BIOAVAILABILITY AND SPECIATION OF MERCURY IN SOILS FROM OAK RIDGE, TN

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ABSTRACT

The Oak Ridge Site has identified a need to investigate the bioavailability of mercury compounds in the Oak Ridge ecosystem. DIAL scientists have performed a series of laboratory analyses and greenhouse experiments. Uncontaminated soil was obtained from Roane County, TN (near the Oak Ridge Site) and spiked with three mercury compounds (nitrate, chloride and sulfide) at low, intermediate and high loading levels. Plants were then grown in the media to evaluate the bioavailability of different mercury chemical species in the spiked soil. We have examined solution/liquid phase speciation of mercury in the spiked soil without plants and also after a growing season with Chinese brake fern plants. Redistribution and transformation of solid-phase mercury species in spiked soil were also investigated. The effects of plants and incubation time on bioavailability and stability (especially for mercury sulfide) have been examined as well. Our study to date has demonstrated that soluble ionic mercury compounds readily undergo substitution reactions to form chloride compounds in Oak Ridge soil with the exact composition being a function of aqueous Cl^- concentration present in the soil liquid solution. The rate of plant uptake of Hg from soils contaminated with $Hg(NO_3)_2$ and of $HgCl_2$ are approximately linear with time while the phytoextraction rate of Hg from soils treated with HgS is exponential with time (at least for the time period investigated). Despite its very low solubility and low volatility, significant amounts of Hg as extracted by 4M HNO_3 from soils treated with HgS were found to undergo natural attenuation with time with the possible route including phytoextraction uptake by Chinese brake fern. A conceptual model of mercury speciation and bioavailability in both liquid and solid phases has been proposed and comparison with initial data sets shows significant correlation. We will continue this project during the upcoming growing season and will have extensive numbers of laboratory analyses in the coming months (approximately a thousand samples have been chemically analyzed to date). We expect the outcomes of these studies will benefit our understanding of bioavailability and stability of mercury and mercury compounds in Oak Ridge soils.

INTRODUCTION

Because of mercury's widespread presence in mining ores and coal and because of its common use in everyday items (such as thermometers, batteries, electrical switches, etc.), a significant amount of mercury from anthropogenic sources is present in the pedosphere (1). Historically as part of its national security mission, the U.S. Department of Energy's Y-12 Plant in Oak Ridge, TN 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 Plant. 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 of and surrounding the Y-12 Plant (2,3). 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.

The long-term bioavailability, stability, and mobility of Hg species in contaminated terrestrial and aquatic environments (including soils, sediments, and the interface) of the Oak Ridge ecosystem under a range of biogeochemical conditions are not well understood. Mercury can be expected to be present as various forms (e.g., HgS, Hg(II), methyl-Hg, Hg(O)) (4-8). These species can be transformed from one form into another thus bioavailability, toxicity, and mobility can change as a function of the biogeochemical conditions. The kinetics of these transformations are currently unknown.

In addition, the long-term stability of Hg in rhizosphere soil (i.e., the small-scale root-soil interface region) is not well understood. Plant roots can alter their microenvironment and mobilize otherwise stable Hg compounds. As an outgrowth of our efforts to investigate the phytoremediation and bioavailability of selected heavy metals (9-14), we are investigating and devising monitors for short- and long-term bioavailability, stability and mobility of Hg species and other species of concern sequestered in contaminated soils/sediments, including vadose zone and saturated zone, under different biogeochemical conditions by varying redox, pH, dissolved organic carbon (DOC), and co-cations and anions.

PRELIMINARY RESULTS

Our experiments utilized soil collected from a private farm in Roane County, Tennessee, near Oak Ridge's East Tennessee Technology Park (ETTP) where the K-25 facility is located. Thus our results are indicative of the Oak Ridge biogeochemical environment.

