

Mercury characterization in a soil sample collected nearby the DOE Oak Ridge Reservation utilizing sequential extraction and thermal desorption method

Guangliang Liu^{a,b}, Julio Cabrera^a, Marshall Allen^c, Yong Cai^{a,b,*}

^a Department of Chemistry and Biochemistry, Florida International University, University Park, Miami, FL 33199, USA

^b Southeast Environmental Research Center, Florida International University, University Park, Miami, FL 33199, USA

^c Applied Research Center, Florida International University, University Park, Miami, FL 33199, USA

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Abstract

A new attempt to characterize Hg speciation and to evaluate Hg mobility in soils was made by applying operationally defined speciation techniques coupled with fractionation of soil components to a soil sample collected just outside the Y-12 boundary of the Oak Ridge Reservation (ORR) site. The soil sample was fractionated based on redoximorphic features and particle size and a sequential extraction procedure and thermal desorption technique were then applied to the fractionated soil components. The redoximorphic concentration component was observed to have higher Hg concentrations than the redoximorphic depletion component in the soil, and fine particles contained higher concentrations of Hg compared with coarse particles. The preliminary results of using thermal desorption as well as the sequential extraction procedure suggested that Hg⁰ and other “easily” vaporized Hg species accounted for 10–30% of total Hg in the soil. Sequential extraction analysis showed that both soluble and bioavailable Hg fractions were relatively small proportions whereas the organic matter bound mercury fraction constituted the major form of Hg species in the sample. The results suggest that Hg retained in the redoximorphic concentrations was less volatile and labile than Hg in the redoximorphic depletions possibly due to the strong binding affinity of Fe/Mn oxides and organic matter to Hg.
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1. Introduction

Speciation analysis of mercury (Hg) is important in assessing the risk posed by contaminated soils. This is because the fate, transport, and bioavailability of Hg in soil are dependent upon the species in which it is present

(Barnett et al., 1997; Wallschläger et al., 1998a, 1998b). The speciation of Hg in soil and sediment may be defined functionally (e.g. bioavailable fraction) or operationally (e.g. water soluble, exchangeable, and organo-chelated Hg fractions). Hg speciation can also be described to distinguish between specific chemical species (e.g. inorganic Hg and methylmercury) (Martín-Doimeadios et al., 2000; Bloom et al., 2003). The procedures determining functionally or operationally defined Hg species are sometimes called fractionation rather than speciation (Martín-Doimeadios et al., 2000).

* Corresponding author. Department of Chemistry and Biochemistry, Florida International University, University Park, Miami, FL 33199, USA. Tel.: +1 305 348 6210.

E-mail address: cai@fiu.edu (Y. Cai).

Sequential extraction procedures (SEP), thermal desorption analysis, and spectroscopic techniques are three major approaches to determine Hg speciation in soil. Sequential extraction, a widely used method for Hg speciation, can provide useful information related to environmental behavior of Hg in soil, such as solubility, mobility, and bioavailability (Biester and Scholz, 1997; Han et al., 2003; Panyametheekul, 2004). Thermal desorption analysis has also been used for Hg species in solid samples. It offers the advantages of being simple, fast, and cost-effective (Bombach et al., 1994). Spectroscopic techniques, such as X-ray absorption fine structure spectroscopy or X-ray microprobe spectroscopy, can provide a direct observation of Hg speciation. The application of this approach, however, is limited by its relatively poor detection limit (Kim et al., 2000, 2003). Combinations of these techniques rather than a single method are often needed to estimate Hg speciation and assess the environmental impact of Hg contaminated sites.

The Oak Ridge Reservation (ORR), especially in the area surrounding the Y-12 Weapons Complex, was heavily contaminated with Hg. In the 1950s and 1960s, an estimation of 108,000–212,000 kg of Hg was released to the headwaters of the East Fork Poplar Creek (EFPC) during the production of Li enriched in ^6Li in the Y-12 Plant, which resulted in a heavy Hg contamination in the floodplains of the EFPC. Efforts have been made to investigate the magnitude, speciation, mobility, and bioavailability of Hg in this area, especially the Lower EFPC (LEFPC) floodplains. The EFPC floodplain soils were found to contain Hg in concentration up to 3000 $\mu\text{g/g}$ and in a combination of various physicochemical forms such as Hg^0 , dissolved ionic Hg, fine Hg particles attached to suspended matter, mercuric oxide, Hg covalently bound to organic matter, and mercuric sulfide (Barnett et al., 1997; Harris et al., 1996; Barnett and Turner, 1995). Among these Hg forms, mercuric sulfide ($\sim 85\%$ of total Hg) had been suggested as the predominant form (Revis et al., 1989), but it was also detected in variable and sometimes relatively lower quantities (Barnett et al., 1995). Due to the severe contamination of Hg, this site was placed on the National Priority List to undergo remediation (Barnett et al., 1997; Morris et al., 1995).

