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Mercury remediation in wetland sediment using zero-valent iron and granular activated carbon

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ABSTRACT

Wetlands are hotspots for production of toxic methylmercury (MeHg) that can bioaccumulate in the food web. The objective of this study was to determine whether the application of zero-valent iron (ZVI) or granular activated carbon (GAC) to wetland sediment could reduce MeHg production and bioavailability to benthic organisms. Field mesocosms were installed in a wetland fringing Hodgdon Pond (Maine, USA), and ZVI and GAC were applied. Pore-water MeHg concentrations were lower in treated compared with untreated mesocosms; however, sediment MeHg, as well as total Hg (THg), concentrations were not significantly different between treated and untreated mesocosms, suggesting that smaller pore-water MeHg concentrations in treated sediment were likely due to adsorption to ZVI and GAC, rather than inhibition of MeHg production. In laboratory experiments with intact vegetated sediment clumps, amendments did not significantly change sediment THg and MeHg concentrations; however, the mean pore-water MeHg and MeHg:THg ratios were lower in the amended sediment than the control. In the laboratory microcosms, snails (*Lymnaea stagnalis*) accumulated less MeHg in sediment treated with ZVI or GAC. The study results suggest that both GAC and ZVI have potential for reducing MeHg bioaccumulation in wetland sediment.

1. Introduction

Mercury (Hg) contamination can negatively affect the health of many faunal species in ecosystems. In natural systems, methylmercury (MeHg) is the Hg species of greatest concern because of its ability to bind to muscle tissue and thereby bioaccumulate in food webs, potentially to the point of toxicity (Chen et al., 2008; Liu et al., 2008; Patra and Sharma, 2000; Watras et al., 1998; Wolfe et al., 1998). MeHg is primarily formed by the methylation of inorganic divalent mercury (Hg(II)) by anaerobic bacteria (Benoit et al., 1999; Compeau and Bartha, 1985; Hamelin et al., 2011; Kerin et al., 2006). Recent studies suggest that plant activity may enhance Hg(II) methylation; therefore, wetlands can be important sources of MeHg contamination to adjacent water bodies (Bowles et al., 2003; Cosio et al., 2014; Hall et al., 2008; Marvin-Dipasquale et al., 2007; St. Louis et al., 1994; Ullrich et al., 2010; Windham-Myers et al., 2009). Low-cost, low-impact, *in situ* treatment of these potential MeHg hotspots is desirable to reduce Hg toxicity in these wetland ecosystems.

Zero-valent iron (ZVI) is an inexpensive material commonly used in permeable reactive barriers to treat ground-water contamination. ZVI treatment has been shown to lower the toxicity of arsenic and chromium through reductive and sorptive mechanisms (Fu et al., 2014). Research on the use of iron (Fe) species for Hg remediation has largely focused on Fe(II) that was shown to reduce Hg(II) methylation in pure culture of sulfate-reducing bacteria (SRB), non-vegetated wetland sediment slurries, and intact wetland sediment clumps (Mehrotra et al., 2003; Mehrotra and Sedlak, 2005; Ulrich and Sedlak, 2010). The effect of ZVI on Hg has been studied in synthetic aerobic and anaerobic systems, where reductions in dissolved Hg concentrations were attributed to adsorption by ZVI (Gibson et al., 2011; Vernon and Bonzongo, 2014; Weisener et al., 2005; Wilkin and McNeil, 2003). To our knowledge, the effect of ZVI on *in situ* MeHg production, and the potential of ZVI as a remediation tool to reduce MeHg uptake by biota have not been studied.

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Several experimental and laboratory microcosm studies have shown that GAC can effectively remove inorganic Hg(II) and MeHg from contaminated sediment (Ghosh et al., 2011; Gilmour et al., 2013; Gomez-Eyles et al., 2013; Hollerman et al., 1999; Zhu et al., 2009). Gilmour et al. (2013) tested the effect of a range of GAC treatment levels on sediment pore-water partitioning of inorganic Hg(II) and MeHg in homogenized sediment microcosms representing a range of salinity and contamination levels. In most instances GAC resulted in a decrease in pore-water MeHg concentration that led to an increase in MeHg partition coefficient ($K_{D,MeHg}$; defined as the ratio of sediment to pore-water MeHg concentrations) and a decrease in MeHg biotic uptake. These results suggest that GAC addition may also be a promising treatment for reducing MeHg uptake by biota.

In this study we evaluated the use of ZVI and GAC as treatment amendments in *in situ* vegetated wetland mesocosms, and in intact vegetated laboratory microcosms. The field mesocosm experiments were conducted to study the effect of ZVI and GAC on *in situ* sediment total Hg (THg) and MeHg concentrations, and on pore-water MeHg concentrations. Additional microcosm experiments were conducted to study the effect of these amendments on the uptake of MeHg by a freshwater snail (*Lymnaea stagnalis*).

2. Materials and methods

2.1. Materials

Zero-valent iron was obtained from Connelly-GPM, Inc. (Chicago, IL), and sieved to <2 mm before application to ensure high surface area. GAC was mix coal/coconut powder, obtained from Siemens Industry Inc., USA, and used as received. Table S1 shows the particle size distribution for the ZVI and GAC. All other chemicals were trace metals grade.

