



# Mercury isotope variations between bioavailable mercury fractions and total mercury in mercury contaminated soil in Wanshan Mercury Mine, SW China

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## ARTICLE INFO

### Article history:

Accepted 17 April 2012

Available online 24 April 2012

### Keywords:

Mercury

Mercury isotope

Water-soluble

Thiosulphate extractable

Soil

## ABSTRACT

In this study, a comparison of the mobility of soil mercury with two different extractable treatments (water-treated and  $(\text{NH}_4)_2\text{S}_2\text{O}_3$ -treated) was carried out in soil samples collected from Wanshan Mercury Mine (WSMM), Guizhou, SW China. Substantially higher levels of mobilized Hg were found in  $(\text{NH}_4)_2\text{S}_2\text{O}_3$ -extracted ( $1.22$  to  $2.41 \mu\text{g g}^{-1}$ ) compared to the water-extracted soil samples ( $0.05$  to  $0.49 \mu\text{g g}^{-1}$ ). To understand the geochemical behavior of Hg during Hg mobilization, and to identify the potential hazard of Hg in soil, Hg isotope compositions of total Hg, water-soluble Hg and  $(\text{NH}_4)_2\text{S}_2\text{O}_3$ -extractable Hg in WSMM soil were measured by using multiple collectors coupled plasma mass spectrometer (MC-ICP-MS). A large variation of mass-dependent fractionation (MDF) of Hg was observed ( $\delta^{202}\text{Hg}$  of  $-0.29$ – $1.59\%$ ) between the extractable Hg species and the total Hg in soil. Mass independent fractionation (MIF) in  $\Delta^{199}\text{Hg}$  ranged from  $-0.07$  to  $0.07\%$ , which were statistically insignificant. The experimental data ( $\delta^{202}\text{Hg}$  values) revealed that water-soluble ( $\delta^{202}\text{Hg} = 0.70 \pm 0.13\%$ ,  $n = 8$ ) and  $(\text{NH}_4)_2\text{S}_2\text{O}_3$ -extractable ( $\delta^{202}\text{Hg} = 1.28 \pm 0.25\%$ ,  $n = 8$ ) Hg species were enriched in heavier Hg isotopes by  $0.72\%$  and  $1.30\%$  relative to total Hg in soil samples, respectively. The results suggest that the bioavailable fraction of Hg in soil possesses heavier Hg isotope values than total Hg in soil. To understand mercury isotope fractionation in the biogeochemical cycling processes in soil, it is of importance to measure Hg isotope compositions of different Hg species.

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## 1. Introduction

Mercury (Hg) is a global pollutant (Fitzgerald et al., 1998). Soil plays an important role in the global biogeochemical cycle of mercury because it acts both as a sink and a source of this metal to biota, atmosphere and hydrological compartments (Davidson et al., 2010). As a consequence of contamination from mercury mining and retorting activities, as well as excessive pesticide application and wastewater irrigation in agriculture, mercury pollution in soil is becoming a serious problem worldwide (Wang et al., 2011).

The geochemical behavior and distribution of Hg in the pedosphere is complex. Most Hg that is released into soil is adsorbed onto the solid phase of organic matter and onto soil minerals, such as sulphides and oxyhydroxides of iron and aluminum (Evans, 1989). A substantial fraction, however, undergoes physical (leaching, erosion, and volatilization) and biochemical transformations (methylation, photochemical and biological reduction) (Morel et al., 1998). Mobilization of Hg can occur through exchange reactions with sulfur-containing ligands and chloride ions, leading to enhanced Hg solubility in soil solution (Schuster, 1991). The mobilized Hg eventually forms complexes to

dissolved organic constituents and reaches aquatic systems, where it can be exported to areas far away from the pollution source (Oliveira et al., 2001). The transformation of inorganic Hg into toxic methyl Hg (Me-Hg) can occur through biotic (Choi et al., 1994) and abiotic processes (Weber, 1993). Once formed, Me-Hg is biomagnified through the food chains and, in top predators such as fish, it can exceed safe levels for human consumption (Southworth et al., 2004).

According to the 'hard and soft' acid-base principle, mercury is regarded as a 'soft metal' (Pearson, 1963). It has a strong affinity for thiol groups and can be readily complexed to the thiosulphate ion (Wilkinson et al., 1987). Hg–thiosulphate complexes are mobile in soils (Wallschläger et al., 1998) and can enhance both Hg bioavailability in soil and Hg uptake by plants (Hinton and Veiga, 2001). In previous studies, thiosulphate-induced plant Hg accumulation has been proposed as a potential strategy for the removal of Hg from contaminated substrates. For instance, *Brassica juncea* was able to accumulate  $40 \mu\text{g g}^{-1}$  of Hg in the shoot tissues following application of ammonium thiosulphate  $[(\text{NH}_4)_2\text{S}_2\text{O}_3]$  to mine tailings with Hg concentration of  $2.8 \mu\text{g g}^{-1}$  (Moreno et al., 2004). Despite the application of chelated-enhanced phytoextraction (Lombi et al., 2001), the existence of the thiol-containing solutions in soil can dissolve the non-mobile Hg phase in soil, and enhance the leaching of Hg to groundwater. Hence, knowledge of the formation of Hg–thiosulphate complexes in soil is critical to evaluate its environmental risk (Moreno et al., 2005).

