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Activated carbon thin-layer placement as an *in situ* mercury remediation tool in a Penobscot River salt marsh

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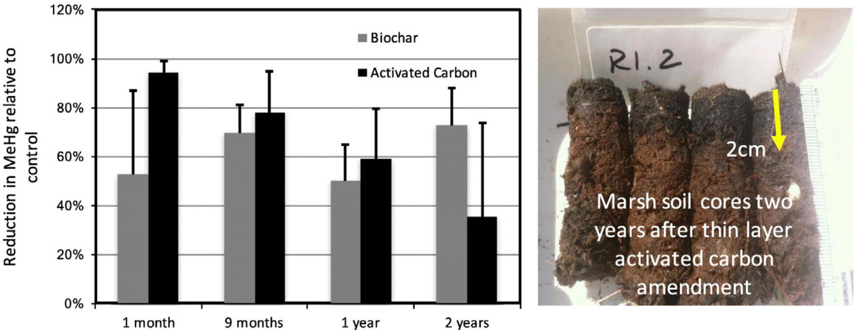
HIGHLIGHTS

- Thin-layer soil amendments were tested as a remediation tool for methylmercury.
- Small plots studies were conducted in a New England salt marsh over 2 years.
- Activated carbon amendments significantly reduced porewater Hg and MeHg.
- Biochar was less effective, but provided significant reductions.
- This is one of the first field trials of *in situ* amendment for Hg remediation.

GRAPHICAL ABSTRACT



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ABSTRACT

The efficacy of thin layer *in situ* soil amendments was tested as a potential tool for methylmercury (MeHg) risk mitigation in Penobscot River, ME, salt marsh. Salt marshes are sites of high MeHg accumulation within the Penobscot, and key targets for remediation. The study was a fully-crossed small plot study, with four treatments (activated carbon (AC), biochar, $FeCl_2$, and lime) and unamended controls at two sites. Plots were monitored for two years. Porewater MeHg concentrations were the main endpoint, with impacts on sediment biogeochemistry as a secondary study goal. AC-based SediMite™ was effective in reducing MeHg, and to a less extent total Hg, in surficial pore waters. AC reduced MeHg concentrations by >90% at the one month time point, and continued to significantly reduce pore water MeHg through about a year. AC was less effective in reducing total Hg in pore water, yielding about 70% reduction at one month, and 50–65% reduction at 8 months. Biochar provided lower, and more variable reduction in porewater MeHg, but was not effective in reducing total Hg. Biochar amendment also increased soil MeHg. Neither $FeCl_2$ nor lime amendments reduced pore water Hg or MeHg levels. About 50% of AC treatment applied as SediMite™ pellets was retained in marsh soils after one year. This study is one of the first field trials of *in situ* amendment for MeHg remediation. Our results show that thin-layer AC placement is a potential remediation tool for Hg risk to biota, especially in marshes where net MeHg accumulation is often strong.

1. Introduction

Currently, there are few remediation options for sediment and soil Hg contamination, short of dredging and capping. Dredging can achieve

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mass removal of Hg from a site (Hosokawa, 1993; Wang et al., 2004), but may resuspend and mobilize contaminants (Bloom and Lasorsa, 1999; Kim et al., 2006). *In-situ* capping can be a low cost remediation practice and may result in fewer adverse environmental impacts than dredging (Nichols et al., 1990; Palermo, 1998). However, buried contaminants may be transported through the capping layer and enter into the overlying water through various natural processes such as bioturbation, tidal pumping, and groundwater flow (Liu et al., 2001). Regulations may not permit changes in elevation, and where they do, elevation changes may alter community structure. Capping may also impact the magnitude and depth of MeHg production (Johnson et al., 2010). Recent field studies show that thin-layer caps that include AC, and AC mixed into surface sediments have limited impact on benthic community structure and density, especially after some re-colonization time (Janssen and Beckingham, 2013; Kupryianchyk et al., 2012; Kupryianchyk et al., 2011; Naslund et al., 2012). Enhanced natural remediation, which is the addition of clean clay-rich material to dilute Hg concentrations in surface sediments, was proposed in the 1980s (Rudd and Turner, 1983) and had been proposed for the Penobscot, but has not had a field trial.

In-situ sorbent amendments, particularly activated carbon (AC) can provide low-cost, low-impact approach for remediation of organic-contaminated sediments (Ghosh et al., 2011). These sorbent amendments are designed to increase contaminant binding to sediments, in turn reducing contaminant bioavailability and transport. The goal of this remediation approach is to reduce the bioavailability and mobility of contaminants *in situ*, rather than removing the contaminants *per se*. Sorbent materials, such as AC, biochar, organoclays, and functionalized substrates can be physically mixed into sediments, added to capping materials, or applied directly to sediment or marsh surfaces. Previous work has explored the effectiveness of a range of amendments such as organic matter, lime, bentonite, fly ash, and various phosphorus containing compounds for the stabilization of Pb in soils (Henry et al., 2015). Apatite amendments to sediments have reduced porewater Cd, Co, Hg, Pb, and U, and increased in desorption of bound As, Se, and Th likely due to competitive exchange of the bound forms with phosphate (Kaplan and Knox, 2004). While a Fe(II) amendments have held promise in reducing marsh MeHg levels in laboratory studies, follow-up tidal marsh microcosm experiments gave mixed results (Mehrotra and Sedlak, 2005; Ulrich and Sedlak, 2010a; Ulrich and Sedlak, 2010b). Field-scale evaluation of amendment addition to sediments is lacking especially for Hg.

