Stability and Bioavailability of Mercury Sulfide in Oak Ridge Soils

F. Han, S. Shiyab, Y. Su, D.L. Monts, C.A. Waggoner
Institute for Clean Energy Technology (ICET)
Mississippi State University, 205 Research Blvd., Starkville, MS 39759
USA

F.B. Matta
Department of Plant and Soil Sciences
Mississippi State University, Mississippi State, MS 39762
USA

ABSTRACT

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 U.S. Department of Energy's Y-12 National Security Facility and in the Y-12 Watershed in Oak Ridge, Tennessee, USA. 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. 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. Specifically, the long-term bioavailability, stability, and mobility of mercury species in contaminated terrestrial and aquatic environments of the Oak Ridge ecosystem under a range of biogeochemical conditions are not well understood. Mercury can be expected to be present in various forms. 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 is currently unknown. We have conducted pilot scale experiments to study the bioavailability of mercury sulfide (HgS) in Oak Ridge soils. The effects of plants and incubation time on chemical stability and bioavailability of HgS under simulated conditions of the Oak Ridge ecosystem have been examined, as has the dynamics of the dissolution of HgS by various extractants. The results show that HgS in contaminated Oak Ridge soils was still to some extent bioavailable to plants.

INTRODUCTION

The Y-12 National Security Facility site encompasses about 324 hectares (ha) (3.24×10^6 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 [1]. The source of the mercury is from 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, including estimates for the 1950

to 1954 period, has been estimated to range from about 75 to 150 metric tons [2]. Most of the contamination around Y-12 is confined to the upper 10 feet (3 m) of soils and fill [1]. Additional studies revealed that about 77,180 kg of mercury are contained in the sediments and floodplain soils of a 15-mile (24-km) length of East Fork Poplar Creek (EFPC), which has its headwaters at Y-12, and that about 227 kg of mercury annually leave this watershed [3]. EFPC flows through the city of Oak Ridge, exposing people to mercury contamination in the easily accessible areas of the floodplains of the creek. The concentrations of mercury in Upper EFPC watershed (soil) range from 0.01 to 7700 mg/kg [4]. In the sediments of EFPC and Lower Poplar Creek, mercury concentrations peaked at depths of 10-20 cm (40 mg/kg) and at 40-60 cm (15 mg/kg mercury), respectively [5]. Some sediment cores contained 460 mg/kg mercury at depths of 80-84 cm [6]. Mercury has been detected at higher than background levels in sediments of the Clinch River and the Tennessee River near Chattanooga, some 118 miles (190 km) downstream of Oak Ridge [3].

A series of remediation efforts have been employed in the Oak Ridge watersheds. These include central pollution control facility, source collection, elimination of untreated discharges, central and east end mercury treatment systems, relining of sanitary and storm sewers, and bank stabilization project [7]. The U.S. Department of Energy (DOE) has removed soil at several locations along the creek where mercury concentrations were particularly high [3]. Mercury can occur as various species (e.g., HgS, Hg(II), methyl-Hg, Hg(O)), but the predominant form of mercury in the floodplain soils of the region is mercuric sulfide (HgS) [8]. 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 bio-availability. HgS, in general, has been considered to be the stable mercury form in soils and sediments since its solubility is limited. The stability and transformation of HgS in Oak Ridge soil might control its solubility, mobility, and bioavailability in both terrestrial and aquatic ecosystems.

Since mercury in floodplain soils across the EFPC in soils now is mainly present in the relatively insoluble HgS [9], it is essential to assess the stability and extractability of HgS in the Oak Ridge soil and its bioavailability to plants. In addition to the Oak Ridge site, mercury-contaminated wastes in many forms are present at virtually every U.S. Department of Energy site and hence potentially there is mercury in their ecosystems. The objectives of this initial study are to investigate solubility and extractability of HgS by various extractants and its distribution among solid-phase components in contaminated soil. Finally, the bioavailability of HgS to plants was also studied as well.

MATERIALS AND METHODS

Soil Sampling and Greenhouse Study

The soil 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. This soil has clay loam texture with pH 5.6 ± 0.2. It contains 4.56 ± 1.5 % organic matter and 1.90 ± 0.007% iron oxides. Surface soils (0 to 15 cm) were sampled from a

private farm in Roane County, Tennessee, near Oak Ridge's East Tennessee Technology Park (ETTP) where the K-25 facility was located. Soil was air-dried and ground to pass a 2-mm sieve. Relevant soil properties are presented in Table I.