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With the development of analytical methods (i.e. Foucher and Hintelmann, 2006, stable isotope geochemistry of Hg represents a new tool to trace sources and transformations of Hg in the environment (Blum and Bergquist, 2007; Yin et al., 2010a). Mercury possesses seven stable isotopes with the following average abundances:  $^{196}\text{Hg}$  (0.155%),  $^{198}\text{Hg}$  (10.04%),  $^{199}\text{Hg}$  (16.94%),  $^{200}\text{Hg}$  (23.14%),  $^{201}\text{Hg}$  (13.17%),  $^{202}\text{Hg}$  (29.73%), and  $^{204}\text{Hg}$  (6.83%). Prior studies have demonstrated that Hg isotope ratios vary significantly between different sources (Hintelmann and Lu, 2003; Smith et al., 2005, 2008; Biswas et al., 2008; Stetson et al., 2009; Zambardi et al., 2009). Isotopic fractionation of Hg can occur during microbial mediated reactions [e.g. microbiological reduction of  $\text{Hg}^{2+}$  (Kritee et al., 2007, 2008), methylation (González et al., 2009) and demethylation (Kritee et al., 2009)]. In addition, isotope fractionation was also observed during abiotic processes including chemical reactions [e.g. photoreduction (Bergquist and Blum, 2007; Yang and Sturgeon, 2009; Zheng and Hintelmann, 2009), chemical reduction (Bergquist and Blum, 2007; Yang and Sturgeon, 2009) and photo-oxidation (Bergquist et al., 2011)] and physical processes [e.g. volatilization (Zheng et al., 2007), evaporation (Estrade et al., 2009) and adsorption (Wiederhold et al., 2010; Jiskra et al., 2011)].

Total mercury is a poor indicator of ecological impact of Hg contamination in soil. The speciation and the way the different species interact with the soil matrix cause changes in solubility, toxicity and bioavailability of this metal (Biestler et al., 2002). As chemical (both biotic and abiotic) transformations and physical processes exert a strong control over Hg isotopic fractionation in the environment, Hg isotope ratios of various Hg species (e.g., dissolved Hg and solid Hg phases) are expected to be different in the soil matrix. In the current study, soil samples collected from Wanshan Mercury Mine, Guizhou Province, SW China were extracted by pure water and  $(\text{NH}_4)_2\text{S}_2\text{O}_3$  solution, and Hg isotope compositions of these two bioavailable fractions were compared with that of total Hg in soil. The objectives of this study were to 1) understand the geochemical behavior of water-soluble Hg in soil; 2) to evaluate the environmental risk of thiosulphate-containing ligands to the mobilization of mercury in soil; and 3) to investigate potential Hg isotope fractionation during soil Hg mobilization.

## 2. Methods and materials

### 2.1. Study area and sampling

As shown in Fig. 1, mercury contaminated soil samples were collected from the Wanshan mercury mining (WSMM) area, Guizhou

province, SW China. Hg mining in WSMM has been documented for more than 3000 years (Feng and Qiu, 2008). Regulated and large scale mining activities completely stopped in this area in 2001, leaving behind significant amounts of mercury contaminated mine wastes as shown in Fig. 1. The large scale Hg mining activities had resulted in serious Hg contamination to the local environment and adjacent ecosystems, including contamination to air, water, soil, and foodstuff (Horvat et al., 2003; Zhang et al., 2004; Qiu et al., 2005, 2008). Eight surface soil samples (0–2 cm) were collected around a mercury tailing named Wukeng (WK) in WSMM in the summer of 2010. All samples were a composite of at least 4 sub-samples to increase spatial resolution. During our sampling campaign, all collected samples were stored in sealed polyethylene bags to avoid cross contamination and then shipped to the laboratory as soon after collection as possible. In the laboratory, after homogenization, milling and riffing, the samples were ground to minus 150 mesh and subsequently sealed in polyethylene bags prior to total Hg concentration (HgT), water extraction,  $(\text{NH}_4)_2\text{S}_2\text{O}_3$ -extraction and Hg isotope analysis.

### 2.2. Water extraction and $(\text{NH}_4)_2\text{S}_2\text{O}_3$ extraction of mercury in the soil samples

Pure water (Mill-Q water, 18.2 MΩ cm) and ammonium thiosulphate [ $(\text{NH}_4)_2\text{S}_2\text{O}_3$ ] solution were selected as chemical extractants. The extraction procedure was performed at room temperature ( $\sim 20^\circ\text{C}$ ). One gram of sieved soil sample was weighed into 50 mL polypropylene centrifuge tubes in replicate. Then, 20 mL of 2 g/L of  $(\text{NH}_4)_2\text{S}_2\text{O}_3$  solution was afterwards added, while pure water was used for the controls. The tubes were rotated in a shaker over night at 3500 rpm per minute and the supernatant was separated after passing through a 0.45 μm microfilter. Finally, concentrated ultrapure  $\text{HNO}_3$  was added to the filtrate to yield 3% (v/v)  $\text{HNO}_3$  content.

### 2.3. Total Hg concentration analysis

Total mercury concentration in soil samples ( $\text{HgT}_s$ ), and the concentrations of water-extractable fraction ( $\text{HgT}_w$ ) and  $(\text{NH}_4)_2\text{S}_2\text{O}_3$ -extractable fraction ( $\text{HgT}_t$ ) were measured. For  $\text{HgT}_s$  analysis, approximately 0.2 g initial soil samples were digested in a water bath ( $95^\circ\text{C}$ ) using a fresh mixture of concentrated HCl and  $\text{HNO}_3$  (3:1, v/v).  $\text{HgT}_s$  was then measured by cold vapor atomic absorption spectrometry (CVAAS) using a F732-S spectrophotometer (Huaguang, China) according to Li et al. (2005). Based on Section 2.2, concentrations of  $\text{HgT}_t$

