 reduction by organic matter (Madison et al., 2013).

1.1.2. Rhenium

Rhenium (Re) behaves conservatively in seawater, is mobile under oxic conditions, and precipitates under mildly reducing conditions (Crusius et al., 1996). It is ideally suited as a redox tracer since its detrital concentration is very low relative to the authigenic deposition; oxic marine sediments have low concentrations of 0.6 ppb or less (Boyko et al., 1986; Koide et al., 1986). Re is not enriched in ferromanganese nodules (Koide et al., 1986), does not show an association with either Fe or Mn oxides (Morford et al., 2005; Schaller et al., 2000), and hydrothermal processes play a negligible role in Re geochemistry (Ravizza et al., 1996). Re is enriched in reducing sediments because dissolved Re(VII)O4 is reduced and precipitates in the solid phase, most likely as Re(IO)2 (Crusius et al., 1996). Re enrichment occurs under both anoxic (Colodner et al., 1993) and suboxic conditions, below the zones of U and Fe reduction and prior to sulfate reduction (Crusius et al., 1996; Morford et al., 2005).

1.1.3. Cadmium

Cadmium (Cd) is a nutrient-like element in seawater, with water column profiles analogous to dissolved phosphate implying an association of Cd with biogenic soft parts. Degradation of Cd-rich organic material results in enrichment of Cd at or just below the sediment–water interface. Authigenic enrichment occurs where Mn is depleted, just below the redox front (Gobeil et al., 1997). Enrichment of Cd is a consequence of precipitation of an insoluble sulfide phase at very low sulfide levels below common analytical detection limits of several μmol/kg (Rosenthal et al., 1995a).

1.1.4. Barium

Barium (Ba) in marine sediments is controlled by several factors. Ba preservation declines under suboxic conditions, with high organic carbon respiration and/or low bottom water oxygen (McManus et al., 1998). Thus, the accumulation rate of marine barite in marine sediments has been used to reconstruct past changes in ocean productivity (e.g. McManus et al., 1999; Paytan and Griffith, 2007). Authigenic barite forms in the water column, as well as within marine sediments and around hydrothermal vents and cold seeps (Griffith and Paytan, 2012), many of which are found in the Northern GoM and is thus of particular importance (Feng and Roberts, 2011; Joyce et al., 2010). Mississippi River water is enriched in barium relative to GoM water (Hanor and Chan, 1977).

Of special relevance to this work, barium is highly enriched in drilling mud, which relies on barite to increase the density (Trocine and Trefry, 1983). In May 2010, an attempt was made to plug the leaking well with more than 105 bbl/day (> 200 × 103 L/day) of high density drilling mud, the so-called “top kill” (National Commission on the BP Deepwater Horizon Oil Spill, 2011). An enrichment of Ba was seen in deep-water plume samples in May 2010 associated with this effort (Joung and Shiller, 2013). Enrichment of Ba in surficial sediments close to the wellhead is evidence of this effort.
2. Methods

2.1. Site description

We collected sediment cores at five stations in the NE GoM aboard the R/V Weatherbird II on a series of cruises from August 2010 to August 2013 (Fig. 1; Table 1). Cores were retrieved with an Ocean Instruments MC-800 multi-corer, which collects up to eight 10 cm diameter cores without disturbing the sediment-water interface. Cores were carefully extruded using a calibrated threaded rod at 2 mm resolution in the top 20 mm, and at 5 mm resolution below 20 mm.

Sediment samples from stations close to the wellhead were retrieved with a box core aboard the RV Pelican leg PE-1031 on May 5–9, 2010, two weeks after the explosion, which we use as a pre-event control since it precedes the large sedimentation pulse. Cores were extruded at 2–3 cm resolution.

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Box cores from the Fisk Basin (PE07-5I; 817 m depth; 27°33.0' N, 92°10.1' W) and Garrison Basin (PE07-2; 1570 m depth; 26°40.5' N, 93°55.5' W) were collected on the R/V Pelican in 2007; a box core beneath a long-term sediment trap mooring in the NGoM was collected in January 2009 (PE09-004 MC1). Linear sediment accumulation rates are relatively high (20–40 cm/kyr) due to large inputs of terrigenous material from the Mississippi River. AMS 14C dates with bomb radiocarbon confirm that the core-top samples include the most recently deposited sediments (Richey et al., 2007).

