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Stabilization of mercury in sediment by using biochars under reducing conditions

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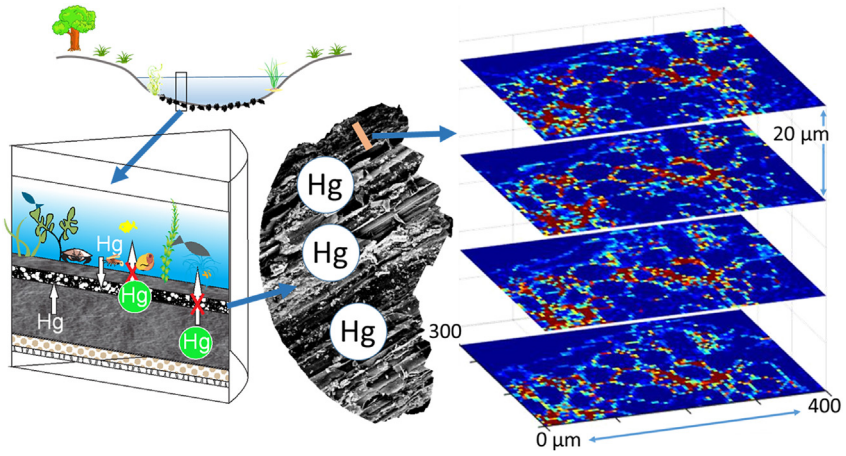
HIGHLIGHTS

- Concentrations of THg and MeHg are lower in biochar amended systems than in controls.
- Distribution of Hg within biochar particles is strongly correlated to S, Fe and Cu.
- Hg stabilization is enhanced under anaerobic conditions.
- Original material of biochar is replaced by elements released from sediment.

GRAPHICAL ABSTRACT



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ABSTRACT

Mercury (Hg) is widely distributed in different localities around the world and poses a serious health threat to humans, especially when ingested in the form of methylmercury (MeHg). Efforts have been directed toward decreasing the production of MeHg by converting Hg to stable forms. Activated carbon and biochar have been evaluated as stabilization agents for Hg in contaminated sediments. However, the long-term fate of Hg stabilized by these materials remains unclear. Here, we compare the effectiveness of Hg stabilization using two biochars prepared from switchgrass at 300 °C (low T) and 600 °C (high T). Experiments were conducted by co-blending biochars and sediment for >600 d under anaerobic conditions. Aqueous concentrations of total Hg and MeHg were greatly reduced in the presence of biochars, with the exception of a spike in MeHg concentration observed at ~440 d in the high-T biochar system. Hg co-occurs with S, Fe, Cu, and other elements within the plant structure of low-T biochar particles, but primarily on the outer surfaces of high-T biochar particles. Our results indicate that the stabilization of Hg may be through an early-stage diagenetic process, suggesting that the stabilization of Hg by biochar may be effective over long time frames.

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1. Introduction

Hg is widely distributed in the environment, and poses serious health risks to humans. MeHg, an organic form of Hg, is much more toxic than inorganic Hg and can cause central nervous system defects [1]. Inorganic forms of Hg can be converted to MeHg by microbes under anaerobic conditions (*e.g.,* sediments and wetlands) [2–5], especially in the benthic zone of lakes, rivers, and oceans just below the oxic/anoxic interface [6]. Many efforts have focused on decreasing the direct release of Hg and the production of MeHg by dredging Hg-contaminated sediment [7], *in situ* capping [8], or by converting Hg to less bioaccessible forms [9–11]. Pyrogenic carbonaceous materials, including activated carbon, are widely used for Hg removal from aqueous solutions [12] and less extensively for Hg stabilization in sediments [10,11].

Biochar, a type of black carbon with properties similar to charcoal, is a low-cost alternative to activated carbon. Biochar can be produced on site and can be used as a soil amendment to improve soil fertility [13], to sequester carbon [14,15], and in water and soil treatment applications [16].

Despite the increasing utilization of biochar for water treatment [12] and stabilization in contaminated sediments [11], the long-term fate of Hg after uptake by biochars remains unclear. We hypothesize that amending contaminated sediment with biochar can reduce aqueous concentrations of Hg and MeHg and can convert a fraction of the Hg to stable forms within the biochar particles. We also hypothesize that the degree of uptake by the biochar is dependent on the pyrolysis temperature used to prepare the biochar. Our specific objective was to investigate the correlation between filtered total Hg (THg) and MeHg with 1) the evolution of aqueous indicators of biogeochemical processes (*e.g.,* Fe, SO_4^{2-}, organic carbon); 2) the evolution of microbial communities; and 3) the changes in binding environment and distribution of Hg within the biochars after extended reaction times.