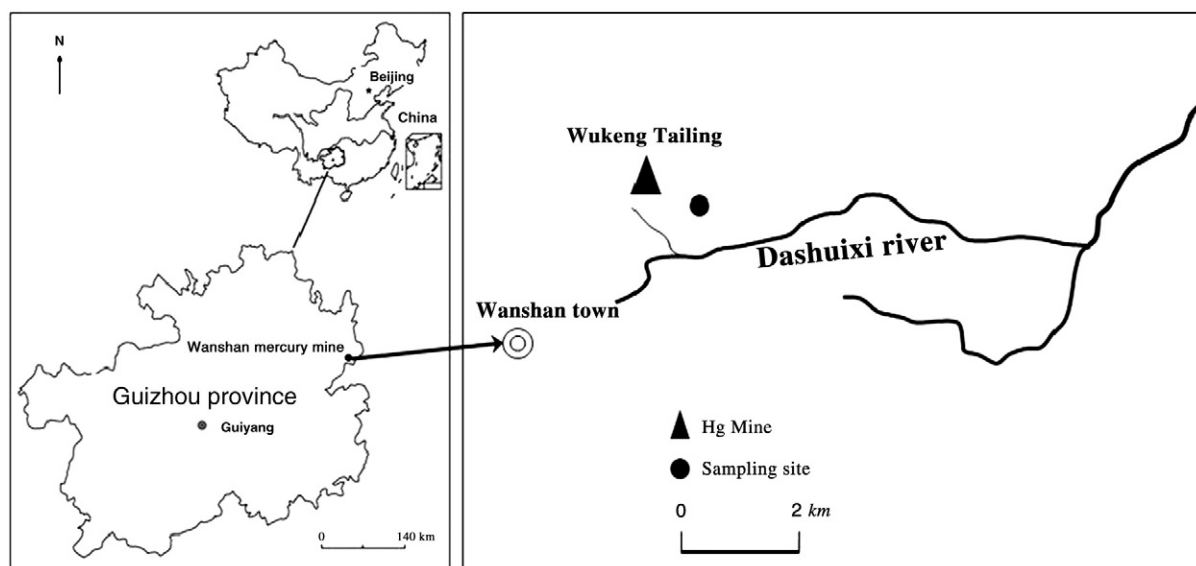


Fig. 1. Location of the Wanshan mercury mining area and soil sampling sites.

and  $HgT_w$  were determined by the dual-stage gold amalgamation method and cold vapor atomic fluorescence spectrometry (CVAFS) using a Tekran 2500 (Tekran Ltd., Canada) (US Environmental Protection Agency, EPA, 1999). Quality control was exercised by using method blanks, blank spikes, matrix spikes, certified reference materials (CRM BCR 580 estuarine sediment) and blind duplicates. The HgT recovery for CRM BCR 580 was in the range of 89–107%, and the relative variability of sample duplicates was <10%. All acids used in this work were of guaranteed grade ( $HNO_3$  and HCl) and Mill-Q water (18.2 M $\Omega$  cm) was used to prepare the final solutions.

#### 2.4. Mercury isotope analysis

Prior to mercury isotope analysis, all digest solutions and leachates were diluted to yield an Hg concentration in the range of 2–5 ng mL<sup>-1</sup> based on Hg concentration listed in Table 1. Hg isotope ratios were determined by MC-ICP-MS using a Nu-Plasma mass spectrometer equipped with twelve Faraday cups (Nu Instruments, Great Britain) at the State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang, China. The sample introduction system consisted of a continuous flow cold-vapor generation system (CV) (HGX-200, CETAC U.S.) coupled to an Apex-Q desolvation unit (Elemental Scientific Inc., U.S.) for Hg and Tl introduction, respectively. SnCl<sub>2</sub> was used as reducing agent and mixed online with Hg standards or sample digests to generate volatile elemental Hg. The Hg<sup>0</sup> vapor from the CV generation system was mixed with a dry Tl aerosol produced via the desolvation device. Instrumental mass bias correction was achieved using Tl as an internal standard (20  $\mu$ g L<sup>-1</sup>, NIST SRM 997) and external standard-sample bracketing with a NIST SRM 3133 Hg solution. An exponential fractionation law

was applied for internal mass bias correction assuming a reference value of 2.38714 for the ratio <sup>205</sup>Tl/<sup>203</sup>Tl. Data were acquired by monitoring <sup>198</sup>Hg, <sup>199</sup>Hg, <sup>200</sup>Hg, <sup>201</sup>Hg, <sup>202</sup>Hg, <sup>203</sup>Tl and <sup>205</sup>Tl isotopes for a period of 10 min (1 block, 100 cycles with 6 s integrations). A typical sequence consisted of measuring the NIST SRM 3133 Hg solution before and after each sample. To ensure optimum results of instrumental mass bias correction, the concentration of the bracketing solution was systematically adjusted to within 10% difference with the Hg concentration in the sample digest (typically 2–5 ng mL<sup>-1</sup>). Instrument blanks were analysed after each sample and each bracketing standard and on-line subtracted. Typical blank values were 10 mV for <sup>202</sup>Hg and 30 mV for <sup>205</sup>Tl, insignificant relative to typical sample and standard signals of 1 V for <sup>202</sup>Hg and 3 V for <sup>205</sup>Tl. A more detailed description of the overall instrumental setup, as well as the parameters and analytical conditions used throughout this study can be found in a previous publication (Yin et al., 2010b).