At the present time, there are no plants known to be able to accumulate large amounts of mercury above ground level. Therefore as part of this effort, we have to date investigated the ability of plants [Indian mustard (*Brassica juncea*), Beard grass (*Polypogon monspeliensis*), Chinese brake ferns (*Pteris vittata* and *Pteris mayii*)] that are known to efficiently uptake other heavy metals to uptake mercury. *Pteris vittata* was chosen for this study because of its demonstrated ability to withstand high concentrations of arsenic (15,16), which is toxic to most plants. Of the plants we have studied to date, *Pteris vittata* has the greatest capability to accumulate mercury above ground (17).

Soil is a mixture of solid-phase components and liquid-phase components. We have investigated the fates of selected mercury compounds both in the soil solution phase and in the soil solid phase. We began our investigation by studying the solubility of selected mercury compounds [$Hg(NO_3)_2$, $HgCl_2$, and HgS] in Oak Ridge soil both with the presence of a plant [Chinese brake fern (*Pteris vittata*)] and without a plant and the results are summarized in Table I. The

experiments were performed by adding a known concentration of a selected mercury compound to a pot of soil and then determining the concentration of mercury in the pot 40 days later in the case of experiments without plants and after one growing period (also about 40 days) for experiments with a plant present. The "total Hg" concentration was determined using two different approaches. The first approach utilized a single extraction using 4 M HNO_3; this approach determines the concentration of mercury from all chemical species (including elemental mercury, but excluding HgS), but does not provide any chemical speciation information. The second approach is a six-step sequential extraction process: (i) exchange fraction using NH_4NO_3; (ii) easily reduced oxide fraction using hydroxylamine; (iii) organic matter fraction using H_2O_2; (iv) amorphous iron fraction using $(NH_4)_2C_2O_4$ buffer; (v) crystalline iron fraction using hydroxylamine with 25% acetic acid; and (vi) the residual fraction. The amount of Hg in each fraction was determined using inductively coupled plasma-atomic emission spectroscopy (ICP-AES). When the amount of Hg from the sequential extraction procedure is summed and plotted versus the amount of Hg determined from a single extraction by 4 M HNO_3, a linear relationship is obtained with a linear least squares slope of 0.9858 and an R^2 goodness-of-fit value of 0.9526 (17). Thus the total Hg concentration determined from a single extraction using 4 M HNO_3 can be used as the total concentration of all mercury species (except HgS). (The concentration of HgS was determined using a single extraction using saturated Na_2S.) As the concentration of Hg added to the soil increased, the amount of mercury remaining in the soil liquid solution at the end of the experiment increased, but significantly more $HgCl_2$ remained in the soil liquid solution when a plant was not present than when a plant was present. When HgS was added, very little HgS was present in the soil liquid solution at the end of the experiment; since the solubility of HgS is very low, the results for HgS are to be expected.

Table I. Mercury concentration (in mg/L) in soil solution as extracted with 1:1 soil/water. The initial mercury compound concentrations are in mg/kg.

Treatment		Without Plants	With Plants
$Hg(NO_3)_2$-100	Avg	0.05	0.06
	SD	0.002	0.038
$HgCl_2$-100	Avg	0.04	0.05
	SD	0.002	0.012
$HgCl_2$-250	Avg	0.06	0.03
	SD	0.002	0.006
$HgCl_2$-1000	Avg	0.98	0.08
	SD	0.002	0.011
HgS-1000		<0.02	<0.02
HgS-2000		<0.02	<0.02

We also determined what mercury species are present 40 days after addition of $Hg(NO_3)_2$ and of $HgCl_2$ to different soil samples; the results are presented in Table II. The dominant mercury species in the soil liquid solution at the end of the 40-day period was aqueous $HgCl_2$ whether $HgCl_2$ or $Hg(NO_3)_2$ had been initially added. This shows that ionic mercury compounds have a

Table II. Distribution of mercury species in soil liquid solution (% of Hg in 1:1 soil/water extracts) of soils contaminated with 100 mg/kg Hg as $Hg(NO_3)_2$ and 1000 mg/kg Hg as $HgCl_2$. DOC is dissolved organic carbon. Concentrations of some species calculated using MINTEQA2 (18).