Despite extensive studies focusing on Hg contamination in the LEFPC floodplains, it is currently not very clear about the magnitude and speciation of Hg present in soils coming from the DOE Y-12 site. The present study was carried out on a soil sample collected just outside the Y-12 boundary of the ORR site. The choice of this site for sample collection was based upon several technical bases. First of all it was the first easily accessible location beyond the Y-12 property and would still

have primarily the fingerprint of any Y-12 manipulations, e.g., fresh addition of Clinch River water for flow management. Secondly, samples taken from this site would have the least exposure to any of the downstream environmental influences, e.g., residual flood plain deposition or Hg reintroduction that might alter the original Hg transport from the Y-12 site. And finally, various engineering activities on the Y-12 site over the years and near this sampling site, e.g., placement of rip-rap in the creek to reduce the transport of fine particulate, has led to a different legacy of Hg contamination at this site than from say the LEFPC floodplains.

A prominent redoximorphic characteristic of soil was observed throughout the area surrounding the Y-12 site, i.e. the soil was clearly composed of two components: a gray part (termed as redoximorphic depletions) and a brownish part (termed as redoximorphic concentrations) (Fig. 1). The concentration, phase association, mobility, and volatility of Hg present in these two components were inferred to be different based on the previous observation that fairly different Hg concentrations were present in these two components. The effect of soil redoximorphic features on Hg concentration and phase association has not been investigated in previous studies dealing with Hg speciation. Most of them applied operationally defined speciation techniques (SEP and/or thermal desorption) to bulk soil samples (wet or dried) (Biester et al., 2000; Biester and Scholz, 1997; Bloom et al., 2003). In the present study, we were trying to make a new attempt to characterize Hg speciation and to evaluate Hg mobility in soils. We first fractionated the soil sample based on redox induced alteration of soil characteristics. Then, we applied SEP and thermal desorption analysis to the fractionated soil components rather than bulk soil sample. The objective of this study is to provide a typical example for

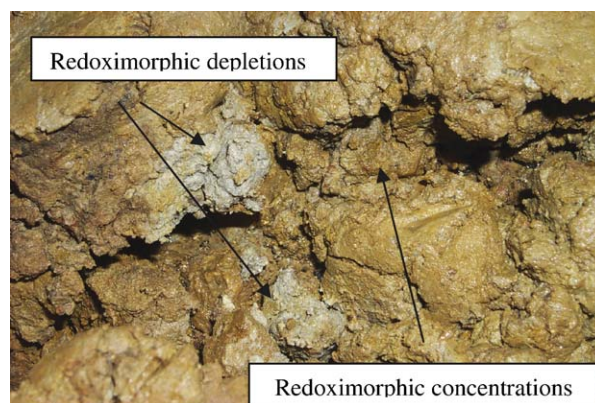


Fig. 1. A picture showing redoximorphic depletion (grey) and redoximorphic concentration (brownish) components in the soil sample.

expanding and detailing the methodology characterizing Hg speciation in soil by applying multiple speciation techniques coupled with fractionation methods. We selected only a typical sample based on the results of previous survey of Hg contamination in the studied area. However, the data generated from various analytical protocols applied in the present study should be potentially useful for investigating the phase association and environmental risk of Hg probably influenced by soil features in the area concerned.

2. Experimental

2.1. Soil sample collection

The soil sample was taken from the EFPC banks at levels 4–8 inches above the water surface using a garden trowel just outside the Y-12 Complex site boundary in Oak Ridge. The sampling site was located approximately a quarter mile offsite, beyond the cement culvert that conveys the stream from the Y-12 site, and directly behind a commercial car wash (Mullins Car Wash). The sample was shipped to FIU on dry ice and stored at -20°C before being analyzed for Hg and Hg speciation.

