Interaction of mercury contaminated soils with iron oxides and potential remediation of river/runoff/storm water by an aquatic plant

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Abstract

Historically as part of its national security mission, the U.S. Department of Energy's Y-12 National Security Facility in Oak Ridge, TN, USA acquired a significant fraction of the world's supply of elemental mercury. During the 1950's and 1960's, a large amount of elemental mercury escaped confinement and is still present in the buildings and grounds of the Y-12 Facility and in the Y-12 Watershed. Because of the adverse effects of elemental mercury and mercury compounds upon human health, the Oak Ridge Site is engaged in an on-going effort to monitor and remediate the area. The main thrust of the Oak Ridge mercury remediation effort is currently scheduled for implementation in FY09. In order to more cost effectively implement those extensive remediation efforts, it is necessary now to obtain an improved understanding of the role that mercury and mercury compounds play in the Oak Ridge ecosystem.

Most recently, concentrations of both total mercury and methylmercury in fish and water of lower East Fork Poplar Creek (LEFPC) of Oak Ridge increased although the majority of mercury in the site is mercury sulfide. This drives the US DOE and the Oak Ridge Site to study the long-term bioavailability of mercury and speciation at the site. The stability and bioavailability of mercury sulfide as affected by various biogeochemical conditions, such as presence of iron oxides have been studied. We examined the kinetic rate of dissolution of cinnabar from Oak Ridge soils and possible mechanisms and pathways in triggering the most recent increases of mercury solubility, bioavailability and mobility in Oak Ridge site. The effects of pH and chlorine on oxidative dissolution of cinnabar from cinnabar-contaminated Oak Ridge soils is discussed.

On the other hand, aquatic plants might be good candidate for phytoremediate contaminated waste water and phytofiltration of collective storm water and surface runoff and river. Our greenhouse studies on uptake of Hg by water lettuce (*Pistia stratiotes*) show that water lettuce is effectively removing Hg from water solution and Hg was mostly stored in roots. One day of growing could remove 93-98% of Hg from water solutions. However, Hg causes acute toxicity to water lettuce as indicated by decreases in fresh biomass and moisture contents.

Key Words

Mercury, Oak Ridge, iron oxides, mercury sulfide, water lettuce.

Introduction

The Y-12 National Security Facility site encompasses 3.24 x 10^6 m^2 near the city of Oak Ridge, Tennessee, USA. Y-12 is a manufacturing and developmental engineering facility that formerly produced components for various nuclear weapons systems. Mercury contamination is ubiquitous in the Y-12 watershed and has been identified as a key contaminant in soil, sediment, surface water, groundwater, buildings, drains, and sumps (Han *et al.* 2006). The source of the mercury is from elemental mercury used during the 1950s and early 1960s for the manufacture of nuclear weapons. Mercury was a key element used to capture enriched lithium by separating the lithium isotopes. The total mercury release to the environment has been estimated to range from about 75 to 150 metric tons. Most of the contamination is accumulated in the upper 3 m of floodplain soils and the sediments of a 24-km length of East Fork Poplar Creek (EFPC), which has its headwaters at Y-12. The concentrations of mercury in the Upper EFPC watershed (soil) range from 0.01 to 7700 mg/kg. Some sediment cores contain 460 mg/kg mercury at depths of 80-84 cm. Mercury has been detected at higher than background levels in sediments of the Clinch River and the Tennessee River near Chattanooga, some 190 km downstream of Oak Ridge.

A series of remediation efforts have been employed in the Oak Ridge watersheds. The U.S. Department of Energy has removed soil at several locations along the creek where mercury concentrations were particularly high (1). The predominant form of mercury in the floodplain soils of the region is mercuric sulfide (cinnabar and meta-cinnabar forms) (1). This indicates that after long-term transformation and redistribution, mercury is finally transferred into the insoluble sulfide form with decreasing mobility, volatility and phyto- and bioavailability. Mercury sulfide, in general, has been regarded to be the stable mercury form in soils and sediments since its solubility is limited. However, the concentration of total mercury in fish and water of the lower East Fork Poplar Creek (EFPC) of Oak Ridge has recently increased. It was reported that dissolved organic carbon increased dissolution of mercury from HgS (1) and thus increased mercury bioavailability in soils. Other inorganic (chloride and sulfate) and organic ligands (salicylic acid, acetic acid, EDTA, or cysteine) were not found to enhance the dissolution of mercury from the mineral cinnabar. Due to interaction of cinnabar and various soil organic and mineral in soil environment, solubility and extractability of mercury sulfide mineral in soil has been found to be enhanced compare to pure cinnabar mineral (1).

Phytoremediation has been accepted and utilized widely because of cost-effectiveness, permanent removal and protection of nature. Our laboratory has investigated uptake and accumulation of Hg by Indian mustard (*Brassica juncea*), Beard grass (*Polypogon monospeliensis*), Chinese brake fern (*Pteris vittata*) and Boston fern (*Nephrolepis exaltata*) as well as its oxidative phytotoxicity (Chen *et al.* 2009; Han *et al.* 2004). All these plants are upland plants. No detailed studies have been done on application of aquatic plants to phytofilter Hg from river, lake and storm waters. The objectives of this study were to 1) investigate effects of chloride and pH on solubility of soil mercury sulfide in contaminated Oak Ridge soil reacted with iron oxides and 2) uptake of Hg by water Lettuce (*Pistia stratiotes*) from water.

