

Mercury speciation and mobility in mine wastes from mercury mines in China

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Abstract Mercury (Hg) speciation and mobility were determined in calcines and waste rocks collected from 9 Hg mines in China. Total Hg (THg) concentrations in the mine wastes varied widely in different Hg mines (with a range of 0.369 to 2,620 mg kg⁻¹). Cinnabar is the dominant form of Hg in the mine wastes. However, Hg²⁺ and Hg⁰ concentrations in the calcines were significantly higher than these in the waste rocks, which suggested the retorting can produce large amounts of by-product Hg compounds. The THg and Hg⁰ concentrations in certain mine wastes exceeded soil guidelines recommended by US Environmental Protection Agency; while total soluble Hg concentrations of leachates in certain mine wastes exceeded National Surface Water Quality Standard of China. Mine wastes are important Hg pollution sources to the aquatic ecosystem and atmosphere.

Keywords Mercury · Speciation · Mobility · Mine waste · Calcines · Waste rocks

Introduction

Mercury (Hg) occurs naturally in the earth's crust. But centuries of anthropogenic activities have been dramatically

mobilizing the geochemical cycle of Hg over the surface of the planet (Schuster et al. 2002; Mason and Sheu 2002). Different from other heavy metals, gaseous phase is the main form of Hg in the atmosphere (Fu et al. 2012). Since gaseous elemental Hg can undergo long-range transport, it is a global pollutant (Lindberg et al. 2007). In the form of methylmercury, it is a potent neurotoxin which can pose risks to human health through fish and rice consumption (Mergler et al. 2007; Feng et al. 2008).

The Hg mining areas are considered as hot spots of Hg pollution (Gray et al. 2006). The Hg deposits are globally distributed in three mercuriferous belts associated with plate tectonic boundaries (Bailey et al. 1973). It includes Almadén in Spain; Idrija in Slovenia; Monte Amiata in Italy; Nevada, Alaska, and California Coast Range in the USA; Wanshan and Wuchuan in China; and Palawan in the Philippines (Rytuba 2003).

The Hg retorting is generally carried out in a retort furnace with a temperature of 600–700 °C. It can easily convert cinnabar (HgS) to Hg vapor, which was condensed to obtain liquid Hg. The mine wastes generated are defined as calcines or mine waste calcines after roasting (calcination) (Gray et al. 2006). The mine waste generally contains unconverted HgS, Hg⁰, and secondary Hg phases formed during the thermal processing (Biester et al. 1999; Kim et al. 2000, 2004). Moreover, the secondary Hg phases in the calcines are more soluble than HgS and can cause a greater extent of Hg contamination to the surrounding environment. The mine wastes are significant sources of Hg contamination to the surrounding aquatic ecosystems (Li et al. 2008; Zhang et al. 2010a) and the atmosphere (Gustin et al. 2003; Wang et al. 2007). The Hg pollution in the mine wastes, air, water, and soils have been widely studied in the Hg mines worldwide: Almadén (Gray et al. 2004) and Asturias (Loredo et al. 2005, 2006) in Spain; Idrija (Gosar and Tersic 2012) in Slovenia; Monte Amiata (Rimondi et al. 2012) in Italy; Nevada (Gray et al. 2002), Alaska (Gray et

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al. 2000), and California Coast Range (Ganguli et al. 2000; Kim et al. 2004) in the USA; and Palawan (Gray et al. 2003) in the Philippines.

China is rich in Hg resource. Guizhou Province is the most important Hg production center with 80,000 tons of Hg reserves. Hg has been used in China for about 2,000 years as an amalgamation agent (Liu 2000). It was thought to prolong life, heal fractures, and maintain good health (Hylander and Meili 2003). The trends in annual Hg production in recent years in China are shown in Fig. S1 provided in the Electronic supplementary material (ESM). The annual production was around 800 tons from 1980 to 1997 and declined from 1998 to 2002 since a few Hg mines closed during this period. However, the demand has increased because of large use in polyvinyl chloride plastic manufacturing (Jian et al. 2009). Since 2003, domestic Hg production has increased steadily to meet the internal demand (Fig. S1 provided in the ESM).

The Hg pollution resulted from Hg mining has been widely investigated in Wanshan (Horvat et al. 2003; Qiu et al. 2005; Zhang et al. 2010a, b), Wuchuan (Qiu et al. 2006a; Li et al. 2012), Tongren (Li et al. 2008), Lanmuchang (Qiu et al. 2006b) in Guizhou Province and Xunyang Hg mines (Zhang et al. 2009; Qiu et al. 2012) in Shaanxi Province in China. Long-term Hg mining has generated large quantities of mine wastes. In Wanshan Hg mine, there were about 125.8 million tons of calcines without proper treatments (Liu 1998).