2.2. Fractionation of soil sample

In order to evaluate whether Hg concentration and speciation in this soil sample was affected by soil composition, the redoximorphic depletions and concentrations were manually separated. In the low-chroma gray redoximorphic depletions part (Fig. 1), Fe and Mn oxides or a combination of Fe and Mn oxides and clay appeared to have been partially removed via redox processes related to seasonal saturation. The brownish redoximorphic concentrations part seemed to contain more Fe and Mn oxides. The analysis for major elements in these two components confirmed that redoximorphic concentrations contained higher concentrations of Fe, Mn, Ca, and Mg than redoximorphic depletions. The mass amount of redoximorphic concentrations was much larger than redoximorphic depletions as observed during the separation process of these two components. Although these two components were not separated completely in the laboratory, differences in Hg concentration and association with soil caused by these two components, if any, should be observed.

Part of the two separated components was stored in a freezer and another part was freeze-dried for 72 h. The dried samples were then ground with a mortar and separated into fine and coarse particle fractions in order to investigate the effect of particle size on Hg distribution. No.

35 and No. 60 sieves were used to separate coarse particles ($<500\ \mu\text{m}$) and fine particles ($<250\ \mu\text{m}$), respectively.

Contents of major elements (Al, Mg, Ca, Mn, Fe) in the fractionated samples were determined by inductively coupled plasma mass spectrometry (ICPMS) (Mg, Ca, Mn) or atomic absorption spectrometry (AAS) (Al and Fe) following $\text{HNO}_3/\text{H}_2\text{O}_2$ digestion (Cai et al., 2002). Organic carbon contents in these samples were determined by subtracting inorganic carbon content from total carbon content. Clay speciation and mineral identification were also conducted on the four fractionated subsamples using X-ray diffraction analysis (Phillips PW 1050 diffractometer) at Activation Laboratories Ltd. (Ontario, Canada).

2.3. Reagents and instrumentation

A cold vapor atomic fluorescence spectrometer (CVAFS) system (Merlin10.035, PS Analytical, UK) was used for Hg analysis. A Gyrotory shaker (model G2) from New Brunswick Scientific Co., Inc. (Edison, NJ) and a Blue M oven (Blue Island, IL) were used for sequential extraction and thermal desorption. A certified Hg standard (1000 ppm in 1.8% HNO_3) was purchased from Fischer Scientific (Fair Lawn, NJ). Another certified Hg standard (1000 ppm in 10% HNO_3) from a second source (SPEX CertiPrep, Metuchen, NJ) was used for calibration check. A river sediment standard reference material (SRM) NIST 8406, with nominal values of 60 ng/g for Hg and 5.50% for Al, 2.96% for Fe, and 0.043% for Mn, was purchased from the National Institute of Standard and Technology (Gaithersburg, MD). Trace metal grade of HCl and HNO_3 , analytical grade of potassium bromide, potassium bromate, stannous chloride, and other reagents were purchased from Fisher Scientific.

2.4. Determination of Hg in fractionated samples

Samples (0.1 to 0.3 g wet or dry) were placed inside a 10 ml Wheaton glass ampoule to which 1 ml of H_2O and 2 ml of concentrated HNO_3 were added (Jones et al., 1995). The samples were allowed to settle for 20 min, then sealed using an Ampulmatic Ampule Sealer, and digested in an autoclave at 120°C for 1 h. The samples were analyzed after cooling down. All results were calculated based on dry weight unless stated otherwise.

2.5. Thermal desorption experiments

Thermal desorption experiments were performed on NIST 8406 and on the wet and dry redoximorphic depletions and redoximorphic concentrations of the ORR soil sample without further differentiation into particle

Table 1
Extractants and Hg fractions used in the sequential extraction procedure

Fraction ID	Extractant	Extractant:soil ratio	Hg fraction
F1	Deionized water	100:1	Water soluble Hg
F2	0.1 M CH ₃ COOH + 0.01 M HCl	100:1	Human stomach acid soluble Hg
F3	1 M KOH	100:1	Organic matter bound Hg
F4	12 M HNO ₃	100:1	Hg ⁰
F5	Aqua regia	32.5:1	Mercuric sulfide

Extractions were conducted at room temperature (20 °C) for 24 h.

size. Soil samples (0.1 to 0.2 g) were weighed into a 10 ml Wheaton glass ampoule. The thermal desorption experiments were performed at temperatures ranging from 60 to 180 °C for a period of 15 h inside an oven. The glass ampoules were then removed from the oven and allowed to cool. The concentration of Hg remaining in the samples were determined using HNO₃ digestion–CVAFS procedure as described above. Triplicates of the sample and three blanks were carried out for each temperature. Each ampoule was analyzed three times.