Materials and methods

Soil sampling and laboratory experiments

The soil at the study site is Armuchee soil (clayey, mixed, thermic Ochreptic Hapludults). This is a moderately deep soil with a clayey subsoil. Armuchee soils are formed in residuum of shale. The total Hg concentration of this soil was 0.20 ± 0.15 mg/kg, indicating that the soils has not been contaminated.One gram of iron oxides (magnetite, Fe_3O_4, 325 mesh or hematite Fe_2O_3, 325 mesh) were used to react with either 0.1 g pure mercury sulfide cinnabar mineral or 5 g of contaminated Oak Ridge soil. Soil contained 2000 mg/kg Hg as HgS. For the experiment with various pHs, 35 ml of 0.01 M $NaNO_3$ at pH 4, 6 and 8 was added to the mixture and the mixture was shaken for 24 hours and then centrifuged. Supernatant was filtered with 0.45 um filter for analyses. For the experiment with various Cl concentrations, 35 ml of 0.01, 0.1 and 1 M NaCl was added to the mixture.

Greenhouse study with water lettuce (pistia stratiotes)

Water lettuce (*Pistia stratiotes*) plants with a similar size (4-5 full leaves) were collected from a clean water pond for the experiment. Hg was not found in the pond water. The plants were transferred into 1000 mL of modified Hoagland's solution containing $HgCl_2$ and grew for 7 days. The pH of the nutritant solution is 5.5. $HgCl_2$ with different Hg concentrations (1, 5, 10, and 20 mg/l) was used. After seven days, plant samples were collected and roots were washed by 1% (v/v) HCl and distilled water to remove the mercury adhering to the surface of the roots. Plants were dried for 48h at 70ºC, and then weighed for mercury content analysis.

Results and discussion

Effects of Cl and pH on reaction of HgS and iron oxides in pure mineral systems and in HgS-contaminated oak ridge soil

We observed the increase in SO_4 concentrations in pure HgS cinnabar-iron oxide (both magnetite and hematite) systems. The SO_4, Fe and Hg concentrations in (NaCl) solution increased with increasing in Cl concentrations (Figure 1). This clearly indicates that Cl promoted oxidation-induced dissolution of Hg and S from HgS cinnabar mineral surface via surface complexing. The possible mechanisms of dissolution of HgS were suggested to include surface complexation of mercury and oxidation of surface sulfur species by trivalent iron atoms from iron oxide. This mechanism was proposed to explain the increase in dissolution of Hg by the organic matter. The complexing of Cl with iron and dissolved Hg may promote the oxidation-induced dissolution reaction. This resulted in a significant decrease in pH from 4.9 to 4.1.

The similar increase in SO_4 was observed in HgS contaminated Oak Ridge soil reacted with iron oxide (magnetite). Significant pH decrease was also found in the soil system with increasing Cl. The possible reactions may be as follows:

$\text{HgS (cinnabar)} + Fe^{3+} \text{ (iron minerals)} \rightarrow HgSO_4 + FeSO_4$

$\text{HgS (soil)} + Fe^{3+} \text{ (iron minerals)} + Cl \rightarrow HgCl_2 + FeCl_2 + SO_4$

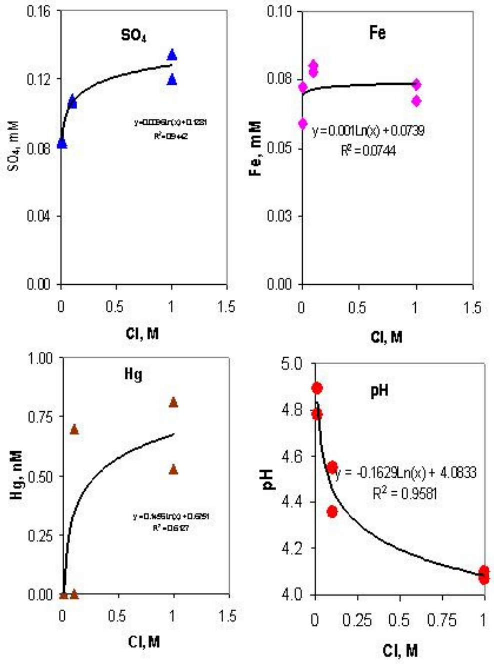

Figure 1. Changes in SO_4, Hg and Fe concentrations in NaCl extracts and pH in the HgS cinnabar-Fe_3O_4 mineral systems with increasing Cl concentration (NaCl).

The effects of initial pH on concentration of SO_4 released from Oak Ridge soils were observed, but not significant. A slight increase in SO_4 release from contaminated soils reacted with magnetite was found with increase in initial pH of the suspension.