About 1.5 kg of air-dried soil was weighed and transferred into plastic pots. Nitrogen, phosphorous, potassium (N:P:K = 1:1:1) were added to soils as base fertilizers. Chemical grade HgS was added to soils at 1000 and 2000 mg/kg in May, 2004. After 17 days of equilibrium of the mercury compounds in soil, a 4-5 month old Chinese brake fern (*Pteris mayii*) from Edenspace (Edenspace Inc. Dulles, VA) was transferred into the pots. The plants grew for 48 days and were then harvested. A second season of brake ferns was planted in spring, 2005 and plants grew for 60 days. The third growing season for this soil involved Indian mustard (*Brassica juncea*)(two varieties, Florida broadleaf and longstanding). The Indian mustard was planted in spring, 2006 and grew for 53 days. All pots were watered and kept at field capacity moisture throughout the growing seasons. Each treatment had twelve duplicates. Two replicates of both plant samples and soil samples were taken for analyses after one, two, and four weeks of planting and the rest were harvested 48 days after the transfer. Total incubation experiment lasted for 65 days. Roots and shoots were sampled and soil samples were collected for analyses. After harvest, roots were washed with distilled water, followed by diluted acid. Both roots and shoots were oven-dried for analyses at 80^{o}C for 48 hours. Dry shoots and roots were ground and weighed.

Table I. Relevant soil physico-chemical properties and mercury concentrations of a soil from Oak Ridge, TN, USA.

pH		5.6 ± 0.2
Cation exchange capacity (CEC)	$cmol_c\ kg^{-1}$	4.2 ± 0.34
Organic matter	%	4.35 ± 1.34
Hygroscopicity	H_2O%	0.84
Free Fe oxide	Fe_2O_3%	1.90 ± 0.007
Free Si oxide	SiO_2%	0.05 ± 0.0005
Free Al oxide	Al_2O_3%	0.52 ± 0.001
Free Mn oxide	MnO_2%	0.24 ± 0.001
Total Hg	mg/kg	0.20 ± 0.147
Texture[a]		Clay Loam
Sand	%	22
Silt	%	41
Clay	%	37

Plant and Soil Analysis

Plant samples (shoots or roots, approximately 0.2-0.5 g) were digested on a hot plate with concentrated HNO_3 and H_2O_2 [10]. The digested solution was filtered and then analyzed

for mercury concentration using inductively coupled plasma-atomic emission spectrometry (ICP-AES) (Perkin Elmer Instruments, Optima 4300DV) and cold vapor atomic absorption spectrometry (CVAAS) (FIMS 100 CVAAS, Perkin Elmer Instruments). Plant uptake of mercury per pot was the sum of mercury uptake by shoots and roots, which was calculated from the products of mercury concentrations in either shoots or roots multiplied by its dry biomass.

Soil pH was measured by electrodes in 1:1 water extracts and cation exchange capacity (CEC) was determined with NH_4Cl-KNO_3 method [11]. Organic matter was measured by $K_2Cr_2O_7$-H_2SO_4 and free Fe (Mn/Al/Si) oxides were analyzed by citrate-bicarbonate-dithionite method [10]. Fresh soil samples were used for all soil mercury analyses. Saturation paste extraction (1:1 soil: deionized water ratio) was conducted to study mercury speciation in soil solution. Anions (Cl, NO_3, SO_4, and PO_4) in the extracts were determined by ion chromatography (Dionex LC 20, Sunnyvale, California). Cations (Ca, Mg, K, and Na) were measured by ICP-AES. Soluble mercury in the extracts was analyzed by CVAAS. Dissolved organic carbon was determined by UV persulfate total organic carbon (TOC) analyzer (Tekmar Dohrmann Phoenix 8000) and soil solution pH was measured by a pH electrode.

Mercury fractions in soils have been determined by sequential dissolution extractions, which have been widely used to study the binding forms, mobility and bioavailability of heavy metals including mercury in soils and sediments [12-17]. Mercury in soils was assumed to be present in six operationally defined solid-phase fractions, which are obtained by selective sequential dissolution (SSD). The protocol employed in this study was developed based on the procedures by Tessier *et al*. [12], Shuman [13], and Han *et al*. [17]. Compared to the traditional sequential dissolution extraction procedures by Tessier *et al*. [10] and Biester and Scholz [18], we added one fraction at the end aiming at extraction of the cinnabar HgS form: saturated Na_2S-extractable fraction. The residual fraction (RES) with 4M HNO_3 before the cinnabar fraction may extract mercury remaining from all previous steps (except for HgS) due to incomplete extraction, such as humin-binding mercury. The modified sequential dissolution extraction procedure clearly distinguishes mercury as cinnabar HgS form (by saturated Na_2S) from humic/humin-binding Hg in the RES fraction.