2.6. Sequential extraction procedure

A sequential extraction procedure reported previously by Bloom et al. (2003) was conducted on the fine and coarse freeze-dried redoximorphic depletions and redoximorphic concentrations. Listed in Table 1 are the definitions of the five different fractions and the corresponding extractant used in each step. An aliquot of approximately 0.4 g of sample was used in the sequential extraction. For each step, 40 ml of extractant was added except for step 5 in which 13 ml of aqua regia was used. The extraction was conducted by shaking on an orbital shaker at 200 rpm at room temperature for 24 h. After centrifuging at 3000 rpm for 5 min, the supernatant was carefully decanted into a 250 ml plastic

bottle and the precipitate was rinsed with 40 ml of the same corresponding extractant by shaking vigorously and followed by centrifugation. The two supernatant solutions were then combined. The concentration of Hg in the supernatants was determined by CVAFS according to the laboratory procedure (Jones et al., 1995).

3. Results and discussion

3.1. Soil characterization

The results of X-ray minerals identification revealed a similar pattern for the manually separated redoximorphic depletions and redoximorphic concentrations, with quartz alpha, sericite, muscovite or mica, and orthoclase the major mineral forms. The X-ray diffraction patterns of the clay speciation for these two components were also similar. However, differences in clay mineral compositions between redoximorphic depletions and redoximorphic concentrations were observed. Vermiculite and kaolinite/dickite or nacrite were present in both components, but interstratified vermiculite/illite was identified only in the redoximorphic concentrations. Additionally, two peaks at 10.09 and 4.96 Å observed in the redoximorphic concentrations clearly indicate the presence of illite. Only one peak at 4.96 Å was found in the redoximorphic depletions, which could not confirm the presence of illite due to the possible interferences of sericite or muscovite. It seemed that the redoximorphic concentrations contained more types of minerals containing Fe/Mg than the redoximorphic depletions.

The concentrations of some major elements (Al, Mg, Ca, Mn, Fe) in the redoximorphic depletions and redoximorphic concentrations were different as seen in Table 2. As expected, significantly higher concentrations of non-silica mineral elements such as Mg, Ca, especially Mn and Fe, were observed for the redoximorphic concentrations compared with redoximorphic depletions. This seemed to be related to the presence of more types of Fe/Mg minerals

Table 2
Content of major elements and organic carbon in fractionated subsamples

Subsample type			Major elements (%)					Organic carbon (%)
			Al	Mg	Ca	Mn	Fe	
Redoximorphic depletions	Coarse	Mean	0.25	0.08	0.08	0.01	0.98	0.08
		SD	0.01	0.00	0.00	0.00	0.06	0.01
	Fine	Mean	0.30	0.09	0.10	0.01	1.05	0.06
		SD	0.01	0.00	0.00	0.00	0.01	0.01
Redoximorphic concentrations	Coarse	Mean	0.37	0.10	0.11	0.08	2.11	0.17
		SD	0.01	0.00	0.00	0.01	0.04	0.01
	Fine	Mean	0.34	0.09	0.11	0.04	1.70	0.10
		SD	0.001	0.00	0.01	0.00	0.01	0.01

Table 3

Hg concentrations in the redoximorphic depletions and redoximorphic concentrations from the ORR soil sample with different particle size

	Redoximorphic depletions				Redoximorphic concentrations			
	Wet	Dry	Fine	Coarse	Wet	Dry	Fine	Coarse
Hg concentration (ng/g)	91.8	57.3	76.7	50.5	206.6	235.9	203.2	121.9
SD	11.6	1.2	3.8	5.7	57.8	7.8	13.7	22.9

such as illite and interstratified vermiculite/illite in the redoximorphic concentrations. The organic carbon content in the redoximorphic concentrations was also higher than the redoximorphic depletions.

3.2. Hg in the redoximorphic depletions and redoximorphic concentrations with different particle sizes

It was observed that loss of Hg occurred for the redoximorphic depletions during the freeze-drying process (Table 3). The concentration of Hg in wet redoximorphic depletions sample (91.8 ± 11.6 ng/g) was significantly different ($P < 0.01$) from that in the freeze-dried sample (57.3 ± 1.2 ng/g). For the redoximorphic concentrations, there was no significant difference between Hg concentrations before and after freeze-drying (206.6 ± 57.8 versus 235.9 ± 7.8 ng/g). The high standard deviations for the wet samples could be attributed to the lack of homogeneity of the sample used. As discussed in the following paragraph, the redoximorphic concentrations has stronger binding affinity to Hg resulting from higher Fe/Mn and organic carbon contents than redoximorphic depletions. This appeared to be partially responsible for the difference of Hg loss during freeze-drying process between redoximorphic depletions and redoximorphic concentrations.