Mercury sulfide is stable in soils under normal conditions. The solubility product constant of HgS is $10^{(-52)-(-54)}$ (Han *et al.* 2008). Thus,many common chemical extractants are not able to solubilize and extract mercury from pure HgS. Strong acids, such as 4M HNO_3 and 12 M HNO_3, only extracted <0.033% and <0.086% of Hg from commercial chemical HgS, respectively (3). The extractability of HgS from HgS-contaminated Oak Ridge soil significantly increased. However, neutral salts, such as NH_4OAc, and other weak extractants (e.g., $NH_2OH{\cdot}HCl$, pH 2) did not extract any detectable amounts of Hg from pure chemical or from HgS-contaminated soils (3). EDTA also effectively released mercury from cinnabar-contaminated Oak Ridge soils (3).

Phytofilteration of Hg from water with water lettuce

Water lettuce effectively removed Hg from Hg solution in the range of 0-20 mg/L. Kinetics of Hg concentrations showed that even first day of reaction effectively removed a majority of Hg (Figure 2)

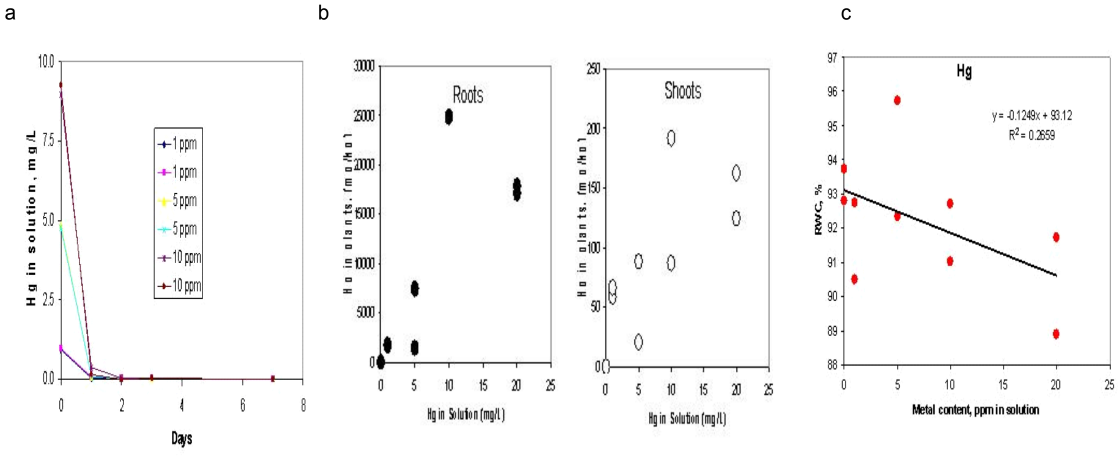

Figure 2. a. Kinetics of mercury concentrations in water with days of growing of plants; b. Uptake of mercury by shoots and roots of water lettuce; c. Relationships between relative moisture contents of shoots and mercury concentrations in water.

After the end of 7 days of cultivation, no any mercury residual was found in solution (Figure 2).Of course, some of Hg may be evaporated into the air, but the majority of Hg was cumulated in roots of plants. The maximum Hg accumulation in roots of water lettuce could be up to 2.5%. Mercury concentrations in both roots and shoots increased with Hg in solution (Figure 2). However, Hg phytotoxicity was also found in water lettuce over the experiment. Both fresh weight and relative moisture contents decreased with increase in Hg concentrations in solution (Figure 2). Relative moisture (water) contents (RWC) of shoots have been suggested to be correlated to phytotoxicity of Hg and other heavy metals in plants (2). Significant decrease in RWC due to exposure to Hg was also observed in ferns and Indian mustard (4).

Our preliminary experiments showed increased oxidation-induced dissolution of Hg from both pure HgS cinnabar mineral surface and HgS contaminated Oak Ridge soil via Cl complexing. Increases in Cl concentrations resulted in increases in Hg, Fe, and SO_4 concentrations, but decreased pH in the pure and soil systems. However, the detailed mechanisms and kinetics require further study. On the other hand, water lettuce proves a very promising candidate for phytofiltering Hg from contaminated lake/river/story water from the site.

References

Han FX, Su Y, Monts DL, Waggoner CA, Plodinec MJ (2006) Binding, Distribution, and Plant Uptake of Mercury in a Soil from Oak Ridge, Tennessee, USA. *Science of Total Environment* **368***,* 753-768.

Chen J, Shiyab S, Han FX, Monts DL, Waggoner CA, Yang ZM, Su Y (2009) Bioaccumulation and Physiological Effects of Mercury in *Pteris vittata* and *Nephrolepis exaltata. Ecotoxicology* **18**, 110-121

Han FX, Shiyab S, Chen J, Su Y, Monts DL, Waggoner CA, Matta FB (2008) Extractability and bioavailability of mercury from a mercury sulfide contaminated soil from Oak Ridge, Tennessee, USA. *Water, Air and Soil Pollution* **194**, 67-75.

Han FX, Sridhar BBM, Monts DL, Su Y (2004) Phytoavailability and Toxicity of Trivalent and Hexavalent Chromium to *Brassica juncea L. Czern. New Phytologist* **162**, 489-499.