2.2. Visual core descriptions

Cores collected in the NE GoM on August 2010 and later reveal a surficial dark brown layer, 1–10 cm thick, overlying a lighter, tan colored layer, which extends to the base of the sediment core. Within the dark brown surface layer, at least one and sometimes two distinct darker brown-black bands are present. The sediment–water interface for core DSH-08 (February 2011) was at an incline, with a 5–7 mm offset from one side to another. Thus, the interval that we report at 7 mm depth was at the sediment water interface and exposed to bottom water on one side of the core barrel.

2.3. Solid phase analyses

Subsamples (~0.2 g) were freeze dried, weighed, then digested in a Milestone Ethos EZ microwave oven in closed Teflon® digestion
vessels with 10 mL concentrated trace metal grade HNO₃ at 165 °C and high pressure (~25 bar) for 15 min according to standard methods (US EPA method 3051a). The digest was diluted 1:10 with MQ ultrapure H₂O, and filtered with 0.45 μm PVDF syringe filters. Since HF was not used in the digestion method, the digest does not include refractory components such as aluminosilicates, but does include authigenic phases, crude oil, organic phases, FeMn oxides, and carbonates.

The samples were analyzed using an Agilent 7500cx ICP-MS with an octopole reaction cell in helium mode for Mn, Fe, and Cd to reduce isobaric interferences and in no-gas mode for Mo, Ba, and Re. Prior to analysis, samples were spiked with an internal standard containing Ge, In, and Bi in order to correct for instrumental drift during analysis. Elemental concentrations were determined using a 6-point external calibration line. Triplicate samples were typically measured for one or two depth intervals in each core with an average relative precision of ±2%, ±4%, and ±4% (1σ) for Mn, Re, Cd and Ba, respectively. Long-term analytical precision based on analyzing the same sample 3 times each run over 1.5 years of ICP MS analyses is ±3%, ±5%, and ±2% (1σ) for Mn, Re, Cd, and Ba, respectively. A complete data set collected under this project, including all elements determined by ICP-MS, is stored with the Gulf of Mexico Research Initiative Information and Data Cooperative (GRIIDC) and available at https://data.gulfresearchinitiative.org. The data set used in this paper is available as a supplementary data set at http://www.pangaea.de.

3. Results

3.1. Pre-impact results

Our first task is to establish natural, pre-event levels of redox sensitive metals and the normal depth of the redoxcline before the spill. Determining this is a challenge, since sediment cores near the wellhead were not sampled at high resolution before the event. We identify pre-event conditions using sediment cores at three sites located in the Northern GoM: Garrison and Fisk Basin, and site PE 09-004, where a sediment trap is moored. We also obtained a suite of four cores near the wellhead taken less than two weeks after the explosion and before substantial sedimentation occurred; the site closest to the wellhead is presented here. Authigenic metal data are presented graphically in Fig. 2a–d, and in supplementary data Table 1.

3.1.1. Garrison basin

(Fig. 2a; 1570 m): Mn values are at a low baseline value in the top 120 mm, increase to a distinct peak at 162 mm, then decrease back to baseline levels. Both Re and Cd remain low with no enrichment at depth. These profiles indicate a redoxcline at 170–180 mm, where bulk Mn begins to decrease, with no enrichment of either Re or Cd associated with reducing conditions. Ba values

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Table 1
Sample sites.

<table>
<thead>
<tr>
<th>Site ID</th>
<th>Latitude</th>
<th>Longitude</th>
<th>Water depth (m)</th>
<th>Collection date</th>
</tr>
</thead>
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<tr>
<td>DSH-08</td>
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<td>87° 52.064W</td>
<td>1143</td>
<td>December 2010</td>
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<tr>
<td></td>
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<td>August 2013</td>
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<td>87° 15.973W</td>
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<td>89° 4.17W</td>
<td>1187</td>
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<td>88° 23.237W</td>
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<td>93° 55.5W</td>
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<td>27° 31.508N</td>
<td>90° 10.126W</td>
<td>1132</td>
<td></td>
</tr>
</tbody>
</table>

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3.1.2. Fisk basin

(Fig. 2b; 817 m): Shallower and situated closer to the mouth of the Mississippi River than Garrison Basin, Fisk Basin shows a shallower redoxcline, at 90–120 mm, as indicated by the Mn peak centered at 80 mm. Re is constant at 0.4 ppb from the surface to 110 mm, where it increases to the base of the core. Cd decreases from the surface to 170 mm, and then increases to 0.4 ppm at the bottom of the core, likely associated with CdS(s) formation. In both Garrison and Fisk Basin, Ba decreases from surface values of 300 and 600 ppm, respectively, to ~200 ppm in the top 10–40 mm.