In addition to conventional X-ray absorption spectroscopy (XAS) measurements, confocal X-ray micro-fluorescence imaging (CXMFI), which is an emerging non-destructive technique [17], was employed. CXMFI provides compositional and structural information from precise locations on the surface of, and within, intact particles, with greater spatial precision than can be obtained using conventional micro x-ray fluorescence (μ-XRF) methods [18]. Limited applications of CXMFI are reported for natural materials; examples include the characterization of Se accumulation in fish eye lens [19]; W, Pt, and Fe in particles embedded in a mineralogical matrix [20]; K, Ca, and Fe in rice grains [21]; and U-Th-Pb for dating of geological materials [22].

Two biochars prepared at 300 and 600 °C from switchgrass, a widely available material in North America, were selected for co-blending with Hg-contaminated sediment and river water under anaerobic conditions. Samples of the aqueous and solid phases were collected as a function of time to determine shifts in chemical composition, microbial population, and Hg-binding environment through XAS measurements.

2. Materials and methods

2.1. Materials

The sediment was collected from South River, Virginia, 5.6 km downstream of a historical point (38° 3′49.00″N, 78°53′4.65″W) of Hg release. The river water was collected 300 m upstream of this location. Raw switchgrass was air dried and pyrolyzed for biochar using a kiln at either 300 or 600 °C for 2–3 h under O_2-deficient conditions [23].

2.2. Microcosm experiment

Microcosm experiments were conducted by mixing biochar, sediment, and river water at a ratio of 1:20:160 (5:100:800 g) in amber bottles. Controls included ultra-pure water, river water, sediment mixed with river water, and biochar mixed with river water. The sediment control was duplicated. The experiments were conducted in an anaerobic glovebox.

Unfiltered aqueous samples were collected for analysis of pH and Eh, and samples filtered using 0.45-μm membranes were collected for analysis of alkalinity, anions, cations, dissolved organic carbon (DOC), THg and MeHg. Sample splits were also filtered through 0.2-μm membranes for THg analyses. Solid samples were collected periodically for MeHg and pyrosequencing analyses. Biochar particles were separated from the solid samples at 65, 100, 154, 235, 387, and 600 d.

2.3. Chemical analyses

Determinations of pH were made using a Ross combination pH electrode (Orion 815600, Thermo Scientific). Determinations of Eh were made using a Pt combination Eh electrode (Orion 9678, Thermo Scientific), checked against ZoBell's [24] and Light's [25] solutions. Alkalinity was determined using a Hach digital titrator using bromocresol green-methyl red as an indicator. Concentrations of anions (including short-chain organic acids) were determined using ion chromatography (ICS-5000, Dionex Corp.) with an IonPac AS11 4 × 250 mm column. Cation concentrations were analyzed by inductively coupled plasma-optical emission spectrometry (Thermo Scientific iCAP 6500) and inductively coupled plasma-mass spectrometry (Thermo Scientific XSeries II). DOC was determined using an automated wet chemical oxidation method (Aurora 1030, OI Analytical).

Concentrations of THg were determined using a cold vapour atomic fluorescence spectroscopy technique (CVAFS, Tekran 2600), following EPA method 1631, with a method detection limit (MDL) of 0.2 ng L^{-1}. MeHg in the aqueous phase was analyzed through distillation (Tekran 2750), aqueous ethylation, and purge and trap using the CVAFS technique (Tekran 2700) following EPA method 1630. Determination of MDL for MeHg was performed for each run and an average MDL of 0.02 ng L^{-1} was calculated. Solid samples for MeHg analyses underwent distillation by mixing with a solution containing 20% KCl and 8 M $CuSO_4$ to improve recovery [26].

The C/S content of the sediment and biochar was analyzed using a resistance furnace (Eltra CS-2000) and elemental composition was obtained following EPA Method 3052. The total organic carbon (TOC) of the sediment was analyzed using a segmented flow analyser (Skalar, Netherlands) following EPA Standard Method 5310C.

2.4. Pyrosequencing analysis

Genomic DNA was isolated and purified from solid-phase samples using commercial extraction kits (UltraClean Soil DNA Kit; MO BIO Laboratories). Purified DNA was shipped to MR DNA Laboratory (Shallowater, Texas) for pyrosequencing analysis. Detailed information on the selected primers (515/806 for bacteria and archaea), the processes and conditions of polymerase chain reaction and sequencing, and data processing procedures is provided in the Supporting Information. Fermenters, iron-reducing bacteria (FeRB), sulfate reducing bacteria (SRB) and methanogens were extracted from the pyrosequencing results. Potential Hg methylators were also extracted based on the methylators identified by Oak Ridge National Laboratory [27] (Table S1).