Hg concentrations in the redoximorphic concentrations were significantly higher than in the redoximorphic depletions ($P < 0.01$) (Table 3). The Hg concentration in the fine redoximorphic concentrations (203.2 ng/g) was almost three times that of the fine redoximorphic depletions (76.7 ng/g), whereas the Hg concentration in the coarse redoximorphic concentrations (121.9 ng/g) was twice that in the coarse redoximorphic depletions (50.5 ng/g). This is not unexpected because the redoximorphic concentrations contained higher Fe and Mn than the redoximorphic depletions (Table 2). The minerals of Fe and Mn such as iron hydroxide and hydrated manganese oxides have been known to have high affinity for Hg (Andersson, 1979; Dudas and Pawluk, 1976). Organic matter present in soils could also strongly bind Hg (Andersson, 1979). It was observed that organic carbon was higher in the redoximorphic concentrations than in the redoximorphic depletions for both fine and coarse

particle sizes (Table 2). Although organic carbon content in the studied sample seems to be low (0.06–0.17%), such an organic carbon content was likely high enough for combining an accountable portion of Hg. This presumption was based on a previous observation that binding of Hg to organic carbon, the predominant process of Hg sorption in the studied soils, showed no correlation with soil organic carbon content (Biester et al., 2002). It was reported that about 82.5% of total Hg was found as humic/fulvic acid-bound form in a soil sample with 0.28% of organic carbon content whereas only 21.8% was found in another soil sample with 0.69% of organic carbon content (Biester et al., 2002).

Particle size had an apparent effect on Hg distribution in the soil sample. For both redoximorphic depletions and redoximorphic concentrations, fine particles contained higher concentration of Hg compared with coarse particles (Table 3). The difference in Hg concentration between coarse and fine fraction was statistically significant as confirmed by *t*-test ($P < 0.01$). Apparently the specific surface area of fine particles was higher than that of coarse particles, which was likely the reason for higher Hg concentration in the fine fraction. It has often been observed that adsorption of Hg is increased with decreasing particle size and increasing specific surface area (Andersson, 1979).

3.3. Thermal desorption experiments

Illustrated in Fig 2 is the Hg concentration for wet and dry redoximorphic depletions and redoximorphic concentrations of the ORR soil sample and NIST 8406 after thermal treatment at different temperatures. The differences in Hg concentration between untreated and thermally treated samples indicated the amount of Hg released. As expected, thermal treatment released certain amounts of Hg and the amounts of Hg vaporized varied with sample types and temperatures. Significant Hg release was observed only when treatment temperature was 140 °C or higher except for the wet redoximorphic depletions subsample. For this sample, significant ($P = 0.05$) reduction in Hg concentration was not observed after thermal treatment from 80 to 180 °C, whereas an unexpected significant ($P < 0.05$) increase in Hg concentration was observed for