NH_4OAc-extractable Mercury. This fraction includes soluble plus exchangeable mercury (**EXC**). Twenty-five mL of a 1 M ammonium acetate solution (pH adjusted to 7.0 with NH_4OH) were added to 1.1 g of air-dried soil (equivalent to 1 g of oven-dried soil) in a 50-mL Teflon centrifuge tube. The mixture was shaken for 30 min at 25^{o}C, and then centrifuged. The supernatant was decanted and filtered through a 0.45-μm filter. The soil residue was kept for the next analysis/dissolution step. The same centrifugation-decantation steps were used after each of the following extractions.

$NH_2OH{\cdot}HCl$-extractable Mercury. This fraction mainly targets mercury bound to easily reducible oxides, such as Mn oxides, (**ERO**) [13]. Twenty-five mL of a 0.1 M $NH_2OH{\cdot}HCl$ + 0.01 M HCl solution (pH 2) were added to the soil residue and shaken for 30 min. This acid might attack some organic matter, resulting in underestimation of the

organically bound metal. However, after extraction of the exchangeable fraction, this attack is less serious.

H_2O_2-oxidizable Mercury. This fraction mainly targets mercury bound to organic matter (**OM**) [13, 16] as well as Hg^0 and some extent of HgS [18]. Three mL of a 0.01 M HNO_3 and 5 mL of 30% H_2O_2 were added to the soil residue. The mixture was digested in a water-bath at 80 ^oC for 2 hrs. An additional 2 mL of H_2O_2 were added and the mixture was heated for one hour. Fifteen mLs of a 1 M ammonium acetate solution were then added and the sample agitated for 10 min.

Oxalate-extractable Mercury. This fraction extracts mercury bound to amorphous iron oxides (**AmoFe**). Twenty-five mL of a 0.2 M oxalate buffer solution (0.2 M $(NH_4)_2C_2O_4$– 0.2 M $H_2C_2O_4$ at pH 3.25) were added to the soil residue and the sample shaken in the dark for 4 hours [13].

Hot $NH_2OH{\cdot}HCl$ and HOAc-extractable Mercury. This fraction extracts mercury bound to crystalline iron oxides (**CryFe**). Twenty-five mL of 0.04 M $NH_2OH{\cdot}HCl$ in a 25% acetic acid solution were added to the soil residue and the sample digested in a water bath at 97-100 ^oC for 3 hours.

HNO_3-extractable Mercury. 4M HNO_3 extracts the residual non-cinnabar mercury (**RES**) from the incomplete extraction of previous fractions (mostly from the organically bound mercury, such as humin bound mercury) as well as Hg^0 [18]. Twenty-five mL of 4 M HNO_3 were added to the residue or soil and the sample was transferred to a glass digestion tube. Digestion was conducted in a water bath at 80 ^oC for 16 hours [13, 16]. The same procedure was used to determine total non-cinnabar mercury (**TOT_{HNO3}**).

Cinnabar mercury (HgS). Four mL of saturated Na_2S were added to the residue soil and the sample was mixed and reacted overnight. The extraction is repeated twice [19].

RESULTS AND DISCUSSIONS

Extractability of HgS from Cinnabar-Contaminated Soil

HgS is stable in soils under normal conditions. The solubility product constants of HgS is $10^{(-52)-(-54)}$ [20]. 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 pure chemical HgS, respectively (Table II, Fig. 1).

However, the extractability of HgS in contaminated soils increased. 4M HNO_3 extracted 0.6-6.1% of mercury from cinnabar-contaminated soils, while 12 M extracted 3-4% of mercury from the soil. Extractability of HgS in contaminated soils was higher than that of pure chemical. However, neutral salts, such as NH_4OAc, and other weak extractants did not extract HgS. 1M NH_4OAc and $NH_2OH.HCl$ (pH 2) could not extract Hg from HgS contaminated soils (Table II, Fig. 1).

Table II. Extractability of pure chemical HgS and contaminated Oak Ridge soils with cinnabar by various chemical reagents (% of the HgS).

Reagents	Pure HgS	Contaminated soils
Na_2S (saturated)		99-100%
EPA method ($HCl:HNO_3:H_2O$, 1:6:7)		98-100%
12 M HNO_3	0.001-0.086%	0.47-3.25%
4M HNO_3	0.008-0.033%	0.69-6.08%
H_2O_2		0.13-5.13%
NH4OAc	0	0
$NH_2OH.HCl$, pH 2	0	0

Saturated solution of Na_2S extracted more than 99-100% of HgS from cinnabar-contaminated Oak Ridge soils with 1000-2000 mg/kg Hg (Table II). USEPA method 3200 (1:6:7 $HCl:HNO_3:H_2O$), which was recommended for extracting HgS from solid waste, extracted 98.9-100% of mercury from the current soil with 1000 mg/kg Hg. Revis *et al*. [19] reported that saturated solution of Na_2S extracted 98% of added HgS from soils and sediments while concentrated HNO_3 only extracted 1% of HgS. They suggested saturated Na_2S is suitable for extracting HgS from soils and sediments.