Hg Species	$Hg(NO_3)_2$-100	$HgCl_2$-1000
$Hg(OH)_2$	0.022	
$HgCl^+$	0.056	
$HgCl_2$ (aq)	94.9	94.3
$HgCl_3^-$	0.397	5.38
$HgCl_4^{-2}$		0.155
HgClOH (aq)	3.22	0.134
Hg^{+2}DOC	1.36	

strong tendency to undergo substitution reactions to form mercury chloride compounds. The effect of Cl^- concentration as calculated using MINTEQA2 (18) is presented in Fig. 1. As the $Cl^-_{(aq)}$ concentration increases to about 2 mM, the concentration of aqueous $HgCl_2$ increases. Thereafter as the Cl^- concentration increases, the aqueous $HgCl_2$ concentration decreases. The $HgClOH_{(aq)}$ concentration decreases with increasing Cl^- concentration and the $HgCl_3^-{}_{(aq)}$ concentration monotonically increases with increasing $Cl^-_{(aq)}$ concentration. Thus the $Cl^-_{(aq)}$ concentration determines the concentration and speciation of soil liquid solution phase mercury compounds.

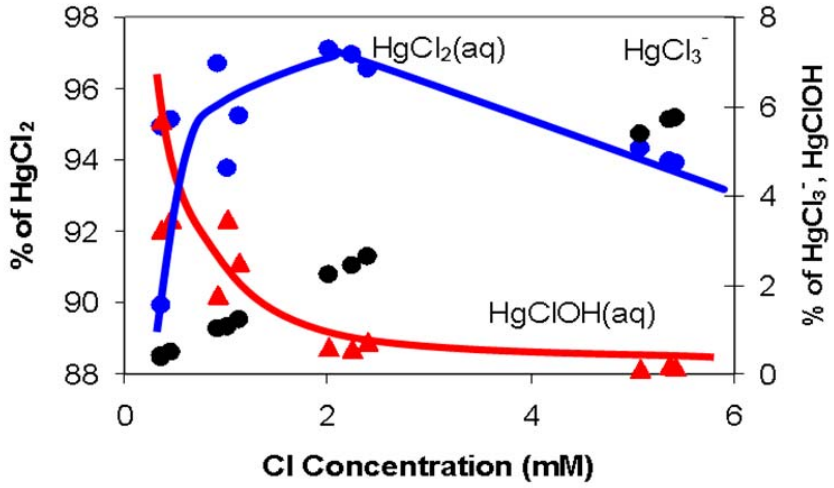

Fig. 1. The effect of chloride ion concentration on the aqueous concentrations of $HgCl_2$ (blue spheres), $HgCl_3^-$ (black spheres), and HgClOH (red triangles) in soil liquid solution phase as calculated using MINTEQA2 (18).

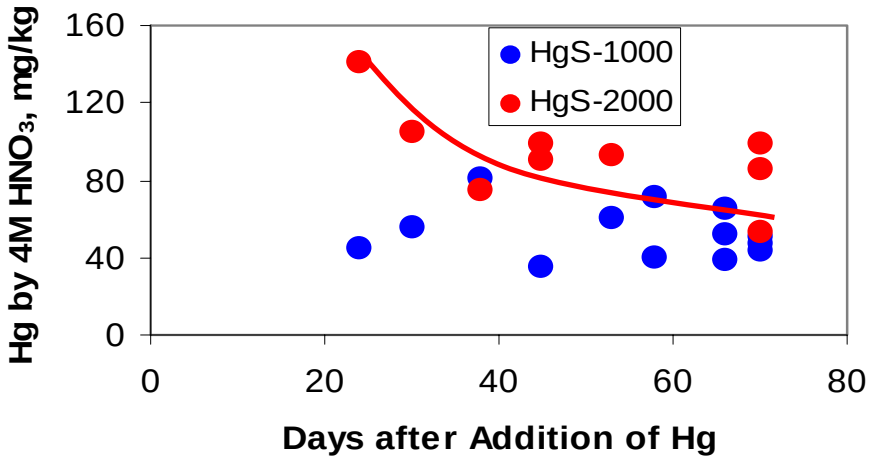

Fig. 2. Natural attenuation of Hg in HgS-treated soil as a function of time and as a function of initial HgS concentration (in ppm). The amount of "total mercury" was determined from a single extraction in 4 M nitric acid.