Hg isotopic variations are reported here in delta notation in units of per mille (‰) and referenced to the NIST SRM 3133 Hg standard (analysed before and after each sample) shown as Eq. (1):

$$\delta^{xxx}Hg \left( \text{‰} \right) = \left\{ \left[ \frac{^{xxx}Hg/^{198}Hg_{\text{sample}}}{^{xxx}Hg/^{198}Hg_{\text{NISTSRM3133}}} \right] - 1 \right\} \times 1000 \quad (1)$$

where xxx is mass of each Hg isotope between 199 and 202 amu. Here only  $\delta^{202}Hg$  values will be reported to indicate mass-dependent fractionation (MDF) as they show the most significant differences among samples. For the odd isotopes (<sup>199</sup>Hg and <sup>201</sup>Hg), the measured isotope ratios occasionally deviated from MDF. In these instances, mass-independent fractionation (MIF) of mercury is reported in “capital delta” notation ( $\Delta^{xxx}Hg$ , deviation from mass dependency in units of per mille, ‰) and is the difference between the

**Table 1**  
Mercury isotope composition and total mercury concentrations of initial soil samples, W-extractable, T-extractable and reference materials.

Sample ID	n	$\delta^{199}Hg$ (‰)	2SD (‰)	$\delta^{200}Hg$ (‰)	2SD (‰)	$\delta^{201}Hg$ (‰)	2SD (‰)	$\delta^{202}Hg$ (‰)	2SD (‰)	$\Delta^{199}Hg$ (‰)	2SD (‰)	$\Delta^{200}Hg$ (‰)	2SD (‰)	$\Delta^{201}Hg$ (‰)	2SD (‰)	HgT $\mu$ g g <sup>-1</sup>
<i>Initial soil Hg</i>																
S1	2	-0.03	0.04	-0.08	0.08	-0.10	0.08	-0.19	0.09	0.02	0.02	0.02	0.01	0.04	0.04	10
S2	2	-0.05	0.06	-0.12	0.09	-0.17	0.09	-0.29	0.09	0.02	0.03	0.03	0.03	0.05	0.02	12
S3	2	0.04	0.04	-0.01	0.11	0.01	0.11	-0.05	0.15	0.05	0.04	0.02	0.03	0.05	0.05	24
S4	2	0.06	0.07	0.02	0.07	0.05	0.07	0.03	0.11	0.05	0.01	0.00	0.04	0.03	0.03	85
S5	2	0.03	0.03	-0.03	0.03	-0.09	0.03	-0.03	0.13	0.04	0.03	-0.01	0.03	-0.07	0.01	108
S6	2	0.11	0.08	0.08	0.07	0.13	0.07	0.14	0.14	0.07	0.03	0.01	0.02	0.02	0.06	190
S7	2	0.00	0.07	0.10	0.09	0.13	0.09	0.15	0.11	-0.04	0.02	0.02	0.04	0.02	0.03	628
S8	2	-0.03	0.07	0.03	0.08	0.07	0.08	0.09	0.14	-0.05	0.04	-0.02	0.01	0.00	0.07	682
<i>Water-soluble Hg</i>																
W-S1	2	0.10	0.10	0.21	0.08	0.43	0.08	0.50	0.17	-0.03	0.04	-0.04	0.01	0.05	0.04	0.05
W-S2	2	0.28	0.03	0.38	0.05	0.67	0.05	0.82	0.14	0.07	0.01	-0.03	0.04	0.05	0.03	0.05
W-S3	2	0.20	0.04	0.32	0.03	0.60	0.03	0.72	0.08	0.02	0.05	-0.04	0.02	0.06	0.04	0.08
W-S4	2	0.25	0.05	0.36	0.06	0.59	0.04	0.70	0.07	0.07	0.04	0.01	0.03	0.06	0.01	0.14
W-S5	2	0.12	0.08	0.38	0.08	0.63	0.08	0.74	0.19	-0.07	0.02	0.01	0.05	0.07	0.03	0.23
W-S6	2	0.19	0.06	0.33	0.08	0.58	0.08	0.70	0.12	0.01	0.07	-0.02	0.01	0.05	0.03	0.33
W-S7	2	0.14	0.04	0.23	0.05	0.42	0.05	0.52	0.11	0.01	0.03	-0.03	0.03	0.03	0.01	0.41
W-S8	2	0.26	0.06	0.40	0.03	0.70	0.09	0.86	0.16	0.04	0.02	-0.03	0.01	0.05	0.04	0.49
<i>Thiosulphate extractable Hg</i>																
S-S1	2	0.25	0.05	0.43	0.09	0.66	0.11	0.89	0.13	0.03	0.03	-0.02	0.01	-0.01	0.02	1.22
S-S2	2	0.34	0.08	0.81	0.06	1.23	0.06	1.59	0.15	-0.06	0.04	0.01	0.04	0.03	0.03	1.64
S-S3	2	0.33	0.03	0.57	0.05	0.88	0.05	1.15	0.09	0.04	0.04	-0.01	0.03	0.02	0.03	1.79
S-S4	2	0.38	0.11	0.74	0.16	1.17	0.09	1.52	0.11	0.00	0.03	-0.02	0.02	0.03	0.01	1.79
S-S5	2	0.35	0.04	0.69	0.07	1.07	0.12	1.31	0.13	0.02	0.02	0.03	0.03	0.08	0.03	1.96
S-S6	2	0.30	0.06	0.53	0.09	0.81	0.09	1.09	0.12	0.03	0.03	-0.02	0.02	-0.01	0.04	2.01
S-S7	2	0.25	0.03	0.61	0.10	0.95	0.10	1.19	0.16	-0.05	0.01	0.01	0.04	0.06	0.02	2.26
S-S8	2	0.41	0.04	0.74	0.10	1.17	0.10	1.51	0.14	0.03	0.01	-0.02	0.01	0.03	0.03	2.41
<i>Standard materials</i>																
UM-Almadén	7	-0.15	0.07	-0.25	0.07	-0.36	0.08	-0.51	0.10	-0.01	0.07	0.03	0.07	0.02	0.08	

measured  $\delta^{\text{xxx}}\text{Hg}$  and the theoretically predicted  $\delta^{\text{xxx}}\text{Hg}$  value using the following formulas (Blum and Bergquist, 2007):

$$\Delta^{201}\text{Hg} \approx \delta^{201}\text{Hg} - (\delta^{202}\text{Hg} * 0.752) \quad (2)$$

$$\Delta^{199}\text{Hg} \approx \delta^{199}\text{Hg} - (\delta^{202}\text{Hg} * 0.252) \quad (3)$$