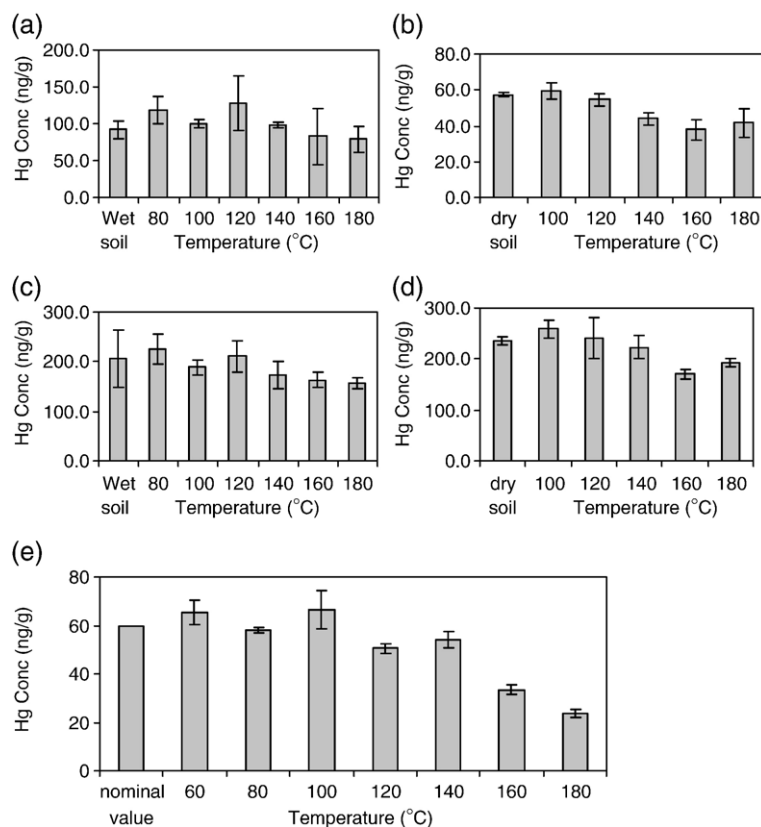


Fig. 2. Hg concentration in the ORR soil sample and SRM NIST 8406 after thermal desorption treatments. (a) Wet redoximorphic depletions; (b) freeze-dried redoximorphic depletions; (c) wet redoximorphic concentrations; (d) freeze-dried redoximorphic concentrations; (e) NIST 8406.

80 and 120 °C treatments. The reason for the increase in Hg is not very clear. However, it is plausible that the difficulty of obtaining a homogenized sample from the wet soil could cause the sample to be unrepresentative. As for the amount of Hg released, about 20–30% of total Hg was released from the freeze-dried samples after heating at 180 °C for 15 h. The percentage of the released Hg was somewhat lower (10–25%) from the wet redoximorphic concentrations through the same treatment. It was observed that placing wet soil in ampoules generated relatively large and dense soil particles after drying at high temperatures. The presence of these large particles was thought to affect the release of Hg under varying temperatures. Therefore, it is likely that Hg was released more from the freeze-dried compared to the wet soil samples when heated. Compared with the freeze-drying process, less Hg was lost for the wet redoximorphic depletions during thermal desorption treatments. This could be attributed to the inhomogeneity of wet sample or formation of these large and dense particles. It was also noted that much more Hg (>50%) was released in NIST 8406 after 180 °C treatment compared with the ORR soil sample possibly due to the differences of soil properties and Hg binding forms between them (Fig. 2).

Since different Hg species present in solid samples are expected to be released at different temperatures (Bombach et al., 1994; Windmüller et al., 1996), thermal desorption may provide some information on Hg species present in soils. It has been reported that Hg^0 , Hg_2Cl_2 , HgCl_2 , HgS , and Hg associated with organic matter could be released at <150, 170, 220–250, 300–400, and 200–300 °C, respectively (Windmüller et al., 1996; Bombach et al., 1994; Biester et al., 2000). Therefore, it can be assumed that thermal desorption with temperature lower than 180 °C adopted in the present study would primarily release Hg^0 and Hg_2Cl_2 , and probably a small portion of other forms of Hg such as HgCl_2 , $\text{Hg}(\text{NO}_3)_2$, HgO (Windmüller et al., 1996; and references cited therein). It is estimated that Hg^0 and/or other “easily” vaporized Hg species appeared to account for 10–30% of Hg species in the soil studied. Although a large amount of Hg^0 was initially discharged to the environments in the studied area (Barnett et al., 1997), it may have been converted to other Hg species during discharge or aging processes in the complex environments. In addition, lack of significant Hg release at less than 120 °C indicated that the Hg in this soil was relatively thermally stable and would not be

Table 4

Concentrations of different Hg species in different fractions of the ORR soil and SRM NIST 8406 by using sequential extraction procedure

Subsample type		Hg concentrations (ng/g) in different fractions						Recovery (%)	
		F1	F2	F3	F4	F5	Sum	Total Hg	
Redoximorphic depletions	Fine	3.4±0.1	2.5±0.4	44.0±2.8	16.6±1.0	5.9±0.8	72.4	76.7	94.3
	Coarse	3.7±0.8	2.0±0.1	35.6±3.6	15.0±1.8	6.8±0.4	63.1	50.5	125.1
Redoximorphic concentrations	Fine	3.8±0.7	3.2±0.5	117.4±1.3	47.3±9.1	20.4±4.8	192.1	203.2	94.5
	Coarse	5.4±1.1	3.1±0.1	77.4±6.9	33.3±6.7	10.4±1.6	129.6	121.9	106.3
NIST 8406		1.7±0.2	1.3±0.2	23.6±1.5	10.2±0.8	4.5±0.4	41.3	60.0	68.8

F1: water soluble Hg; F2: human stomach acid soluble Hg; F3: organic matter bound Hg; F4: Hg⁰; F5: mercuric sulfide.

thermally released under real-world environmental conditions. Temperature higher than 180 °C was not tested in the present study because this study was designated to investigate Hg species with high mobility or volatility simulating the real environment.