The extractability of HgS from contaminated soils by 4M HNO_3 and 12 M HNO_3 increased with increasing reaction time (Fig. 1).The gradual increases in dissolution of mercury from cinnabar-contaminated soil by HNO_3 indicate that mercury has been transformed from HgS form into other more soluble and HNO_3-extractable form(s). It is noted that dissolution of Hg from pure chemical grade HgS also initially increased in the first four hours and thereafter its dissolution reached a plateau. The initial dissolution may be from surface impure mercury form other than HgS. However, dissolution of mercury by 4M and 12 M HNO_3 from contaminated soils continued to increase with time, even after 15 hours. Various mechanisms, including effects of dissolved organic matter and microorganisms on stability of Hg, may be involved; these will be discussed below.

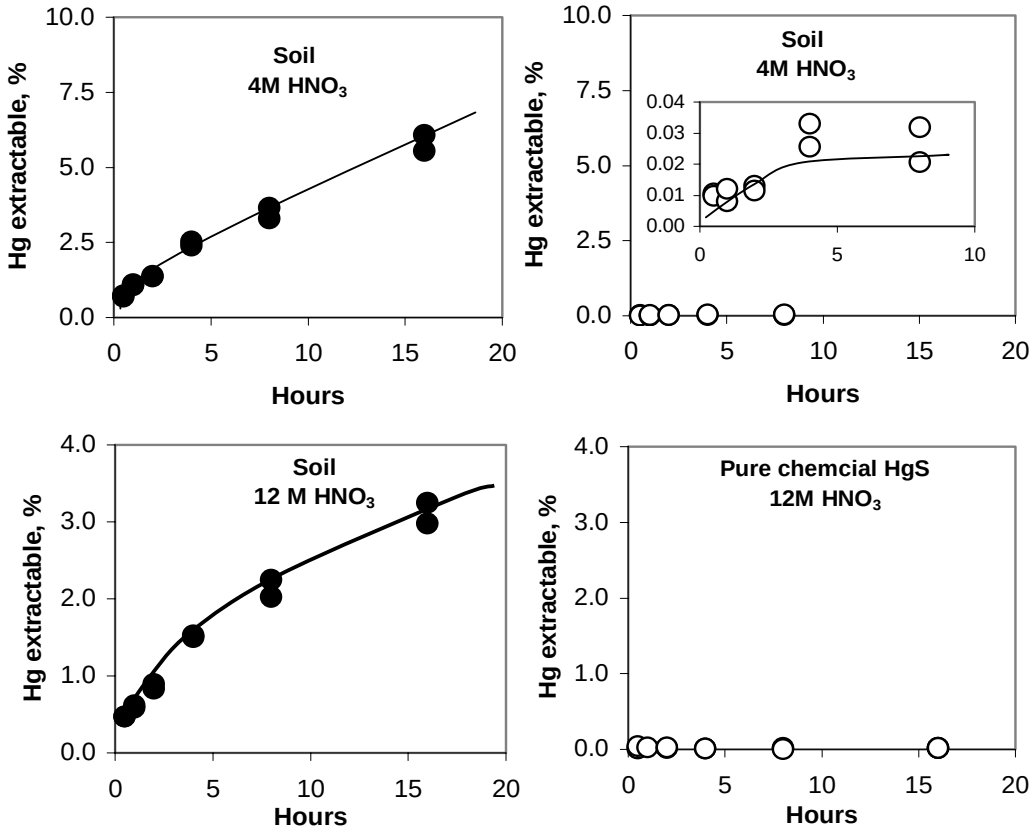

Figure 1. Kinetics of dissolution of HgS by 4M HNO_3 and 12 HNO_3 from cinnabar-contaminated Oak Ridge soils.

Solid-phase Distribution of Hg in HgS-Contaminated Soils

Mercury in HgS-contaminated Oak Ridge soils was mainly distributed in the cinnabar form (HgS) (86-97%). However, H_2O_2-extractable Hg accounted for 2 - 5% and 4M HNO_3-extractable Hg was in the range of 2 - 8.5% (Table III, Figure 2). There are two factors contributing to H_2O_2-extractable Hg: (1) soil organically bound Hg was present in soils; and (2) some extent of oxidation of sulfide in soils by H_2O_2.

