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Effects of organic matter addition on methylmercury formation in capped and uncapped marine sediments

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ABSTRACT

In situ subaqueous capping (ISC) of contaminated marine sediments is frequently proposed as a feasible and effective mitigation option. However, though effective in isolating mercury species migration into overlying water, capping can also alter the location and extent of biogeochemical zones and potentially enhance methylmercury (MeHg) formation in Hg-contaminated marine sediments. We carried out a boxcosm study to investigate whether the addition of organic carbon (OC) to Hg-contaminated marine sediments beneath an in situ cap would initiate and/or enhance MeHg formation of the inorganic Hg present. The study was motivated by ongoing efforts to remediate ca. 30,000 m^2 of Hg-contaminated seabed sediments from a Hg spill from the U864 WWII submarine wreck. By the time of sinking, the submarine is assumed to have been holding a cargo of ca. 65 tons of liquid Hg. Natural organic matter and petroleum hydrocarbons from fuels and lubricants in the wreck are potential sources of organic carbon that could potentially fuel MeHg formation beneath a future cap. The results of our study clearly demonstrated that introduction of algae OC to Hg-contaminated sediments, triggered high rates of MeHg production as long a there was sufficient OC. Thus, MeHg production was limited by the amount of organic carbon available. The study results also confirmed that, within the six-month duration of the study and in the absence of bioturbating fauna, a 3-cm sediment clay cap could effectively reduce fluxes of Hg species to the overlying water and isolate the Hg-contaminated sediments from direct surficial deposition of organic matter that could potentially fuel methylation.

1. Introduction

Mercury (Hg) contamination in natural waters and sediments is a global problem. A number of mitigation strategies have been applied to remediate both Hg-contaminated waters (Herrero et al., 2005; Zhang et al., 2005) and sediments (Hosokawa, 1993; Palermo, 1998). For remediation of Hg-contaminated sediments, in situ subaqueous capping (ISC) offers a feasible and efficient management option (Palermo, 1998). The use of an ISC involves placing a layer of clean fill material at the sediment-water interface to prevent contaminant release and contact with benthic macrofauna and overlying surface water. In situ subaqueous caps have been successfully used to manage Hg-contaminated sediments in Minamata Japan (Hosokawa, 1993) and Hamilton harbor Canada (Azcue et al., 1998). The application of an ISC can however, alter the location and extent of biogeochemical zones (Johnson et al., 2010; Randall et al., 2013a) and potentially increase MeHg formation under sulfate reducing conditions if organic carbon (OC) is available (Randall et al., 2013a). There are multiple potential sources of OC to Hg-contaminated sediments including natural organic matter and petroleum hydrocarbons from natural seeps and oil spill from sunken ship wrecks (Monfils et al., 2006), leakage from underground storage tanks (Boopathy, 2004); or purposeful addition of emulsified vegetable oil for reductive bioremediation of aquifer sediments contaminated with chlorinated organic compounds (Borden, 2007). This study was therefore carried out to investigate whether; (i) introduction of OC to Hg-contaminated marine sediments would affect Hg speciation and cycling, (ii) how a combination of OC addition and capping would affect Hg methylation dynamics.

Methylmercury is mainly produced in anoxic sediments and soils, primarily by dissimilatory sulfate- and iron-reducing bacteria (DSRB and DFeRB) (Bravo et al., 2015; Gilmour et al., 2011) and to some extent methanogens (Gilmour et al., 2013). In addition to Hg and a suitable terminal electron-accepting process (TEAP) anaerobic microbial MeHg formation usually requires the presence of an

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appropriate organic substrate i.e. an electron donor (Bravo et al., 2015; Johnson et al., 2010; Randall et al., 2013a).

The relationship between organic matter content in marine sediments and MeHg formation is however complex. A number of studies have reported both a positive (Graham et al., 2012; Mitchell and Gilmour, 2008; Schartup et al., 2013) and negative (Driscoll et al., 2012; Hammerschmidt and Fitzgerald, 2004; Schartup et al., 2013) correlation between sediment organic matter content and MeHg formation rates. The quality of the organic matter has also been suggested to control MeHg formation in marine sediments (Mitchell and Gilmour, 2008). We are aware of only two studies (Johnson et al., 2010; Randall et al., 2013a) that have investigated how the application of an ISC affects the TEAP and MeHg formation in the underlying sediments (Johnson et al., 2010; Randall et al., 2013a) The mesocosm study by Randall et al. (2013a) used freshwater sediments where (unlike in marine systems), DSRB activity can be sulfate limited. The study by Johnson et al. (2010) did not investigate possible limitation of DSRB activity (and hence MeHg formation) by sediment organic matter content.

The aim of this study was therefore to investigate how introduction of allochthonous OC to Hg-contaminated sediments with low autochthonous OC content, would affect methylation of in situ Hg. We hypothesized that laying an ISC over such contaminated sediments would alter the MeHg formation-demethylation balance leading to an increase in MeHg concentration relative to controls without ISC. We designed our boxcosm study to reflect both the current in situ sediment conditions around the U-864 wreck site; and after possible application of an ISC over the sediments. In our boxcosm study, we amended the Hg-contaminated sediment (grainy sand with low native OC content) with varying doses of a labile OC (chlorella algae; ca. 50 wt % carbon). We believe this is the first study to systematically investigate the effect of OC addition to Hg-contaminated marine sediments addition on; (i) MeHg formation and (ii) the effect of capping on Hg methylation dynamics beneath an ISC.