This study was designed to: (1) evaluate Hg speciation in the mine wastes from Hg mines in China and (2) simulate the mobilization of Hg by runoff under the environmental conditions. This study can provide scientific data to understand Hg geochemical cycle and take effective measures to reduce Hg pollution in the Hg mines.

Materials and methods

Study area

A total of nine Hg mines in China were selected in this study (Fig. 1). The detailed information about these Hg mines is given in Table 1. Wanshan, Danzhai, Xiushan, and Xunyang are ranked as super-large Hg mines. Wanshan Hg mine is located in eastern Guizhou Province. It was the largest one in China before the closure in 2003 and known as the “capital of Hg.” Total Hg production was estimated to be 30,000 tons from the 1950s to 2003. Xunyang Hg mine is located in southern Shaanxi Province. It is the only large-scale Hg mine that is still in operation in China. Two large (Tongren and Chatian) and three medium scale (Sandu,

Yulan, and Xinhuang) Hg mines were also chosen in this study.

Samples collection

A total of 132 mine wastes were collected from these nine Hg mines. There are two main types of mine wastes: calcines and waste rocks. The calcines are the residues of HgS ores after high temperature retorting and may contain trace amount of Hg. The waste rock is the sterile fraction of mine production. It contains variable but usually minor level of Hg. The samples included 91 calcines and 41 waste rocks. Three profiles were collected at Wanshan Hg mine to evaluate vertical distribution and homogeneity in the mine wastes. The mine wastes were collected as grab samples about 25–50 cm below the surface to avoid near-surface oxidized environment. Before geochemical analysis, the mine waste samples were air dried, ground, and sieved to minus 100 mesh in the laboratory.

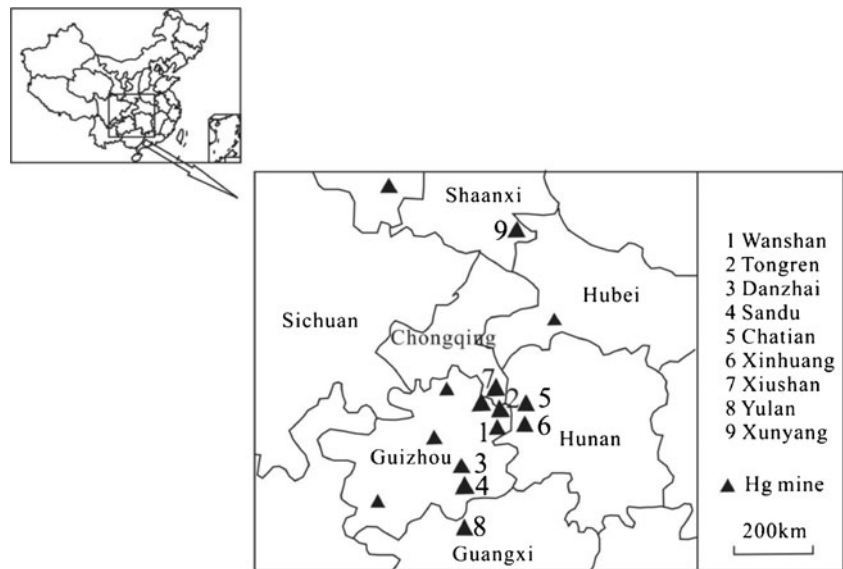
Analytical methods

Total Hg (THg) concentrations in the mine wastes were analyzed by the RA-915+ Hg analyzer coupled with PYRO-915+ attachment (Lumex, Russia). It is based on the atomization of Hg by thermal decomposition and subsequent detection by Zeeman Atomic Absorption Spectrometry (Sholupov et al. 2004).

Among 132 samples, 17 calcines and 15 waste rocks were selected for Hg speciation analysis and leaching experiments. Samples with high, medium, and low THg concentrations obtained from different Hg mines were included. There was no significant difference in THg concentrations between two selected groups (Table 2). The Hg^{2+} concentrations were determined with cold vapor atomic absorption spectrometry following room temperature leaching for 18 h with 1 N HCl using a liquid to solid ratio of 10:1 (Gray et al. 2006). This operationally defined technique liberates most Hg not bound in HgS or Hg^0 . The Hg^0 concentrations were measured by a pyrolysis technique following Biester and Scholz (1997). It derived from the difference between THg concentrations before and after 24 h heating at 180 °C (García-Sánchez et al. 2009; Wang et al. 2011a). The HgS concentrations in the mine wastes were obtained by subtracting the Hg^{2+} and Hg^0 concentrations from the THg concentrations.