The latter is excluded since the initial mercury in the organically bound fraction was in the range of 25 to 102 mg/kg in soils contaminated with HgS, while after a growing season, the organically bound mercury decreased to 1.9 - 3.5 mg/kg. After 24 days of initial incubation, 25-30 mg/kg (average: 27 mg/kg) and 40-102 mg/kg (average: 60 mg/kg) mercury were found to be in the organically bound fraction in soils contaminated with HgS at 1000 and 2000 mg/kg, respectively. Two possible processes might govern the decrease of mercury in the organically bound fraction in HgS-contaminated soils. One is DOC-enhanced dissolution and plant uptake and the other is transformation and redistribution of mercury from the organically bound fraction into both amorphous and crystalline iron oxide bound fractions.

Table III. Distribution of mercury in Oak Ridge soils contaminated with cinnabar (HgS) among solid-phase components (% of the total Hg).

HgS	Days of Planting	EXC	ERO	OM	AmorFe	CryFe	No-Cinnabar RES	Cinnabar HgS
1000	7	0.00	0.00	2.68	0.02	0.11	2.63	94.56
	7	0.00	0.00	2.98	0.03	0.11	2.25	94.64
2000	7	0.00	0.00	2.02	0.02	0.18	2.92	94.86
	7	0.00	0.00	5.13	0.04	0.24	8.43	86.16
1000	48	0.00	0.00	0.15	0.03	0.36	2.37	97.09
	48	0.00	0.00	0.14	0.06	0.29	2.42	97.09
	48	0.00	0.00	0.19	0.03	0.40	2.64	96.74
2000	48	0.00	0.00	0.18	0.01	0.38	2.03	97.40
	48	0.00	0.00	0.14	0.03	0.35	2.56	96.92
	48	0.00	0.00	0.13	0.04	0.13	3.16	96.54

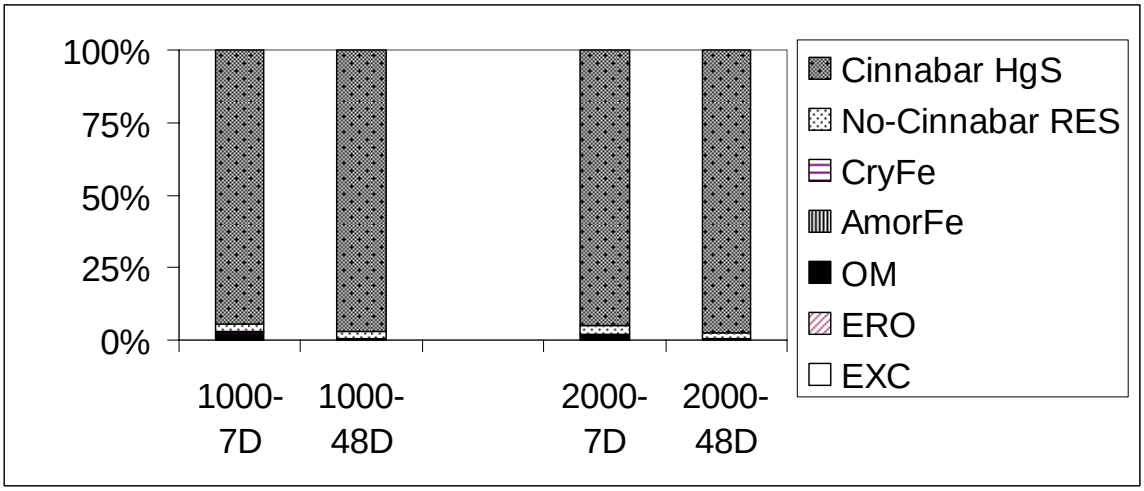

Figure 2. Distribution of mercury among solid phase components in Oak Ridge soils contaminated with HgS.

If H_2O_2 oxidizes some HgS, the oxidization process should release a similar amount of mercury in soils over the experimental period. But after the end of the growing season, H_2O_2-extractable Hg significantly decreased (Table II). However, Shannon and White [21] reported that during oxidation of organic materials in sediments, H_2O_2 extracted 69% and 104% of the Fe and S, respectively, added as FeS; and 92% and 80% of the Fe and S, respectively, added as pyrite (FeS_2). About 77% of the total carbonate of the sediments was selectively extracted in the oxidation step of the organic material [21]. Based on the present study, we can conclude that the contribution from oxidization of HgS during the extraction of the organically bound fraction is minimal. Further study will be needed to confirm the observations here.