Hg retained in different soil mineral fractions was believed to have different mobility potential due to difference in texture of soil fractions (Andersson, 1979). It was observed that Hg retained in the redoximorphic concentrations had stronger interactions with the matrix and thus was less mobile than Hg in the redoximorphic depletions for the ORR soil sample. An apparent Hg release occurred from 140 °C for the freeze-dried redoximorphic depletions compared with 160 °C for the freeze-dried redoximorphic concentrations. Moreover, 30.7% of total Hg was released for the redoximorphic depletions at 180 °C while 18.1% was observed for the redoximorphic concentrations after the same treatment. This could indicate that Hg retained in the redox-

imorphic concentrations was less volatile than Hg in redoximorphic depletions.

3.4. Sequential extraction

Hg extracted in each step (F1–F5), representing different forms of Hg associated with different soil phases, is presented in Table 4. The sum of the amount removed by each extractant was in good agreement with the amount released by digestion with concentrated nitric acid with recoveries ranging from 94.3 to 125.1%. In addition, a recovery of 68.8% for SRM NIST 8406 was achieved, suggesting higher residual Hg left after these five extraction steps.

The distribution of Hg in each fraction showed considerable similarities for all four subsamples of the ORR soil and SRM NIST 8406. Fig. 3 shows the percentage of Hg extracted in each step calculated against the sum of Hg recovered in all five steps. In all cases the most

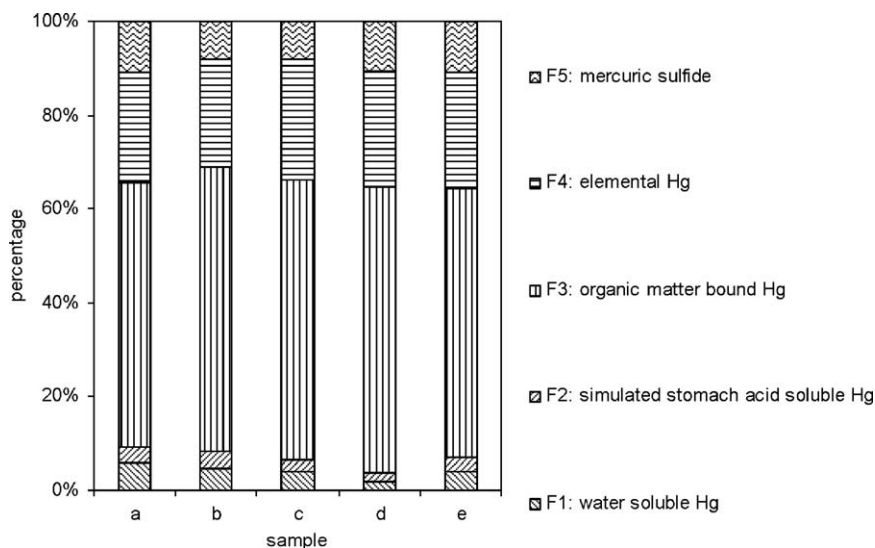


Fig. 3. Distribution of Hg in the freeze-dried subsamples from the ORR soil sample and the SRM NIST 8406 using sequential extraction. (a) Coarse redoximorphic depletions; (b) fine redoximorphic depletions; (c) coarse redoximorphic concentrations; (d) fine redoximorphic concentrations; (e) NIST 8406.

abundant Hg fraction was organic matter bound Hg fraction (F3) with percentage higher than 50% of total Hg. The second highest fraction was F4 (20–30%), representing Hg^0 based on the fact that all free Hg^0 present in a sample could be dissolved in cold 12 M HNO_3 (Gerlach et al., 1995; Bloom et al., 2003). It should be noted that some other classes of Hg compounds such as Hg(I) , Hg associated with amorphous organo-sulfur, Hg–Ag amalgams, and Hg associated with crystalline Fe/Mn oxide phases may be extracted into F4 fraction. Besides F3 and F4, the aqua regia soluble Hg fraction, F5, operationally termed as mercuric sulfide (HgS) including both cinnabar and metacinnabar and mercuric selenide (HgSe), also contributed an accountable portion to total Hg in the samples (about 10%). The first two sequentially extracted fractions F1 and F2, representing water soluble and human stomach acid soluble Hg, respectively, were relatively small portions.