The reproducibility of the isotopic data was assessed by measuring replicate sample digests (typically  $n=2$ ). We also analysed the UM-Almadén as a secondary standard in addition to the bracketing standard NIST 3133. Hg in UM-Almadén was measured the same way as other samples in each analytical session. The overall average and uncertainty of  $\delta^{202}\text{Hg}$  was  $-0.51 \pm 0.10\%$  (2 SD,  $n=7$ ), of  $\Delta^{201}\text{Hg}$  was  $0.02 \pm 0.08\%$  (2 SD,  $n=7$ ) and of  $\Delta^{199}\text{Hg}$  was  $-0.01 \pm 0.07\%$  (2 SD,  $n=7$ ) for all UM-Almadén measurements, which agreed well with data reported in Blum and Bergquist (2007). Uncertainties given in the figures and tables of this paper represent the larger value of either 1) the measurement uncertainty of replicate sample digests, or 2) the uncertainty of repeated measurements of the same digest at different analysis sessions. In case, the calculated uncertainty was smaller than that of the replicate analyses of the reference material of UM-Almadén, the uncertainty reported for the specific material was used instead.

### 3. Results and discussion

#### 3.1. Total Hg and water-soluble Hg in WSMM soil samples

$\text{HgT}_s$  and  $\text{HgT}_w$  concentrations in soil samples were shown in Table 1 and Fig. 2.  $\text{HgT}_s$  of the investigated soil samples in WSMM ranged from 10 to  $680 \mu\text{g g}^{-1}$ , which is much higher than the maximum upper limit for mercury content ( $1.5 \mu\text{g g}^{-1}$ ) in agriculture soil in China (CNEPA, 1995) and the soil can therefore be regarded as heavily polluted (Horvat et al., 2003; Zhang et al., 2004; Qiu et al., 2005).

The water-extractable mercury ( $\text{HgT}_w$ ) concentrations in WSMM soil samples ranged from 0.05 to  $0.49 \mu\text{g g}^{-1}$  as shown in Table 1. As shown in Fig. 2A, there is a significant exponential correlation between the  $\text{HgT}_s$  and  $\text{HgT}_w$  ( $r^2=0.93$ ). The fraction of water-soluble Hg released from each soil sample was small, usually less than 0.5% of the total. This indicates that the majority fraction of mercury in soil is primarily associated with the solid phase (Peakall and Lovett, 1972; Wiener et al., 2003). This is also observed in other soil studies at Hg mining sites (Sánchez et al., 2005; Millán et al., 2006). Although

the water-soluble mercury fraction is not entirely identical to in situ soil pore water concentration, it can be used as a first indicator for potential groundwater pollution or risk of metal leaching from soil. The speciation of mercury in soil solution is still unknown, but it is expected that the complexes  $\text{HgCl}_2$ ,  $\text{Hg}(\text{OH})_2$  and  $\text{HgOHCl}$  would dominate over other Hg forms in the soil solutions (Schuster, 1991; Wallschläger et al., 1998). Although the water-soluble Hg fraction contributed a minor part of  $\text{HgT}_s$ , the importance of this fraction should not be underestimated, since it is more mobile, more toxic and more readily bio-accumulated than any other mercury species (Han et al., 2003). Considering that the majority of these soils in WSMM are predominantly used for agricultural purposes (Zhang et al., 2010; Rothenberg et al., 2011), the presence of mobile and toxic mercury species, even in low concentrations, may be of concern.

#### 3.2. Impact of addition of $(\text{NH}_4)_2\text{S}_2\text{O}_3$ solution in soil on mercury mobilization

The  $(\text{NH}_4)_2\text{S}_2\text{O}_3$ -extractable fraction  $\text{HgT}_t$  concentrations in WSMM soil samples are shown in Table 1 and Fig. 2B. The  $\text{HgT}_t$  concentrations in soil ranged from 1.22 to  $2.41 \mu\text{g g}^{-1}$  and were significantly higher than the water-soluble fraction  $\text{HgT}_w$  ( $P<0.001$ ) by 5 to 32 times. As shown in Fig. 2B, a significantly exponential correlation between the  $\text{HgT}_t$  and  $\text{HgT}_s$  ( $r^2=0.87$ ) was also observed.