Leaching experiments were performed by shaking 20 g of samples for 24 h end to end in 250 mL polyethylene centrifuge bottles with 200 mL of deionized water (pH 5.7). After centrifugation (2 h, 3,000 RPM), all leachates were filtered through a 0.45- μm filter. The Hg concentrations in the solution were determined using the RA-3000F

Fig. 1 The spatial distribution of studied Hg mines in China



Automatic Hg Analyzer (Nippon Instruments Corporation, Japan) and defined as total soluble Hg (TSHg) (Biester et al. 1999). The pH in the leachates was measured by a pH electrode.

Quality control

Quality control consists of method blanks, blank spikes, matrix spikes, certified reference materials (CRMs), and blind duplicates. Limits of detection were 0.02 mg kg^{-1} for THg, Hg^{2+} , and Hg^0 in mine wastes, whereas the limit of detection was 0.02 ng L^{-1} for TSHg in the leachates of mine wastes in the leaching experiments. The averages of THg concentration in GBW070009 and NIST 2710 were 2.18 ± 0.08 and $32.3 \pm 1.7 \text{ mg kg}^{-1}$, respectively, which were in a good agreement with the certified values of 2.2 ± 0.4 and $32.6 \pm 1.8 \text{ mg kg}^{-1}$. Recoveries for Hg^{2+} on blank and matrix spikes ranged from 88 to 105 %. The average of the relative percentage difference was $<5 \%$ for THg, Hg^0 , Hg^{2+} , and TSHg in the mine waste duplicate samples.

Results and discussion

THg

THg concentrations in the mine wastes varied widely from 0.369 to $2,620 \text{ mg kg}^{-1}$ and followed a log-normal distribution pattern with a geometric mean of 18.8 mg kg^{-1} . THg concentrations in the mine wastes were significantly higher than the baseline of 0.35 mg kg^{-1} in rocks reported in Wanshan Hg mine (Hua and Cui 1994). Among these samples, 45.5 % (60/132) exceeded the screening level of inorganic Hg for residential soil set by US Environmental Protection Agency (2011) (23 mg kg^{-1}); 3.8 % (5/132) exceeded that for industrial soil recommended by US Environmental Protection Agency (2011) (310 mg kg^{-1}). The geometric means of THg concentrations in the calcines and waste rocks were 18.2 and 20.1 mg kg^{-1} , respectively. The waste rocks showed significantly higher THg concentrations than the calcines ($p < 0.01$), which indicated the probable existence of HgS in the waste rocks.

Table 1 The basic information of studied Hg mines (data from CMA 2011)

No	Mine	Location	Accompanying element	Reserves/tons	Scale	Grade/%	Status
1	Wanshan	Guizhou	Se	37,000	Super large	0.3	Closed in 2003
2	Tongren	Guizhou	Zn	6,700	Large	0.16	Closed in 1989
3	Danzhai	Guizhou	Au	14,000	Super large	0.5	Closed in 1985
4	Sandu	Guizhou	Au	1,900	Medium	0.5	Closed in 1984
5	Chatian	Hunan	Pb and Zn	4,990	Large	0.15–0.33	Closed
6	Xinhuang	Hunan	Se and Zn	3,500	Medium	–	Closed in 2003
7	Xiushan	Chongqing	–	11,760	Super large	0.19	Closed
8	Yulan	Guangxi	Tl and Ga	1,980	Medium	0.2–2	Closed in 1991
9	Xunyang	Shaanxi	Sb and Au	14,800	Super large	0.3–0.5	Active since 1998