Xia *et al.* [22] used synchrotron-based X-ray absorption spectroscopy and found the importance of reduced sulfur functional groups (thiol (R-SH) and disulfide (R-SS-R)/disulfane (R-SSH)) in humic substances in the complexation of Hg(II). They further

observed the involvement of oxygen ligands, such as carboxyl and phenol, in addition to the reduced S ligands in the complexation of Hg(II) due to the low density of reduced S ligands in humic substances. Ravichandran [23] and his coworkers [24] suggested that mercury is strongly bound to reduced sulfur sites (such as polysulfide, sulfide, and thiol groups) within the organic matter. The present soil contained 4.65% organic matter. If we assume a total sulfur content of 1% (of organic matter) and a reduced sulfur content of 20% (of total sulfur) [23], the molar concentration of reduced sulfur sites in organic matter is estimated to be 2.72 mM/kg soil. In the soils after seven days of incubation, mercury concentration in the organically bound fractions ranged from 26 to 102 mg/kg, equaling 0.12 -1.9 mM Hg/kg soil. The molar ratio of reduced sulfur to total mercury bound in soil organic matter fraction is about 1.4 to 20. However, the molar ratio of reduced sulfur to mercury changed with mercury loading levels and time. When the capacity for bonding to the reduced sulfur is filled, mercury may be attached to $–NH_2$ and –COOH by weaker bonds. It is observed that soils contaminated with insoluble HgS had 5-20 ratio of reduced sulfur to mercury bound in organic matter. As showed in Fig. 2 and Table II, mercury in the organically bound fraction decreased with time. Therefore the ratios of reduced sulfur to the organically bound Hg increased with time after a growing season in soils. This ratio drastically increased from 6-20 initially to 150-400 in soils contaminated with HgS. The mercury kept in the organically bound fraction may increase its stability with time. The conditional stability constants for mercury-organic sulfur complexes are between 10^{25} and 10^{32} [23]. In addition, the present study may provide an explanation of the observation that the majority of the total soil mercury is concentrated in the organic rich A horizon [25, 26]. Lindberg [26] has shown that in the forest ecosystem of the Walker Branch watershed (Tennessee), the largest mercury pool resided in the soil and about 75% of the total mercury soil pool was in the organic A horizon.

As indicated earlier, 4M HNO_3 extracted only < 0.033% of Hg from pure chemical HgS. However, 4M HNO_3 extracted 2-8% of Hg from HgS-contaminated soils and increased with extraction periods. Oxalate-extractable and hot $NH_2OH{\cdot}HCl$ + HOAc-extractable mercury was <0.06 and 0.4%, respectively. This indicates a series of reactions takes place in the soil matrix when HgS enters the soil. These reactions may release some mercury from very stable HgS into other forms (organically bound, soil humin bound), which were extracted by H_2O_2, oxalate, hot $NH_2OH{\cdot}HCl$ + HOAc-, and 4M HNO_3.

Bioavailability of Hg in HgS-Contaminated Soils

Mercury in soils contaminated with insoluble HgS is to some extent bioavailable (Table IV). Higher mercury concentrations were observed in both shoots and roots of fern and Indian mustard grown in HgS-contaminated soils than control soils. Mercury concentrations in fern grown in control soils after a growing season were higher than those in background plants (mercury concentrations in shoots and roots of fern at the onset of the experiment were below the detection limits).

Table IV. Mercury concentrations in plants grown in Oak Ridge soils contaminated with HgS.

Plant (variety)	Year	Treatment HgS		Shoots mg/kg	Roots
Pteris vittata	Spring, 2004	CK	Avg	4.1	7.4
(48 Days growing)			Stdev	1.6	2.9
		1000	Avg	14.3	36.9
			Stdev	5	5.8
		2000	Avg	10.6	45.5
			Stdev	1.6	8.7
Pteris vittata	Spring, 2005	CK	Avg	0.79	
(60 Days growing)			Stdev	1.76	
		1000	Avg	13.35	132.38
			Stdev	14.36	75.58
		2000	Avg	24.17	296.80
			Stdev	24.71	228.89
Indian mustard	Spring, 2006	CK	Avg	0.20	
(Long standing)			Stdev	0.32	
(53 Days growing)		1000	Avg	26.78	84.01
			Stdev	25.24	39.35
		2000	Avg	15.18	205.39
			Stdev	23.24	45.52
Indian mustard	Spring, 2006	CK	Avg	0.95	
(Florida broadleaf)			Stdev	1.07	
(53 Days growing)		1000	Avg	34.65	17.14
			Stdev	29.16	11.12
		2000	Avg	78.77	86.96
			Stdev	50.77	42.68

Direct foliage absorption of mercury vapor from the air was observed in trees and mosses [27]. Direct uptake of elemental Hg via stomata is controlled by stomatal and mesophyll resistances [27]. Lindberg *et al*. [28] observed a dual mechanism of mercury uptake by alfalfa: roots accumulated Hg in proportion to the soil levels and aerial plant shoots absorbed Hg vapor directly from the atmosphere. Therefore mercury in ferns/Indian mustard grown in the control soils may have contributions from direct absorption of airborne mercury vapor, which originated from volatilization of mercury from soils as well as from fern foliage of fern in soils with soluble mercury. The direct uptake of mercury vapor from air may also contribute to some mercury in ferns grown in HgS-treated soils. However, mercury concentrations in both shoots and roots of ferns grown in HgS-treated soils were significantly higher than those in control soils, indicating some bioavailability of mercury in soils treated with HgS and that the major contribution was through root uptake.