According to the 'hard and soft' acid-base principle (Pearson, 1963), mercury is a 'soft metal' and has a strong affinity to form complexes with sulfur-containing functional groups and organic ligands. In flooded soil with a condition of anoxic, high pH and in the presence of sulphide ions, Hg speciation will be completely dominated by Hg thiol complexes (Morel et al., 1998). Hg thiol complexes are mobile in soil (Wallschläger et al., 1998) and therefore are highly bioavailable and easily uptake by organisms (Hinton and Veiga, 2001). Thioligand-induced plant Hg accumulation has been proposed as a potential strategy for the removal of Hg from contaminated substrates (Moreno et al., 2005). For instance, in a case study by Wang et al. (2011), the uptake of mercury by *C. glaucum* L. can be enhanced through the addition of  $(\text{NH}_4)_2\text{S}_2\text{O}_3$  at a rate of 2 g of chemical per kg of soil five days before the harvest of the plants. They further proposed that thiosulphate-assisted phytoextraction by plant was able to decrease the amount of soil mercury associated with the oxide-bound fractions. Moreno et al. (2004) also demonstrated that the oxide-bound mercury fraction may represent a pool of potentially bioavailable mercury which could be transformed into a more bioavailable form. Our study further confirmed that the addition of  $(\text{NH}_4)_2\text{S}_2\text{O}_3$  in soil increased the mobility of Hg in soil. Under the conditions of high pH and anoxic recorded for the Wanshan soil (Qiu et al.,

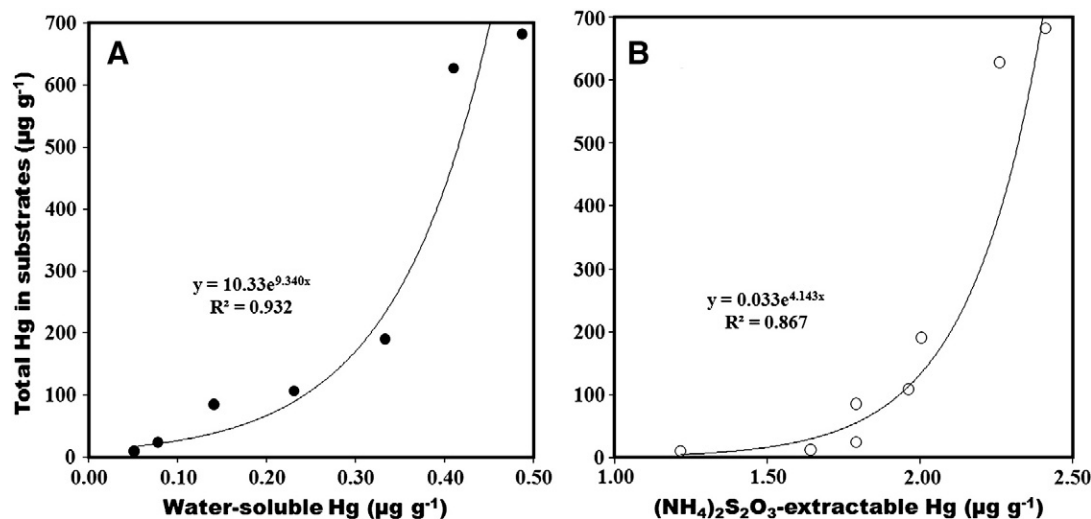


Fig. 2. Exponential correlations between total mercury concentration and water-extractable Hg concentration (A) and thiosulphate-extractable Hg concentration (B).

2005; Rothenberg et al., 2011), thiosulphate could be a stable counter ion (Bowell and Muinonen, 1993). The existence of a water-extractable Hg fraction in the original soil (mentioned in Section 3.1) indicates that Hg was available for exchange reactions with thiosulphate-containing ligands in the substrate solution. Thus, when  $(\text{NH}_4)_2\text{S}_2\text{O}_3$  is added, a new ligand is present that can form a stable soluble thio-Hg complex which is likely to be  $\text{Hg-S}_2\text{O}_3$  (Wang et al., 2011).

### 3.3. Hg isotope compositions of total Hg, water-soluble Hg and $(\text{NH}_4)_2\text{S}_2\text{O}_3$ -extractable Hg in WSMM soil samples

#### 3.3.1. Hg isotope compositions of total Hg in soil

The  $\delta^{202}\text{Hg}$  values of total Hg in soil samples varied from  $-0.29$  to  $0.15\%$ , with a mean of  $-0.02 \pm 0.16\%$  ( $n = 8$ ). MIF in  $\Delta^{199}\text{Hg}$  ranged from  $-0.05$  to  $0.07\%$ , which were small and statistically insignificant. So far, the major processes known to induce MIF are photo-reactions of Hg (Bergquist and Blum, 2007; Bergquist et al., 2011). Considering the very high Hg concentrations in the soil samples in WSMM, photochemical processes would only affect a very minor fraction, and we would not expect a detectable MIF in this large Hg pool. Recent studies reported that the Hg isotope compositions of river sediment collected downstream from the Idrija Hg mine, Slovenia, were similar to that of cinnabar ore at the mine upstream (Foucher et al., 2009). In the Idrija Hg mining area, the sediment of the downstream river contained a large amount of cinnabar, and thus, the Hg isotope composition of cinnabar was successfully used to trace the contamination source of Hg in the sediment of downstream river of the Idrija mine (Foucher et al., 2009). However, due to the fact that a large volume of calcine piles occur at WSMM, the Hg isotopic composition of nearby soil is most likely to be dominated by the Hg isotopic composition of mine waste calcines, but not the cinnabar ore. In a parallel study, we investigated mercury isotope composition of cinnabar ( $\delta^{202}\text{Hg} = -0.74 \pm 0.11$ ,  $n = 14$ ) and calcine ( $\delta^{202}\text{Hg} = 0.08 \pm 0.20\%$ ,  $n = 13$ ) in WSMM (Yin et al., 2010a, 2010b, in press), and a significant Hg isotope fractionation occurred during Hg retorting process. As shown in

Fig. 3, the  $\delta^{202}\text{Hg}$  values of total Hg in soil are identical to those of total mercury in calcines in WSMM, suggesting that the major Hg contamination source in soil is the nearby calcines.