In this study, a set of small plots were used to test the efficacy of thin-layer placement of AC and other soil amendments as a potential tool for Hg risk mitigation in a New England salt marsh. The experiment was done in Mendall Marsh, a salt marsh complex in the mesohaline reach of the macrotidal Penobscot River in Maine, USA. The Penobscot is the second largest drainage basin in New England (~22,400 km^2), and it empties into the largest estuary in Maine. The Penobscot is recovering from decades of pollution from pulp and paper mills, sewage, *etc.* (Haefner, 1967; Rabeni et al., 1985) that led to anoxic conditions and depletion of fisheries. The river flows for about 35 miles below the head of tide near Bangor before emptying into Penobscot Bay. Most salt marshes on the tidal and estuarine Penobscot are small fringe marshes on protected coves (Jacobson et al., 1987). However, there are two larger marsh complexes, the Mendall Marsh complex on the Marsh River and the Orland River marsh complex (Fig. 1). Both marsh systems are net depositional environments (Turner et al., in review, this volume) and traps for riverine particulate Hg. The large western platform of Mendall Marsh was chosen as the study site.

The Penobscot River is contaminated with Hg mainly as the result of operations of a former chlor-alkali plant in Orrington, ME, a few miles downstream from Bangor (Bodaly et al., in review, this volume; Merritt and Amirbahman, 2007; Merritt and Amirbahman, 2008; Turner, in review, this volume; Yeager et al., in review, this volume). Mendall Marsh, about 15 miles downstream from Orrington, has accumulated Hg-contaminated sediments since the late 1960s when plant operations began (Santschi et al., 2017, this volume). Although the highest Hg concentrations occur at depth in marsh soils, new materials deposited to the surface of the marsh remain elevated in Hg. In 2009, Hg in Mendall marsh surface soils averaged about 650 ng/g (range ~200–1000) based on sediment coring surveys (Yeager et al., in review, this volume). Mass sedimentation rates in the marsh averaged about 0.5–0.7 cm y^{-1} (Santschi et al., 2017, this volume; Yeager et al., in review, this volume). The marsh acts as trap for river sediments, especially sediments from the highly mobile mudflats just outside the marsh entrance, at the sharp bend in the river at Frankford Flats. Field studies of MeHg concentrations and production rates in sediments and soils across the Penobscot system pointed to salt marshes as sites of particularly high methyl Hg production and accumulation, and therefore a key target for remediation (Gilmour et al., in review, this volume). For Hg-contaminated sediments and soils where direct inorganic Hg toxicity to invertebrates is not a concern, risk derives mainly from the bioaccumulation of MeHg (Wiener and Suchanek, 2008).

Until recently, sorbents have not been widely tested for the remediation of sediment contaminants other than hydrophobic organic compounds, including mercury. Several lines of evidence suggest that MeHg should be amenable to *in situ* remediation with AC. Activated carbon has strong binding constants for both Hg (log K_d roughly 6–7) and MeHg (log K_d roughly 5–6) (Gomez-Eyles et al., 2013). The concentration of natural organic matter in sediments is a strong predictor of sediment:water partitioning (K_d) for both total Hg and methyl Hg (Hammerschmidt and Fitzgerald, 2004; Hammerschmidt and Fitzgerald, 2006; Hollweg et al., 2010; Ogrinc et al., 2007). The sediment:water partition coefficient for Hg or MeHg can be a strong predictor of bioavailability to benthic fauna (Wang et al., 1998; Williams et al., 2010). The bioaccumulation of methyl Hg by polychaetes (Wang et al., 1998), amphipods (Lawrence and Mason, 2001) and sipunculans (Zhong and Wang, 2008) is negatively related to sediment organic content. These characteristics led us to believe that AC amendment might be effective in Hg remediation in contaminated sediments and soils, by reducing pore water Hg and MeHg concentrations. Our laboratories studies with AC amendments suggest that porewater MeHg concentration may be a good predictor of MeHg bioavailability to benthic infauna (Gilmour et al., 2013). If AC or other *in situ* amendments can reduce pore water Hg concentrations, and/or enhance partitioning to sediments, they should be effective in reducing bioavailability to benthic organisms. Based on these laboratory studies, the mechanism of AC remediation appears to be reductions in MeHg bioavailability to worms, rather than by reductions in sediment MeHg production or bulk sediment MeHg concentration.

Small plot studies were selected as a first approach to testing *in situ* amendments in Mendall Marsh. Small-scale studies offer advantages in cost and in the ability to replicate treatments, facilitating statistical tests of response. They also help to smooth the impacts of small elevation changes across the marsh surface on redox and therefore MeHg production. Four amendments were tested: activated carbon (formulated into SediMite™ pellets with sand and clay), a pine dust biochar, ferrous chloride ($FeCl_2$), and lime. The carbon treatments were chosen based on previous laboratory studies demonstrating their ability to reduce pore water Hg and methyl Hg concentrations, and uptake by benthic infauna (Gilmour et al., 2013). The lime treatment was designed to alter pH, as Hg methylation rates tend to be higher at lower pH (Miskimmin et al., 1992). Ferrous iron may impact sulfur chemistry (Mehrotra and Sedlak, 2005) and/or the change microbial respiration pathways in soils.

The study design was a fully-crossed small plot study, with four amendment treatments plus an un-amended control, each in triplicate, at each of two sites in Mendall Marsh. The sites were chosen to represent two different vegetation complexes, and associated biogeochemical conditions, in the marsh. The study sampling design was based on two objectives. The first was to determine if amendments reduced potential risk by reducing pore water total Hg and MeHg concentrations and sediment water partition coefficients. A secondary objective was to evaluate