It was reported that dissolved organic carbon increased dissolution of mercury from HgS [23, 24] and thus increased mercury bioavailability in soils. Hydrophobic acid (a mixture

of both humic and fulvic) dissolved more mercury than hydrophilic acids and other nonacid fractions of dissolved organic matter [24]. The possible mechanisms of dissolution of HgS were suggested to include surface complexation of mercury and oxidation of surface sulfur species by the organic matter [24]. However, 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 [24]. This all indicates the positive effects of the rhizosphere on biavailability and stability of HgS in soils. Plant roots can alter their microenvironment and mobilize otherwise stable Hg compounds.

SUMMARY

Our preliminary experiments showed to some extent bioavailability of mercury sulfide (HgS) in Oak Ridge soils. Extractability of HgS by 4M HNO_3 and 12 M HNO_3 in cinnabar-contaminated Oak Ridge soils was significantly higher than pure HgS. The extractability of HgS by HNO_3 increased with extraction time. Planting seems to increase the extractability and bioavailability of HgS. In cinnabar-contaminated Oak Ridge soils, mercury was mainly present in HgS form. However, a considerable amount of mercury was present in H_2O_2-extractable (0.13-5.1%) and 4M HNO_3-extractable (2-8.5%) forms. Further studies on effects of rhizosphere chemistry on stability and bioavailability of Hg will be performed.

ACKNOWLEDGEMENTS

We wish to thank Dr. Elizabeth C. Phillips (Oak Ridge Operations) and Dr. Paula G. Kirk (Oak Ridge National Laboratory) for providing us with assistance and information for these efforts. We also wish to thank Mr. Michel E. Okhuysen (Mississippi State University) for his suggestions and his comments on this manuscript. This research is supported by U.S. Department of Energy's Office of Science and Technology through Cooperative Agreement DE-FC26-98FT-40395.

REFERENCES

1. U.S. Department Of Energy, *Report on the Remedial Investigation of the Upper East Fork Popular Creek Characterization Area at the Oak Ridge Y-12 Plant, Oak Ridge, Tennessee,* Volume 1, DOE/OR/01-1641/V1&D2, pp. 3-10 to 3-106 (1998).
2. R.R. Turner, C.R. Olsen, W.J. Wilcox Jr, "Environmental Fate of Hg and 137 Cs Discharged from Oak Ridge Facilities," in *Trace Substances in the Environment* (D.D. Hemphill, editor) Elsevier/North-Holland Biomedical Press, New York (1985).
3. U.S. Environmental Protection Agency, *National Priorities List for Uncontrolled Hazardous Waste Sites*, Federal Register **54** (223): 48184 – 48189 (1989).
4. E.C. Phillips, "Upper East Fork Poplar Creek Watershed," U.S. Department of Energy Mercury Workshop, Oak Ridge, TN (2004).
5. T.L. Ashwood, C.R. Olsen, I.L. Larsen, and P.D. Lowry, "Sediment Contamination in Streams Surrounding the Oak Ridge Gaseous Diffusion Plant," Oak Ridge National Laboratory, Oak Ridge, TN (1986).