2.2. Site description

This field study was conducted at a fringing wetland of Hodgdon Pond (Tremont, Maine, USA; Fig. S1), located on the western border of Acadia National Park on Mount Desert Island. This pond has a surface area of 18.2 ha, a perimeter of 3300 m and reaches a maximum depth of 6.7 m. Fish (pickerel) in Hodgdon Pond had an average Hg body burden of 1.4 ppm, one of the highest concentrations among 125 studied lakes and ponds in Maine (Linda Bacon, personal communication, 2014). The pond's eastern shore is part of Acadia National Park and the western shore is privately owned residential land. There are several fringing wetlands and other wetlands in the pond's catchment (Nielsen, 2006). The southern fringing wetland, where this study was conducted, is dominated by grass and sedge vegetation. Water temperature and relative water level in the lake during the sampling period are shown in Fig. S2.

There is no known point source of Hg contamination for this pond; as such, Hg within the pond is derived almost exclusively from atmospheric deposition. The high fish Hg body burden in Hodgdon Pond is thought to be a result of conditions that are conducive to high Hg(II)-methylation rates in this ecosystem, namely the presence of wetlands.

2.3. Field mesocosms

Twelve mesocosms were established along an 18 m transect on the waters edge of the southern fringing wetland of Hodgdon Pond on 8/12/2013 (Fig. S3). Care was taken to locate the mesocosms such that they contained a similar mass of the same plant material. Mesocosms were isolated in the wetland by driving a ~38 cm diameter ~39 cm long PVC pipe to a depth of ~15 cm. Treatments were randomly assigned such that four mesocosms received ZVI (at 5 × estimated sediment total Fe in the top 3 cm), four received GAC (at 1.7% estimated sediment dry weight in the top 0–3 cm interval) and four were left untreated. In the pristine environment of a National Park, any amendments to the sediment should have minimal effects on the background geochemical characteristics and on biological activity of the native flora and fauna. Therefore, the ZVI concentration was based on preliminary experiments in which a range of ZVI concentrations (5–50 × native sediment acid-soluble Fe) were added to the top 3 cm of homogenized wetland sediment (Lewis, 2014). The results showed that the lower end ZVI dosage had the least effect on pore-water chemistry, especially with respect to pH and Fe(II) concentrations, while lowering the pore-water MeHg concentration; in the top ~4 cm, the pore-water pH ranges were 5.6–5.8, 5.8–6.0, and 6.3–6.5 for the control, 5 × and 50 × ZVI, respectively, and the pore-water Fe(II) ranges were 43–53, 80–83, and 229–269 μM for the three treatments, respectively. The added GAC concentration was close to the lowest concentration used in a recent study by Gilmour et al. (2013) on Hg remediation of contaminated sediment. The ZVI and GAC were gently mixed into the surface sediment (top ~0–3 cm interval for ~3 min) of the mesocosms using a plastic spoon taking care not to damage the plants; the surface sediment of the reference treatments was also similarly mixed. The water level was ~4 cm above the sediment surface when the mesocosms were installed (Fig. S2).

Sediment samples were collected as a composite of 3–5 samples from the top 0–3 cm of sediment immediately before treatment applications in August (8/12/2013), and 25 days on September (9/6/2013), and 91 days on November (11/11/2013) after treatment applications. Samples were flash frozen in the field using dry ice until analysis; prior to analysis, they were thawed, homogenized and freeze–dried.

Pore water was sampled in two mesocosms of each treatment in September and November. Equilibrium dialysis samplers (peepers) were used to sample pore water. Peepers are acrylic frames with 5 mL cells on 1.5 cm centers and 0.45 μm Tuffryn HT polysulfone (Gelman Sciences dialysis membranes). Peepers were assembled in the laboratory and bubbled with N_2 for two weeks prior to deployment. They were modified with fittings to allow for *in situ* pore water collection without having to withdraw the peepers and disturb the sediment. Pore-water samples were withdrawn twice from the peepers; the first draw of >3 mL was allocated to ancillary chemistry (including Fe(II), hydrogen sulfide and dissolved organic carbon; Table S2) and the second was allocated to MeHg analysis; total Hg was not analyzed in field samples due to the low sample volume. Following collection, pore-water samples collected for MeHg analysis were transferred into pre-weighed falcon tubes and kept on ice in the dark. Upon return to the lab, samples were preserved with 0.5% HCl (final concentration) by weight and frozen until analysis.

2.4. Laboratory microcosms

Twelve microcosms were established in 1 gal glass aquaria. The aquaria were established using intact sediment clumps containing macrophytes collected on 10/14/2013 from the same wetland where mesocosms were installed. Care was taken to establish microcosms so that they all had approximately the same amount of sediment and plants. Microcosms were maintained at room temperature with overlying water from Hodgdon Pond at a depth of 8–10 cm (Fig. S4). Similar to the field mesocosms, treatments were assigned randomly with four for each treatment (ZVI or GAC) and four untreated microcosms; added ZVI mass was similar to that in field mesocosms, and GAC was added at 1.0% estimated sediment dry weight in the top 0–3 cm interval. Peepers were inserted in two