Natural attenuation of a mercury chemical species present in the soil can occur by three major processes: (i) chemical transformation and redistribution among the soil solid-phase components; (ii) plant uptake; and (iii) volatilization into the atmosphere. In all soils contaminated with $HgCl_2$, $Hg(NO_3)_2$ and HgS, total Hg extracted by 4 M HNO_3 decreased with time. In contrast to soils with aqueous $HgCl_2$ and $Hg(NO_3)_2$, the retention of Hg in soil contaminated with HgS as extraction by 4 M HNO_3 displays a concentration dependence (Fig. 2). At lower HgS concentration (1000 ppm), the amount of Hg extracted by 4 M HNO_3 is basically time independent, while at higher HgS concentration (2000 ppm), the amount of Hg as extracted by 4 M HNO_3 decreased with time. Since the solubility of HgS is so low (solubility product of HgS is ~10^{-52}), it is common to assume that none of the HgS dissociates and that HgS is an

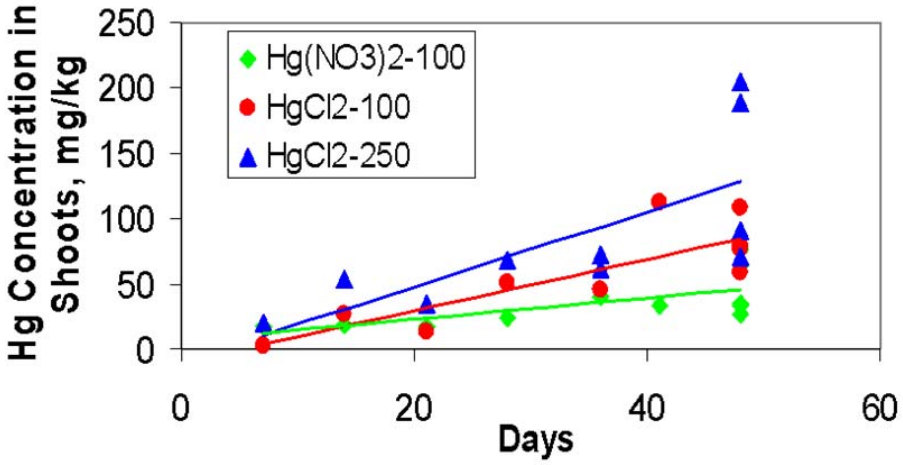

Fig. 3. Uptake into plant shoots of selected mercury compounds as a function of growing time. Initial concentrations of mercury compounds are in ppm. The concentration of mercury in shoots is determined after digestion by HNO_3-H_2O_2.

environmentally stable form. However, the presence of dissolved organic matter (DOC) is known to increase the solubility of HgS (19) and the observed effect is consistent with that observation.

We have also investigated the rate of phytoextraction uptake of various mercury chemical species by Chinese brake fern. As Fig. 3 shows, for equal concentrations (100 ppm) of $HgCl_2$ and of $Hg(NO_3)_2$, the rate of uptake of Hg from soils with $HgCl_2$ is greater than that of $Hg(NO_3)_2$. The results above show that Hg in $Hg(NO_3)_2$ contaminated soils is also present as aqueous $HgCl_2$ in soil solution. Furthermore, Fig. 3 demonstrates that as the concentration increases, the amount accumulating in the fern shoots also increases (at least for the concentrations investigated). With 100 mg/kg treatment of either $HgCl_2$ or $Hg(NO_3)_2$, Chinese brake fern plants (roots and shoots) extracted 1.6-8.5% (average 2.9-3.9%) of the total Hg in the soil during a 48-day growing season. At higher concentrations, the absolute amount of Hg phytoextracted from the soil increased, but the percentage decreased: for 250 mg/kg $HgCl_2$, Chinese brake fern uptake was 0.5-1.3% (average 0.9%) of total Hg in soil during a 48-day growing season; for 1000 mg/kg $HgCl_2$, plant uptake was 0.2-0.5% (average 0.2%) of total Hg in soil during a 48-day growing season. Similarly the concentration of Hg in Chinese brake fern shoots exponentially increases with time in soils contaminated with HgS (as presented in Fig. 4), but is still very small—for both 1000 and 2000 mg/kg HgS treatment, less than 0.02% of the total Hg in the soil was phytoextracted by Chinese brake fern plants during a 48-day growing season.