6. C.R. Olsen, I.L. Larsen, P.D. Lowry, C.R. Moriones, C.J. Ford, K.C. Dearstone, R.R. Turner, B.L. Kimmel, and C.C. Brandt, "Transport and Accumulation of Cesium-137 and Mercury in the Clinch River and Watts Bar Reservoir System," Oak Ridge National Laboratory, ESD Publication, Vol. **3471**, Oak Ridge, TN (1992).
7. J.M. Loar, "State of East Fork Poplar Creek: Status of Ecological Recovery," U.S. Department of Energy Mercury Workshop, Oak Ridge, TN (2004).
8. NCEDR Workshop On Decision-Making Related To Clean-Up Of Mercury Contamination At Lower East Fork Popular Creek, Oak Ridge, TN (1996).
9. N.W. Revis, T.R. Osborne, G. Holdsworth, and C. Hadden, "Distribution of Mercury Species in Soil from a Mercury-Contaminated Site," *Water Air and Soil Pollution* **45**, 105-113 (1989).
10. F.X. Han, Y. Su, D.L. Monts, and B.B.M. Sridhar, "Distribution, Transformation and Bioavailability of Trivalent and Hexavalent Chromium in Contaminated Soil," *Plant and Soil* **265**, 243-252 (2004).
11. D.L. Sparks, "Methods of Soil Analysis, Part 3, Chemical Methods," American Society of Agronomy, Inc., Madison, WI (1996).
12. A. Tessier, P.G.C. Campell, and M. Bisson, "Sequential Extraction Procedure for the Speciation of Particulate Trace Metals," *Analytical Chemistry* **51**, 844-851 (1979).
13. L.M. Shuman, "Separating Soil Iron- and Manganese-Oxide Fractions for Microelement Analysis," *Soil Science Society of America Journal* **46**, 1099-1102 (1982).
14. G. Sposito, L.J. Lund, and A.C. Chang, "Trace Metal Chemistry in Arid-Zone Field Soils Amended with Sewage Sludge: I. Fractionation of Ni, Cu, Zn, Cd, and Pb in Solid Phases," *Soil Science Society of America Journal* **46**, 260-264 (1982).
15. R.P. Eganhouse, D.R. Young, and J.N. Johnson, "Geochemistry of Mercury in Palos Verdes Sediments," *Environmental Science and Technology* **12**, 1151-1157 (1978).
16. F.X. Han, A. Bainin, W.L. Kingery, G.B. Triplett, L.X. Zhou, S.J. Zheng, and W.X. Ding, "New Approach to Studies of Redistribution of Heavy Metals in Soils," *Advance in Environmental Research* **8**(1), 113-120 (2003).
17. F.X. Han, Y. Su, D.L. Monts, C.A. Waggoner, and M.J. Plodinec, "Binding, Distribution, and Plant Uptake of Mercury in a Soil from Oak Ridge, Tennessee, USA," *Science of the Total Environment* **368**, 753-768 (2006).
18. H. Biester and C. Scholz, "Determination of Mercury Binding Forms in Contaminated Soils: Mercury Pyrolysis Versus Sequential Extractions," *Environmental Science and Technology* **31**, 233-239 (1997).
19. N.W. Revis, T.R. Osborne, D. Sedgley, and A. King, "Quantitative Method for Determining the Concentration of Mercury(II) Sulphide in Soils and Sediments," *Analyst* **114**, 823-825 (1989).
20. E. Schuster, "The Behavior of Mercury in the Soil with Special Emphasis on the Complexation and Adsorption Processes – a Review of the Literature," *Water Air and Soil Pollution* **56**, 667-680 (1991).
21. R.D. Shannon and J.R.. White, "The Selectivity of a Sequential Extraction Procedure for the Determination of Iron Oxyhydroxides and Iron Sulfides in Lake Sediments," *Biogeochemistry* **14**, 193-208 (1991).
22. K. Xia, U.L. Skyllberg, W.F. Bleam, P.R. Bloom, E.A. Nater, and P.A. Helmke, "X-ray Absorption Spectroscopic Evidence for the Complexation of Hg (II) by Reduced

Sulfur in Soil Humic Substances," *Environmental Science and Technology* **33**, 257-261 (1999).
23. M. Ravichandran, "Interactions between Mercury and Dissolved Organic Matter - a Review," *Chemosphere* **55**, 319-331 (2004).
24. M. Ravichandran, G.R. Aiken, M.M. Redd, and J.N. Ryan, "Enhanced Dissolution of Cinnabar (Mercuric Sulfide) by Dissolved Organic Matter Isolated from the Florida Everglades," *Environmental Science and Technology* **32**, 3305-3311 (1998).
25. C.T. Driscoll, J.K. Otton, And A. Iverfeldt, "Trace Metals Speciation and Cycling," in *Biogeochemistry of Small Catchments* (B. Moldan and J. Cerry, editors) John Wiley, New York (1994).
26. S.E. Lindberg, "Forests and the Global Biogeochemical Cycle of Mercury," in *Regional and Global Mercury Cycles: Sources, Fluxes and Mass Balance* (W. Baeyens, R. Ebinghaus, and O. Vasiliev, editors) Kluwer, Dordrecht, Netherlands (1996).
27. S.E. Lindberg, R.R. Turner, T.P. Meyers, G.E. Taylor Jr, and W.H. Schroeder, "Atmospheric Concentrations and Deposition of Hg to a Deciduous Forest at Walker Branch Watershed, Tennessee, USA," *Water Air and Soil Pollution* **56**, 577-594 (1991).
28. S.E. Lindberg, D.R. Jackson, J.W. Huckabee, S.A. Janzen, M.J. Levin, and J.R. Lund, "Atmospheric Emission and Plant Uptake of Mercury from Agricultural Soils near the Almaden Mercury Mine," *Journal of Environmental Quality* **8**, 572-578 (1979).