2. Materials and methods

2.1. Sampling of Hg-contaminated sediments from U864 site

Surface sediment samples for this study were collected in January 2013 from the seabed wreck site, which lies about two nautical miles (3.7 km) west of the Norwegian North Sea island of Fedje (Fig. S1). Sediments were sampled using a Van Geen grab mounted on the arm of a Remotely operated vehicle controlled from the deck of the vessel *Skandi Skolten* docked above the U864 wreck site. The sediment was then transported to the shore lab and stored in the dark at a temperature of 5–10 °C until use. The Hg contaminated sediment area around the wrecks is estimated to be ca. 0.03 km^2, with sediment "hot spots" in the immediate vicinity of the wrecks and decreasing away from the wreck.

2.2. Sediment preparation

The sediments were carefully checked for any ammunition, as they were collected from a site in the proximity of a WWII submarine wreck (Kystverket, 2014a, b). All large stones and pebbles were physically removed. The rest of the sediment (which consisted of gravelly sand) was homogenized and aliquoted into eight-6L portions in which 0, 5, 15 and 45 g of pulverized *Chlorella* sp green algae with a carbon content of ca. 47 wt %, was added (corresponding to approximately 0, 25, 75 or 225 g$C$$m^{-2}$ respectively). Each of the eight sediment portions (i.e. three with added algae and one control for capped and uncapped respectively; Figs. S2 and S3) was placed in a wooden tray and set in a freezer at −20 °C for seven days forming frozen 3 cm sediment layers ("frozen sheets") with the same surface area as the boxcosms. An extra four frozen layers were prepared in a similar way but this time with fresh (uncontaminated) marine clay sediment to act as caps for the four capped treatments. The marine clay sediment used for the cap was collected from a reference location in the Outer Oslofjord, remote from any known point source of anthropogenic discharges.

2.3. Boxcosms set up

The boxcosm setup used in this study is depicted in Fig. 1 (and Fig. S2 in the supplementary information). The set up is a slight modification of the one described by Josefsson et al. (2012) for their study of the efficiency of different capping materials for in situ subaqueous capping of contaminated marine sediments. The eight boxcosms in this study were placed in large concrete tank (L 2 m x W 0.8 m x H 0.6 m, Fig. 1 and Fig. S2) with flow-through seawater pumped from 60 m depth, maintaining a temperature of 8–10 °C and a salinity of ~34 throughout the six month experimental period. The water level in the tanks was about 1 cm below the rim of the boxes. The same seawater was also pumped into a header tank from which it was distributed to the four uncapped boxes at an average (±1 standard deviation) flow rate of 0.94 ± 0.05 mL min^{-1}, corresponding to a turnover time of ca. 6.4 days for the overlying water in the uncapped boxcosms. An air-diffusing system, consisting of an airstone diffuser placed in a perforated Plexiglas tube in the center of each box, was used for stirring and aerating the water.

Before adding the various layers, the lids were removed from the eight polycarbonate boxes previously filled to a depth of about 20 cm with fresh uncontaminated clay sediment (same sediment as used for the ISC) leaving about 15 cm of the box filled with seawater (Figs. S2 and S3). Each of the eight frozen sheets was removed from

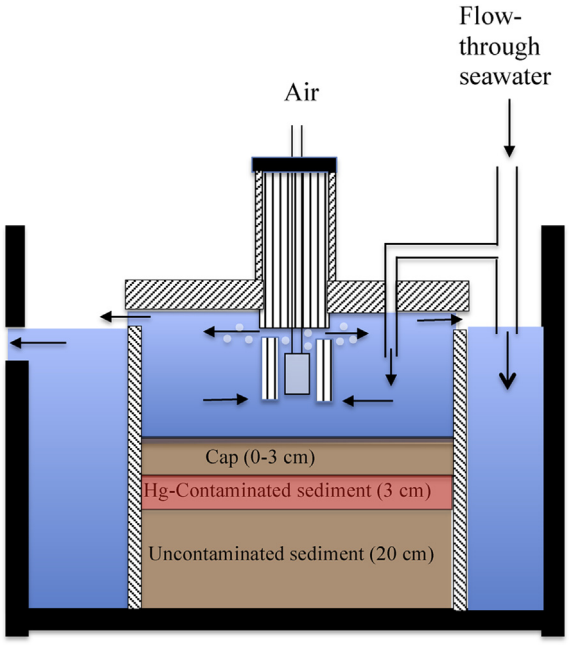

Fig. 1. Set-up showing the experimental boxes (boxcosms) used to study the effect of organic carbon and capping on Hg speciation in contaminated marine sediments. The 3-cm Hg-contaminated sediment layer in three of the four capped and uncapped (control) boxcosms (total of eight boxcosms) was amended with varying levels of organic carbon (as pulverized *chlorella* algae). Both the cap and bottom layers were clay sediment sampled from an uncontaminated site. See text for more details.