3.1.3. Sediment trap site PE09-004

(Fig. 2c; 1132 m): Closer to the wellhead than either Garrison or Fisk Basin, this site adds insight into pre-impact profiles of redox sensitive metals at a depth similar to impacted sites. A distinct Mn peak at 77 mm with Re enrichment directly below this depth indicates a redoxcline somewhat shallower than the two other pre-impact sites. The absence of Cd enrichment is consistent with no sulfide, and therefore no CdS(s).

3.1.4. Proximal to DWH wellhead PE 1031-6

(Fig. 2d; 1380 m): Sediments taken two weeks after the explosion 7 km from the DWH wellhead at site PE 1031-6, show Mn decreasing from 12.6 mg/g at the surface (0–20 mm), to 2.7 mg/g at 65 mm. Re increases from 0.6 ppb in the top 20 mm to 1.4 ppb at 35 mm, followed by more substantial increases to 2.6 ppb at 100 mm and 5.7 ppb at 125 mm. The sample resolution for this core is coarse, 20–30 mm, and is not adequate to resolve the characteristic Mn peak, or allow a detailed comparison to our sampling at 2 mm resolution. Sediments from three additional sites sampled at the same time close to the wellhead were also analyzed as part of our effort and provide insight into pre-event [Re].

3.2. Post-impact results

3.2.1. Time series

Three sites were sampled five to six times between August 2010–August 2013, allowing us to determine how the event impacted surficial sediments and to constrain the temporal evolution of reducing conditions. While Mo, V, and U are enriched in suboxic and anoxic sediments and are frequently part of the suite of redox sensitive trace metals, downcore changes in these elements were associated primarily with changes in Mn oxide (e.g., Hem, 1978) and did not provide geochemical insight into other processes. We do not discuss changes on Mo, V, and U since they primarily reflect changes in bulk Mn in the surficial sediments affected by the depositional event. Rather than present figures of all 17 downcore metal profiles from each time different stations were sampled, we describe general trends and present downcore results that are representative of element profiles at the three different stations. In each figure, the surface 30 mm is shown in greater detail to reveal more subtle changes in down core concentrations. A complete data set with metal data from each station are provided in supplementary data Table 1. Temporal evolution of reducing conditions is best described by changing [Re] over time.

3.2.2. DSH-10

Bulk Mn is typically characterized by two peaks in the top 5–30 mm, separated by about 15 mm (Fig. 3a–c). In December 2010 and August 2013 profiles, there is a broad Mn maximum spread between 5 and 19 mm, rather than two distinct peaks; the surficial Mn peak at 11 mm in the February 2011 profile is characterized by just one point, with a relatively small increase of 3 mg/g (25%). In most profiles, there is a modest Re enrichment of 0.1–0.3 ppb coincident with the Mn minimum defined by the two peaks. This is either not significant or nonexistent in September 2011, August 2012, and August 2013. Except for September 2011, Re increases to a distinct relative maximum just below the
second Mn peak, then decreases before increasing again at depth, typically at ~100 mm. For August 2010 and February 2011, a secondary Cd peak of 0.08 ppb and 0.05 ppb exists at 5 mm and 19 mm, respectively, in addition to the broad Cd enrichment below the deeper peak common in all profiles. This secondary Cd peak is reduced in the September 2011 and August 2012 profiles.

Fig. 3. Redox sensitive metal and Ba profiles at time series site DSH 10, 1520 m for (a) August 2010, (b) December 2010, and (c) August 2012.
3.2.3. **DSH-08**

As with DSH-10 there are two Mn maxima in the surface 30–40 mm for samples taken in December 2010 and February 2011. Re increases from the surface by ~0.2–0.4 ppb to a maximum coincident with the Mn minimum (Fig. 4a and b). In February 2011, there is also a Re peak at 29 mm, at the base of the second Mn peak. The last three sample dates (September 2011, August 2012, August 2013) show a single Mn peak, or a very subtle second peak, rather than a distinct double Mn peak, with a more gradual decline in Mn to the baseline values at depth. In August 2013, Re has a distinct peak at 15 mm where Mn is decreasing. Below the relative minimum at 19 mm, Re then gradually increases to the base of the core.