#### 3.3.2. Hg isotope compositions of water-soluble Hg

Hg isotope measurements of the water-soluble Hg are presented in Table 1. The  $\delta^{202}\text{Hg}$  of water-soluble Hg varied from  $0.50$  to  $0.86\%$  with an average value of  $0.70 \pm 0.13\%$  ( $n = 8$ ). In general, the water-soluble Hg was isotopically heavier than the total Hg ( $-0.02 \pm 0.16\%$ ,  $n = 8$ ) as shown in Fig. 3. However, MIF in  $\Delta^{199}\text{Hg}$  ranged from  $-0.07$  to  $0.07\%$ , which is similar with the values of total Hg in soil.

As mentioned in Section 3.1, the water extraction process only dissolved a minor fraction of total Hg in the soil matrix. This is evidenced by the fact that Hg occurred in both organic bound and residual solid phase materials in WSMM soil (Wang et al., 2011). The water-soluble Hg fraction which constituted  $0.07$ – $0.54\%$  of total Hg in soil is generally in the same level with previous studies conducted in WSMM (Wang et al., 2011). We can speculate that water-soluble Hg species may have heavier  $\delta^{202}\text{Hg}$  values than total Hg in soil. In a study by Stetson et al. (2009), the leaching experiment of calcines by simulated water was performed. They demonstrated that during the leaching, the Hg isotope compositions of the dissolved Hg compounds were also much heavier than those of total Hg in calcines.

The speciation of water-soluble mercury in soil is still unknown, but it is expected that the complexes of Hg oxides, chlorides, oxychlorides, and sulfates would dominate over other Hg forms in the soil solutions. These Hg compounds are mobile species and can undergo physical (leaching, erosion, and volatilization) and biochemical transformations (methylation, photochemical and biological reduction) (Morel et al., 1998). In previous studies, mercury isotope fractionation has been reported in multiple geochemical processes. For example, microbial reduction (Kritee et al., 2007, 2008, 2009), evasion processes (Zheng et al., 2007), photoreduction (Bergquist and Blum, 2007), volatilization (Estrade et al., 2009) and adsorption (Wiederhold et al., 2010) preferentially act on the light Hg isotopes,

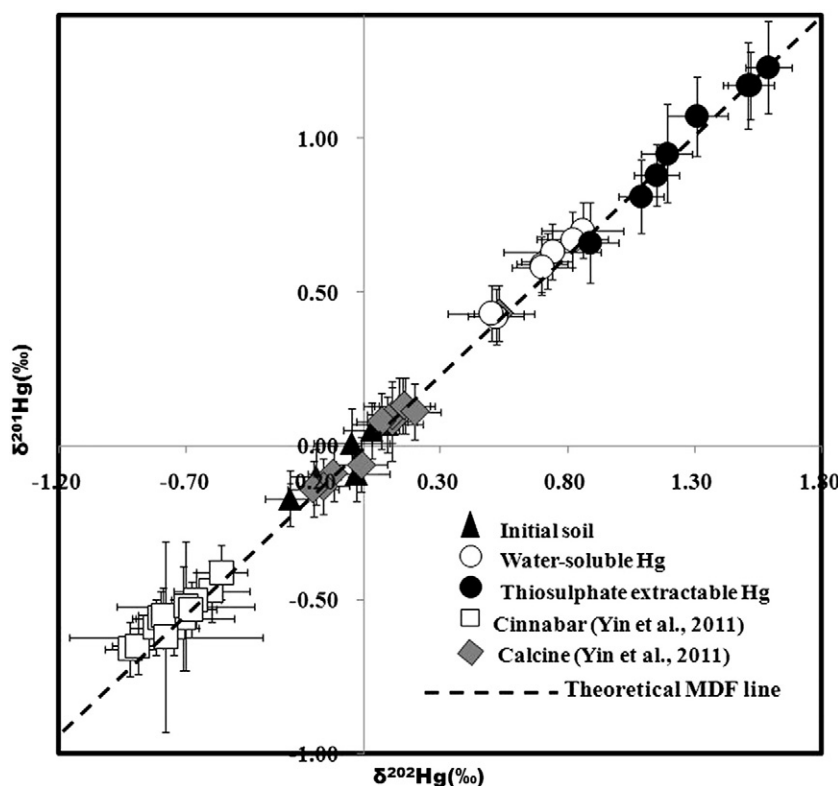


Fig. 3.  $\delta^{202}\text{Hg}$  versus  $\delta^{201}\text{Hg}$  in per mille for total Hg, water-soluble Hg, and thiosulphate extractable Hg in soil samples, cinnabar and calcine samples collected in WSMM.

which subsequently leave the system. Hence, our results of the soil leachate suggest that the minor Hg compounds (e.g. HgCl<sub>2</sub>, Hg(OH)<sub>2</sub> and HgOHCl) that are water soluble could have undergone these geochemical processes prior to being deposited to soils.

### 3.3.3. Hg isotope compositions of (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>3</sub>-extractable Hg

Hg isotope measurements of the (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>3</sub>-extractable Hg are presented in Table 1. The  $\delta^{202}\text{Hg}$  of (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>3</sub>-extractable Hg varied from 0.89 to 1.52‰, with an average value of  $1.28 \pm 0.25\%$  (n = 8). In general, the (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>3</sub>-extractable Hg species have  $\delta^{202}\text{Hg}$  values that are isotopically heavier than those of total Hg and water-soluble fraction in soil as shown in Fig. 3. No significant MIF was observed. The heavier isotope compositions of (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>3</sub>-extractable Hg in our study were generally in agreement with previous leaching studies of other elements, such as Cu and Fe (Mathur et al., 2005; Fernandez and Borrok, 2009).