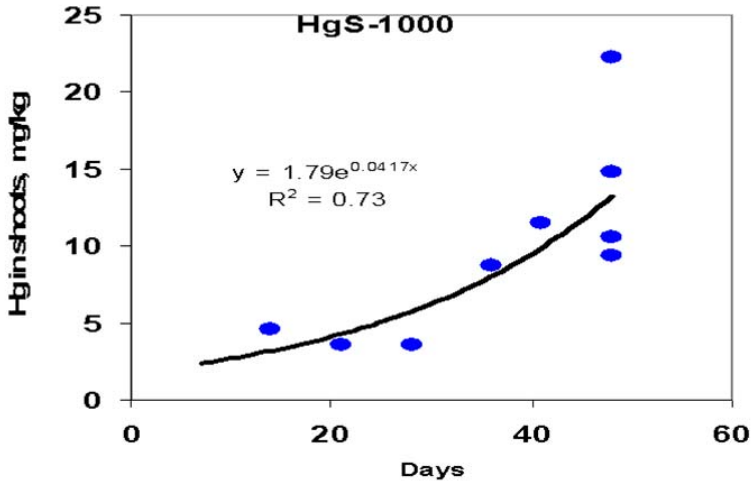

Fig. 4. Uptake into plant shoots of Hg from soil contaminated with HgS as function of growing time. Initial HgS concentration was 1000 ppm. The concentration of mercury in shoots is determined after digestion by HNO_3-H_2O_2.

SUMMARY AND FUTURE EFFORTS

Our study to date has demonstrated that soluble ionic mercury compounds readily undergo substitution reactions to form chloride compounds in Oak Ridge soil with the exact composition being a function of aqueous Cl^- concentration present in the soil liquid solution. The rate of plant

uptake of Hg from soils contaminated with $Hg(NO_3)_2$ and of $HgCl_2$ are approximately linear with time while the phytoextraction rate of Hg from soils treated with HgS is exponential with time (at least for the time period investigated). Despite its very low solubility and low volatility, significant amounts of Hg as extracted by 4M HNO_3 from soils treated with HgS were found to undergo natural attenuation with time with the possible route including phytoextraction uptake by Chinese brake fern.

Our future efforts will include examination of natural attenuation rates for elemental mercury in Oak Ridge soil with and without plants; determination of the volatilization rates of elemental mercury from selected plant species; phytoremediation efficiency of native Oak Ridge plants; and development of a testbed for investigating the transfer and interplay between mercury species in soil, aquatic, and atmospheric media.

ACKNOWLEDGEMENTS

We wish to thank Dr. Elizabeth Phillips (DOE ORO EM) and Dr. Paula Kirk (ORNL) for providing us with guidance with regard to critical closure uncertainties and the type of data that is needed for DOE to make decisions for the Oak Ridge Site. We also wish to thank Mr. Dharmendra K. Singh, Mr. Cheng Wang, Mr. Shyam S. Balasubramaniam and Mr. Thomas W. Hallmark, for their contributions in data collection and plant culture activities. The authors are thankful to Ms. Yunju Xia, Mr. Dean Patterson, and Dr. Thomas Meaker of DIAL for their help in chemical analysis. This research is supported by U.S. Department of Energy's Office of Science and Technology through Cooperative Agreement DE-FC26-98FT-40395.

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