3.2.4. **PCB-06**

In December 2010 (Fig. 5a), double Mn peaks are evident, close to the surface at 5 mm and at 21 mm, a feature which is less pronounced in February 2011 (Fig. 5b), and subdued, or no longer present, in the last three sample efforts (September 2011, August 2012, August 2013). In December 2010, a modest Re enrichment of 0.1 ppb is coincident with the Mn minimum at 7 mm (Fig. 5a). Re enrichment above background values is at the surface in February 2011; surface Re continues to be above background values in September 2011. Subsurface Re peaks at 50–70 mm are evident in all but the February 2011 core. For December 2010, February 2011, and September 2011 a secondary Cd peak exists at 15–17 mm, in addition to the broad Cd enrichment below the deeper peak common in all profiles. Minor variations in Re patterns in August 2012, and 2013 cores seem to show the opposite patterns: modest Re increases are not coincident with Mn minima.

3.2.5. **SW-01, April 2012**

Mn is characterized by two peaks, at 15 mm and 81 mm with a relative minimum at 35 mm (Fig. 6). Re mirrors the Mn profile with a

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**Fig. 4.** Redox sensitive metal and Ba profiles at time series site DSH 08, 1143 m for (a) December 2010 and (b) February 2011.
clear maximum at 35 mm, a minimum at 60–80 mm, then increasing to a maximum of 2.4 ppb at 142 mm. At or below the redoxclines as defined by the Mn minima, Cd increases to a maximum of 0.22 ppm at 35 mm and again at 102 mm. Ba shows an unusual downcore profile, with two distinct maxima; Ba values are consistent with normal, pre-impact concentrations (265 ppm) at the surface, with distinct maxima at 5 mm (1 100 ppm) and at 51 mm (1000 ppm).

4. Discussion

4.1. Pre-impact geochemistry

It is well established that the downward flux of organic carbon to the sediments, and subsequent oxidation, is the driving force for early diagenesis in marine sediments, resulting in the reduction of a series of electron acceptors: oxygen, nitrate, Mn oxides, Fe oxides, then sulfate, in order of decreasing energy per mole organic carbon (e.g. Emerson et al., 1980; Froelich et al., 1979). After oxygen is nearly depleted, nitrate is reduced, followed by reduction of Mn(IV) oxides to Mn(II). The dissolved Mn(II) diffuses upward, is reoxidized to Mn(IV) by pore water oxygen, and then trapped within the sediment. Under steady-state conditions, this leads to the formation of a single Mn peak, which typically defines the depth of the redoxcline (e.g. Burdige and Gieskes, 1983). The redox state of surface sediments and the depth of the redoxcline is controlled by the flux of organic carbon to sediments, bottom water oxygen concentration, and the degradation rate constant for the carbon (e.g. Emerson et al., 1985). This single Mn peak typical of continental slope sediments is clearly observed in cores we sampled before the event from the Sediment Trap Site, Fisk Basin, and Garrison Basin, at 77 mm, 80 mm, and 165 mm, respectively. Re increases below the Mn peak, consistent with Re enrichment in mildly reducing sediments. This characteristic Mn peak is considerably shallower in cores near the wellhead (e.g. PE-1031-6) since they are closer to the Mississippi River, with its high nutrient load and resulting high productivity and high sedimentation rate.

4.2. Post impact – organic geochemistry

Following the blowout event, our working hypothesis is that the accumulation of marine snow resulted in a substantial sedimentation pulse. In addition to an increase in sedimentation rate,
Figure 6. Redox sensitive metal and Ba profiles at site SW-01, 1187 m; April 2012.
4.4.1. Evolution of Re enrichment