These five Hg fractions have different mobility and potential bioavailability. The first two fractions (F1 and F2) were probably the most important Hg classes in view of environmental concerns. Water soluble (F1) Hg fraction is likely the most labile and able to migrate in interstitial soil solutions (Kot and Matyushkina, 2002), and even moves downward into deeper soil layer or groundwater. F2 fraction, simulating human stomach acid soluble Hg species, was determined as the fraction of Hg in soil potentially available for absorption in the human digestive system. This kind of absorption through the gastrointestinal tract appears to be the most critical endpoint and exposure pathway for the human community around Hg contaminated soil sites (Barnett and Turner, 1995). Compared with the first two Hg fractions that were weakly associated with soil phase, F3 (Hg bound to organic matter) was regarded as a stronger complex (Wallschläger et al., 1998a) and thus has limited mobility and bioavailability. Due to its very low solubility, F4 (Hg^0 likely plus other slightly soluble Hg species associated with soil particles) and F5 (insoluble mercuric sulfide) were not subject to transport or availability for chemical or biological transformation. It also should be borne in mind that: (1) Hg bound to organic matter (F3) could include methylmercury species (mainly monomethylmercury) in spite of being a very small proportion in general (Bloom et al., 2003); (2) organo-chelated Hg (F3) was observed to be strongly correlated with methylation potential and thus seems to play an important role in the biogeochemical cycle of Hg in some cases (Bloom et al., 2003; Kocman et al., 2004); and (3) Hg fractionation (and speciation) in soil/sediment is dynamic (Wallschläger et al., 1998a, 1998b) and subject to shift with alteration of environmental conditions

including physical, chemical factors, and especially microbial population and activities. For example, it has been reported that the presumably non-soluble cinnabar appeared to become soluble and form aqueous complexes with sulfide if it accumulated to a high enough concentration (Ravichandran et al., 1998; Jay et al., 2000) due to sulfate reduction mediated by sulfate reducing bacteria (SRB) (Mason and Benoit, 2003).

It was observed again that Hg in the redoximorphic concentrations was less labile than Hg in the redoximorphic depletions. In the redoximorphic depletions, the sum of F1 and F2 fraction (labile and bioavailable Hg fractions) accounted for 11.4% for coarse particles and 7.7% for fine particles. Lower proportions of F1 together with F2 were observed for the redoximorphic concentrations (7.7 and 3.4% for coarse and fine particles, respectively).

3.5. Environmental implications

Thermal desorption analysis showed that approximately 10–30% of total Hg in the ORR soil sample was Hg^0 and other “easily” vaporized Hg species. Such a proportion was comparable with F4 fraction (about 20–30%) obtained in the sequential extraction procedure. The identical results obtained in these two different methods of speciation analysis provided a good estimation for Hg^0 and other “easily” vaporized Hg species present in the ORR soil sample. Despite such an accountable “volatile” proportion, Hg in the studied soil seemed to be unfavorable to volatilization or to toxicity via inhalation due to bonding with solid matrix. Lack of significant Hg release at less than 120 °C indicated that Hg in this soil was relatively thermally stable and would not be thermally released under real-world environmental conditions.

The results of the present study suggested that both labile and bioavailable Hg fractions with high environmental risks were relatively small proportions in the studied ORR soil sample. Mercuric sulfide, previously reported as the dominant form of Hg, was found not to be the most abundant form (~ 10% of total Hg) in the studied soil sample. Such differences in Hg speciation could be attributed to the differences in sampling locations selected and probably, to a lesser extent, to the different sequential extraction procedures employed.

4. Conclusions

The redoximorphic concentrations contained higher Hg than the redoximorphic depletions. The higher content of Fe/Mn and organic matter was probably responsible for the higher Hg concentration in the redoximorphic

concentrations. As expected, fine soil particles contained higher Hg compared with the coarse ones. The results obtained using thermal desorption and sequential extraction procedure suggested that Hg retained in the redoximorphic concentrations was less volatile and labile than Hg in the redoximorphic depletions. With regards to the speciation of Hg in the soil, 10–30% of Hg species appeared to be Hg⁰ and other “easily” vaporized Hg species whereas the organic matter bound Hg fraction was the major form of Hg species (accounting for 50% of total Hg).

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