

Temperature-dependent formation of metallic copper and metal sulfide nanoparticles during flooding of a contaminated soil

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Abstract

Riparian floodplains in temperate regions are affected by pronounced seasonal variations in soil and water temperature. This affects the rates and interplay of microbial and abiotic geochemical processes that control the fate of metals in contaminated floodplain soils, including potential release into surface and groundwater during periodic flooding. Here, we investigated how temperature affects chalcophile trace metal contaminants (Cu, Cd, Pb) upon flooding of a riparian soil contaminated by past mining activities. In soil microcosms incubated at 23, 14, and 5 °C, the reductive dissolution of Mn(III,IV) and Fe(III) (oxyhydr)oxides and the release of dissolved Mn²⁺ and Fe²⁺ were significantly slower and less intense at the lower temperatures, which was reflected in a decrease of trace metal mobilization via the dissolution of metal oxide sorbents and cation competition for sorption sites. The onset of sulfate reduction was significantly delayed at lower temperatures and the apparent rate of sulfate reduction was decreased, especially at 5 °C. This resulted in elevated high dissolved Cu, Cd, and Pb concentrations over weeks of flooding at 5 °C, whereas colloidal metal sulfide formation dominated Cu, Cd, and Pb pore water dynamics at higher temperatures of 14 and 23 °C due to fast sulfate reduction. Cu K-edge X-ray absorption fine structure spectroscopy revealed metallic Cu(0) as the main colloidal Cu species prior to sulfate reduction at all three temperatures. Analytical electron microscopy showed that Cu(0) particles were associated with suspended bacteria, suggesting biomineralization of Cu(0). Upon onset of sulfate reduction, metallic Cu particles were transformed into Cu_xS with incorporation of smaller amounts of Cd and Pb. Concomitantly, freely dispersed mixed Cu–Cd–Pb sulfide nanoparticles precipitated in the pore water. Other metals with higher metal sulfide solubility products did not react with the limited amounts of biogenic sulfide. The median size of the mixed metal sulfide nanoparticles increased from 21 nm at 23 °C to 70 nm at 5 °C. During ~30 days of soil flooding at 23 and 14 °C, Cu speciation in the soil matrix changed from Cu(II) bound to soil organic matter in the oxic soil to 66% Cu_xS, with intermittent formation of about 14% metallic Cu(0). In contrast, at 5 °C, sulfate reduction and formation of Cu(0) were strongly retarded. After ~30 days of flooding at 23 and 14 °C, nearly all Cd and about 25% of total Pb in the soil, were precipitated in mixed metal sulfides. Our results demonstrate that temperature controls trace metal dynamics during soil flooding via its influence on microbial reduction of terminal electron acceptors. Even at low temperatures, soil flooding may trigger the release of chalcophile metals from contaminated floodplain soils by sorbent reduction, competitive sorption, and formation of nanoparticulate metal-bearing colloids.

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1. INTRODUCTION

The widespread historic contamination of river floodplain soils with trace metals can adversely affect riparian ecosystem health and surface and ground water quality. The bioavailability and mobility of trace metals are strongly affected by periodic soil flooding that triggers major variations in soil chemistry (Kirk, 2004). In a recent study, we demonstrated that flooding of a contaminated soil in laboratory microcosms led to substantial mobilization of colloidal Cu, Cd, and Pb into the pore water (Weber et al., 2009a). A companion study also highlighted that the speciation and solubility of Cu, Cd, and Pb were strongly affected by reductive dissolution of sorbent phases and by competitive precipitation with limited amounts of biogenic sulfide (Weber et al., 2009b). Although these studies identified important mobilization and sequestration mechanisms for chalcophile metals in riparian soils, the experiments (conducted at 23 °C) did not address the possible effects of temperature on the studied processes.