We examined the change in Re for the three stations for which a 36-month long time series exists. Since Re changes substantially with depth, as well as over time, choosing a consistent depth interval is important. For DSH-10 and PCB-06, we chose the distinct Re peak centered at 40 mm and 60 mm, respectively. For DSH-08 where no distinct Re peak exists, we chose [Re] at 50 mm, approximately where the Re peaks occurred at the two other sites. At each site, subsurface authigenic Re concentrations at ~50 mm increase substantially over two years, increasing 3–4 times compared to the pre-impact value for Re (Table 2; Fig. 7). We determined the pre-impact value for Re based on the suite of cores (PE-1031) collected at different water depths just after the explosion occurred, and before substantial sedimentation or deposition of oil (see supplementary data Table 1). These pre-impact Re values are indicated at the y-axis on Fig. 7. The increase in Re demonstrates a clear change in sedimentary redox conditions after the impact, and continuing over the subsequent two years. The Re enrichment suggests persistent reducing conditions due to continued remineralization of organic carbon. The pulse of organic carbon must be incorporated into the sediment, and not simply at the sediment-water interface, for it to have an effect on the oxygen content within the sediment (Gobeil et al., 1997). Since the accumulation of sediment from the pulse was at least 20 mm, this criterion is satisfied. The final Re “peak” value for both DSH 10 and PCB 06 on August 2013, three years after the initial sample, is substantially lower, indicating a return towards pre-impact conditions at DSH 10 and PCB 06 or integration of the subsurface Re peak into adjacent depths.

4.5. Post impact: Cd enrichment

Changing redox conditions is also a control of the dynamic down core concentration profiles of Cd. Distinct Cd peaks of ~0.1 ppb at 15–17 mm in cores from PCB-06 in December 2010, February 2011 and September 2011 are consistent with the presence of low concentrations of sulfide and formation of authigenic CdS (Rosenthal et al., 1995b). This near-surface Cd enrichment is also observed in the August 2010 DSH-10 profile and at DSH-08 in December 2010. These peaks are in addition to the deeper, broader, and greater Cd enrichments at ~60 mm and deeper. The shallow, secondary Cd peaks are absent or substantially diminished in later cores from August 2012 and 2013, which suggests oxidation of the free sulfide, burndown of the CdS, and return towards pre-impact conditions.

4.6. Post impact: ecological impact

Down core changes in Mn and Re reveal clear evidence of changes in redox conditions following the event. What is the ecological impact of such changes on the benthic community? Given that redox changes occurred at the mm scale, benthic foraminifera are potentially sensitive indicators of the changes in reducing conditions. We have documented changes in the density of benthic foraminifera at two sites, DSH-08 and PCB-06, in December 2010 and February 2011 (supplementary data Table 2). Where Mn and Re indicate significant reducing conditions by Mn depletion and Re enrichment, there is a clear decrease in density of the dominant genera of benthic foraminifera.

At site DSH-08 in December 2010, a 40–60% reduction in both Bulimina spp. and Uvigerina spp., the most abundant genera of benthic foraminifera, occurs between 13–17 mm (see supplementary data Table 2). This is coincident with the Mn minimum, and a modest (0.20 ppb; 35%) Re enrichment (Fig. 4a). At the surface, a significant decrease in density of benthic foraminifera occurs, while a modest (0.16 ppb; 30%) Re increase and Mn minimum occurs, consistent with reducing conditions (Fig. 4a). On the subsequent sampling date, February 2011, a dramatic reduction in the most abundant genera, Bulimina spp., Uvigerina spp., occurs at 13 mm, coincident with the Mn minimum and a 0.14 ppb increase in Re (Fig. 4b). A similar large reduction in “other species”, primarily Brizalina spp. and Bolivina spp., also occurs at this depth.

Site PCB-06 reveals a similar relationship between redox sensitive metals and benthic foraminiferal density. In December 2010 a 60% reduction in Brizalina spp. and Bolivina spp. (“other species”) occurs at 8 mm, coincident with the Mn minimum and a 0.07 ppb (15%) increase in Re. In February 2011, a dramatic decrease in density of the dominant three genera occurs in the surface 0–8 mm, entirely consistent with decreases in Mn in that depth range, and an unusual 0.18 ppb (30%) increase in Re in the top 5 mm (Fig. 5b). Decreases in Uvigerina spp. in core PCB-06 December 2010 at shallow depths (~4 mm), are not exactly coincident with changes in Re or Mn. This could be an offset between the two multicores, since the redox sensitive metals and the foraminifera were sampled in different cores. Alternatively, another mechanism may be responsible for changes in foraminiferal density. PAH compounds and other toxic organic compounds found in the crude oil and/or dispersant may be another reason for the changes in foraminiferal density.