Recent experiments have demonstrated distinct isotopic fractionation of Hg during a variety of abiotic (Bergquist and Blum, 2007; Zheng et al., 2007; Estrade et al., 2009; Yang and Sturgeon, 2009; Zheng and Hintelmann, 2009; Wiederhold et al., 2010; Bergquist et al., 2011) and biotic (Kritee et al., 2007, 2008, 2009; Rodríguez-González et al., 2009) processes. As mentioned in Section 3.2, the mobility of mercury can be significantly enhanced through the addition of (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution in soil. In a study by Wang et al. (2011), the Hg fraction associated with oxides in WSMM soil significantly decreased from  $3.41 \mu\text{g g}^{-1}$  to  $0.74 \mu\text{g g}^{-1}$  after the soil samples were extracted by (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution. However, they (Wang et al., 2011) did not observe a significant difference in the concentrations of mercury associated with the organic bound fraction and the residual fraction between the soil samples were extracted by (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution and the original soil samples. Moreno et al. (2004) proposed that thiosulphate-assisted plantation method was able to decrease the amount of soil mercury associated with the oxide-bound fractions. Therefore, the Hg species extracted by (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution could be specifically associated with the Oxide-bound fractions in soil from WSMM. According to the general principle (Schauble, 2004), heavy isotopes prefer stiff chemical bonds. Typically this means short and strong bonds correlate with “hard” and low atomic anions. Hence, it is likely that Hg isotope compositions of oxide-bound fraction of Hg were heavier than those of total Hg in soil.

Alternatively, our results may indicate mercury isotope fractionation during leaching and/or absorption process. Soil plays an important role in the immobilization of mercury. Environmental changes like acidification, salinization, or land use change can lead to leaching of mineral-bound mercury. To interpret natural processes causing Hg isotope fractionation in soils, Jiskra et al. (2011) investigated the sorption of Hg<sup>II</sup> to goethite (α-FeOOH), an important Fe mineral in most soils, and the corresponding isotope fractionation mechanisms. Their experimental data revealed systematic MDF with an enrichment of light Hg isotopes at the goethite surface ( $\delta^{202}\text{Hg}_{\text{diss}} - \delta^{202}\text{Hg}_{\text{sorb}} = 0.4\%$ ). Similarly, in the Wiederhold et al. (2010) study, the equilibrium absorption experiment between dissolved Hg(II) and absorbed Hg was conducted. The constant difference between the isotopic composition of the solution and absorbed Hg species ( $0.53 \pm 0.15\%$  for the Hg(II)-chloride and  $0.62 \pm 0.17\%$  for the Hg(II)-nitrate, respectively) indicated that significant equilibrium Hg isotope fractionation can occur without redox transition. Our data suggest that light Hg isotopes are preferentially sequestered in soils and we could expect an enrichment of heavy Hg isotopes in the mobile fraction which is leached from soils into surrounding ecosystems.

## 4. Conclusions and environmental implications

In WSMM, the large Hg mining activities had resulted in serious Hg contamination to the soil compartment. In our study, the total mercury concentrations in WSMM soil samples ranged from 10 to

$680 \mu\text{g g}^{-1}$ , which were much higher than the maximum upper limit for mercury content ( $1.5 \mu\text{g g}^{-1}$ ) in agriculture soil in China (CNEPA, 1995). Different Hg species can exist in various forms in soil and different forces keep them bound to soil particles. It is essential to study the interactions because the solubility, toxicity and bioavailability of the metal may strongly depend on the form in which they exist in the environment. The water-extractable mercury concentrations of WSMM soil samples ranged from 0.05 to  $0.49 \mu\text{g g}^{-1}$ . A significant correlation between the Hg<sub>Ts</sub> and Hg<sub>Tw</sub> ( $r^2 = 0.93$ ) was observed. Although the water-soluble Hg fraction contributed a minor portion of Hg<sub>Ts</sub>, the importance of this fraction should not be underestimated. Hg has a strong affinity to form complexes with sulfur-containing functional groups. The concentrations of (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>3</sub>-extractable Hg in WSMM soil samples reached from 1.22 to  $2.41 \mu\text{g g}^{-1}$ . The concentrations of (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>3</sub>-extractable Hg were 5 to 32 times higher than those extracted by pure water. Despite for the application of chelate-enhanced phytoextraction (Lombi et al., 2001), the environmental risk of the thiol-containing solutions in soils should be further considered.

In our study, the  $\delta^{202}\text{Hg}$  values of total Hg in soil are very similar with those of Hg in calcines in the WK tailing, suggesting that the soil were mainly contaminated by the mine waste calcines. In general, both the water-extractable Hg and the (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>3</sub>-extractable Hg have higher  $\delta^{202}\text{Hg}$  values than those of total Hg in soil. Therefore, Hg isotope compositions of more bioavailable fractions of Hg showed different Hg isotope composition with total Hg in soil. This may provide important qualitative and quantitative information for the interpretation of Hg isotope fractionation in the environment. Our study highlighted the importance to investigate Hg isotope compositions of different Hg fractions in soil to better understand Hg fractionation during Hg transformation processes in soil compartment. More studies are urgently needed to understand the mechanisms that control the fractionation of Hg isotope among different Hg fractions in soil.

## Acknowledgments

This research was funded by the Natural Science Foundation of China (40825011, 41120134005, and 41021062) and by the Chinese Academy of Sciences through Hundred Talent Plan.

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