River floodplains in temperate regions experience pronounced seasonal variations in soil and water temperature that affect the rates of microbial and chemical reactions. Temperature markedly influences the decomposition of organic substances during flooding (Yamane and Sato, 1967) and soil respiration rates strongly increase with temperature (Fang and Moncrieff, 2001; Pietikainen et al., 2005), reaching a maximum at ~30 °C (Pietikainen et al., 2005). Following soil flooding, microbial iron reduction and release of dissolved Fe²⁺ was observed to occur earlier and with greater intensity at higher temperatures (Cho and Ponnampuruma, 1971; Meier et al., 2005; Vaughan et al., 2009; Weber et al., 2010). For example, Vaughan et al. (2009) reported that Fe reducing conditions in three flooded soils developed within 2 days of water saturation when temperature was >9 °C, but only after 20 days when temperature was <3.9 °C. In another field study, a marked increase in dissolved Mn²⁺ and Fe²⁺ (and trace metals) has been observed in a wetland from winter to spring and was attributed to increasing reductive dissolution of Mn(III,IV) and Fe(III) (oxyhydr)oxide minerals as temperature increased (Olivie-Lauquet et al., 2001). The simultaneous increase in dissolved organic carbon (DOC) was attributed to microbial decomposition of particulate organic compounds or the release of plant exudates. The rate of microbial sulfate reduction has also been shown to increase with temperature in marine and saltmarsh sediments (Westrich and Berner, 1988; Koretsky et al., 2003), freshwater lake sediments (Bak and Pfennig, 1991), a freshwater pit lake sediment (Meier et al., 2005), an alkaline mine tailing (Praharaaj and Fortin, 2008), and rice paddy soils (Van Bodegom and Stams, 1999). Increasing DOC concentrations at higher temperature provide an ideal substrate for dissimilatory sulfate-reducing bacteria (SRB) that anaerobically oxidize organic matter.

In addition to these microbially mediated biogeochemical processes, temperature also affects abiotic processes occurring in the environment. Increases of chemical reaction rates by a factor of 1.5–3 over an increase in temperature by 10 °C are common (Brezonik, 1994), and also ion

diffusion and adsorption are influenced by temperature (Barrow, 1992). For example, Cd sorption to goethite was shown to increase by 10–30% when temperature was increased from 10 to 25 °C (Johnson, 1990; Angove et al., 1999) and higher sorption of Cu and Pb to ferrihydrite has been observed at 24 °C than at 6 °C, which was partly due to increased micropore diffusion rate at higher temperature (Scheinost et al., 2001).

The chemical speciation and mobility of trace metals during soil flooding is intimately coupled to the aforementioned biogeochemical processes, and therefore, we expect an important influence of temperature on trace metal mobilization and/or sequestration. Microbial reduction of Mn(III,IV) and Fe(III) (oxyhydr)oxides leads to an increase in trace metal concentrations in solution, due to the loss of sorbent phases and increasing competition between dissolved Fe²⁺ and Mn²⁺ and trace metal cations for sorption sites (Olivie-Lauquet et al., 2001; Zachara et al., 2001; Weber et al., 2009b; Van Laer et al., 2010). Sulfide release by SRB, on the other hand, may lead to the sequestration of metals in poorly soluble metal sulfides (Morse and Luther, 1999; Kirk, 2004). However, as pointed out in our recent work (Weber et al., 2009b), sulfate may be limited in freshwater floodplain soils and the amount of biogenic sulfide may not be sufficient for the sequestration of all chalcophile metals. Under such conditions, we found that the thermodynamic stability of metal sulfides plays a major role in controlling the extent to which individual chalcophile metals (Cu, Cd, Pb in the studied soil) react with sulfide. Importantly, we also observed that metal sulfides did not only form in the stationary soil matrix, but also as colloids in the pore water (Weber et al., 2009a). Metal sulfide complexes or nanoclusters (Rozañ et al., 1999, 2000; Luther and Rickard, 2005) and submicrometer-sized ZnS particles (Priadi et al., 2012) have previously been identified in oxic river waters and ZnS nanoparticles were observed in a SRB biofilm (Moreau et al., 2004). Several studies postulated a mobilizing effect of metal sulfide colloids (Horzempa and Helz, 1979; Gammons and Frandsen, 2001; Moreau et al., 2004) and demonstrated their colloidal stabilization by thiol-containing organic ligands (Horzempa and Helz, 1979; Lau and Hsu-Kim, 2008; Deonaraine and Hsu-Kim, 2009; Mullaugh and Luther, 2011). For redox-sensitive Cu, our earlier experiments also provided first evidence for colloidal Cu mobilization by bacterially-driven formation of Cu(0) particles during submergence prior to onset of sulfate reduction (Weber et al., 2009a). Particulate metallic Cu has also been observed before in peat bogs (Loving, 1927; Lett and Fletcher, 1980), in a contaminated stream (Genovese and Mellini, 2007) as well as in and near plant roots (Manceau et al., 2008).

Temperature is expected to have different effects on microbial and abiotic geochemical processes that control trace metal behavior in floodplain soils, but it is currently not known how the coupling of these processes will affect trace metal dynamics in flooded soils at different temperatures. Expanding upon our earlier studies on trace metal dynamics in a contaminated floodplain soil during submergence at 23 °C (Weber et al., 2009a,b), the aim of the present study was to elucidate the influence of temperature

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