5. Conclusions

Downcore concentration profiles of redox sensitive metals from sites in the NE GoM sampled before the blowout event, just after the explosion near the wellhead, or distal from the wellhead after the event, are typical of continental slope sediments. Bulk Mn is distinguished by a single peak caused by reduced Mn(II) at depth diffusing up to oxic sediments where it precipitates, thus defining

<table>
<thead>
<tr>
<th>Date</th>
<th>Re (ppb) DSH-10</th>
<th>Re (ppb) PCB-06</th>
<th>Re (ppb) DSH-08</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before event</td>
<td>1.39</td>
<td>1.1</td>
<td>1.0</td>
</tr>
<tr>
<td>August 2010</td>
<td>2.15</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>December 2010</td>
<td>2.36</td>
<td>1.85</td>
<td>0.94</td>
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<tr>
<td>February 2011</td>
<td>2.64</td>
<td>1.33</td>
<td>0.97</td>
</tr>
<tr>
<td>September 2011</td>
<td>1.89</td>
<td>2.54</td>
<td>1.79</td>
</tr>
<tr>
<td>August 2012</td>
<td>3.79</td>
<td>3.95</td>
<td>2.15</td>
</tr>
<tr>
<td>August 2013</td>
<td>2.64</td>
<td>1.87</td>
<td>2.45</td>
</tr>
</tbody>
</table>

ND: no data since station was not sampled on that date.

* No distinct Re peak.
the depth where sediments become reducing. Immediately below the Mn peak, Re increases above detrital values, followed by increases in authigenic Cd reflecting a CdS phase. Water depth and distance from the Mississippi River have a substantial influence on the depth of the redoxcline and the behavior of these reduct sensitive metals.

Following the blowout event, a substantial marine snow event which lead to a large sedimentation pulse was recorded in NE GoM sediments. Subsequent respiration of the organic carbon associated with the marine snow resulted in reducing conditions, as evidenced by downcore changes in reduct sensitive metals Mn, Re and Cd.

After the event, at three time series sites (DSH-08, DSH-10, and PCB-06) and at SW-01, double Mn peaks are typically present, at ~5 mm and at ~20–30 mm, consistent with the non-steady state behavior associated with a shoaling redoxcline and a relic Mn peak. Some profiles do not show two distinct peaks but reveal shoulders with relatively high Mn values over a broad depth range of 10–15 mm. These double Mn peaks result from the observed changes in the input of organic carbon and possibly a more labile carbon source. Double peaks of Re and Cd are present in several profiles, indicating non-steady state behavior for these reduct sensitive metals as well.

Re concentrations at the subsurface maximum (40–60 mm) increase over two years at all three sites, demonstrating that reducing conditions persist over time. In the last sampling effort in August 2013, [Re] decreased at two sites, suggesting a possible return towards pre-impact conditions. Cd enrichment indicates depths where CdS is precipitating due to presence of sulfide and reducing conditions. In August 2012 no double peak for Mn is seen at PCB-06, and the secondary peak in DSH-08 is minor, another indication that the surface sediments (<30 mm) may have begun toward return to pre-impact conditions.

An assemblage-wide decrease in benthic foraminiferal density occurred at the same depth intervals as reducing conditions suggesting an important consequence of changing reduct conditions in sediments to biotic communities.

Acknowledgments

We dedicate this work to Benjamin Flower, who passed away in July 2012. Ben was careful and caring, hard working and honest, and dedicated to his family, friends, and colleagues. He was an enthusiastic ultimate (Frisbee®) player, who embraced the “Spirit of the Game” in both his professional and personal life.

Many thanks to the numerous Eckerd College undergraduate students who helped in the laboratory and at sea including Shannon Hammaker, Chloe Holzinger, Farley Miller, Claire Miller, and Corday Selden. Grateful acknowledgments to Alan Shiller, who provided important insight at a critical time. A special thanks to Luke McKay and Andreas Teske (University of North Carolina) for collecting and providing valuable sediment samples collected just after the explosion. Thanks to the exceptional crew of the RV/Weatherbird II for their capable assistance at sea collecting samples, and staying safe during the field operations.

We would like to thank the National Science Foundation Rapid Grant program for providing the funding for the Deep Sea Instruments MC-800 Multi-corer. We acknowledge the British Petroleum/Florida Institute of Oceanography (BP/FlIO) Gulf Oil Spill Prevention, Response, and Recovery Grants Program for providing funding for the initial research cruises during 2010 and 2011. This research was made possible by funding from The Gulf of Mexico Research Initiative to both the Deep-C Consortium and to the C IMAGE Consortium. The complete data set can be accessed at the GRIIDC website: http://www.data.gulfresearchinitiative.org/.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.dsr2.2014.12.009.

References