Table 2 Statistical summary of Hg speciation in the calcines and waste rocks

	Type ^a	Number	Min	Max	Mean	STD	Geometric mean
THg (mg kg ⁻¹)	1	17	0.60	267	48.4	67.6	17.8
	2	15	0.40	516	90.5	160	18.1
Hg ²⁺ (mg kg ⁻¹)	1	17	0.0015	3.81	0.52	1.17	0.047
	2	15	0.0030	8.33	0.65	2.13	0.035
Hg ²⁺ /THg (%)	1**	17	0.010	10.6	1.84	3.47	0.26
	2	15	0.030	1.95	0.39	0.51	0.19
Hg ⁰ (mg kg ⁻¹)	1*	17	0.22	79	15.8	22.6	4.9
	2	15	0.14	15	6.2	5.8	2.8
Hg ⁰ /THg (%)	1	17	2.84	72.9	34.5	18.0	27.8
	2	15	2.34	71.2	24.3	20.1	15.7
HgS (mg kg ⁻¹)	1*	17	0.31	185	32.1	46.2	10.8
	2	15	0.23	500	83.7	156	13.1
HgS/THg (%)	1	17	26.2	97.2	63.7	18.9	60.6
	2	15	28.2	97.0	75.3	20.0	72.0
TSHg (μg L ⁻¹)	1	17	0.074	1.9	0.38	0.42	0.28
	2	15	0.012	2.8	0.54	0.75	0.24
TSHg/THg (%)	1	17	0.0026	0.17	0.039	0.058	0.016
	2	15	0.0020	0.61	0.063	0.156	0.013
pH	1	17	6.30	9.86	8.80	1.22	8.71
	2	15	4.94	9.52	8.79	1.36	8.66

p*<0.05; *p*<0.01, compared with 2

^a“1” calcines; “2” waste rock

The distribution pattern of THg concentrations in the calcines and waste rocks from each Hg mine is shown in Fig. 2. THg concentrations varied widely in the mine wastes from different Hg mines. The highest value (2,620 mg kg⁻¹) was found in waste rock from Tongren Hg mine, which was similar to the previous result of 4,400 mg kg⁻¹ reported in Wanshan Hg mine (Qiu et al. 2005). Since waste rocks contain

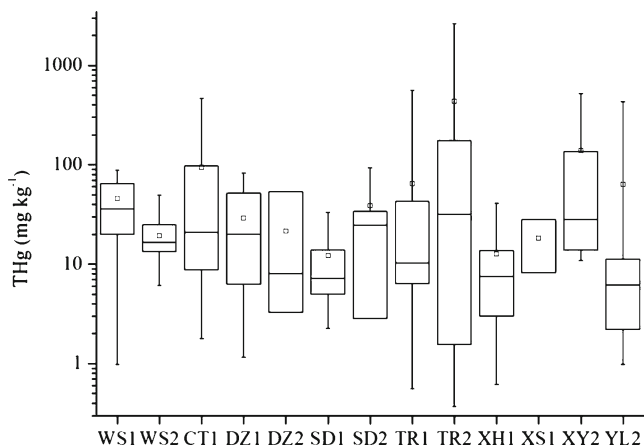


Fig. 2 The distribution pattern of THg concentrations in the calcines and waste rocks from each Hg mine. 1, calcines; 2, waste rock; each box represents interquartile range (25th and 75th percentiles), the band near the middle of the box is the 50th percentile (the median), and the whisker represents 5th and 95th percentiles; WS Wanshan, CT Chatian, DZ Danzhai, SD Sandu, TR Tongren, XH Xinhuang, XS Xiushan, XY Xunyang, YL Yulan

HgS, they are characterized with high THg concentrations. Meanwhile, HgS retorting is an inefficient and incomplete process (Rytuba 2003; Gray et al. 2002, 2004). As a result, mine waste calcines may contain unconverted HgS and other secondary Hg compounds. THg distribution patterns in three profiles show no obvious trend and THg concentrations varied widely in different depths (Fig. 3). The results indicated THg concentrations are clearly unevenly distributed among the mine wastes.

THg concentrations in the mine wastes in this study were comparable to the results from Wuchuan Hg mine, Guizhou, China (3–810 mg kg⁻¹; Qiu et al. 2006a; Li et al. 2012); Palawan Hg mine, Philippines (28–660 mg kg⁻¹; Gray et al. 2003); Hg mines in SW Texas, USA (4.1–480 mg kg⁻¹; Gray et al. 2006); and Monte Amiata Hg mine, Italy (25–1,500 mg kg⁻¹, Rimondi et al. 2012). However, much higher THg concentrations were reported in mine wastes collected from Almadén Hg mine, Spain (up to 34,000 mg kg⁻¹; Gray et al. 2004).

Hg speciation

- a. Hg²⁺
 - Hg²⁺ concentrations in the calcines and waste rocks varied from 0.002 to 3.81 and 0.003 to 8.33 mg kg⁻¹, respectively (Table 2). The calcines showed significantly higher percentages of Hg as Hg²⁺ (with a mean of 1.8 %) than the waste rocks (with a mean of 0.4 %; *p*<0.01). Three

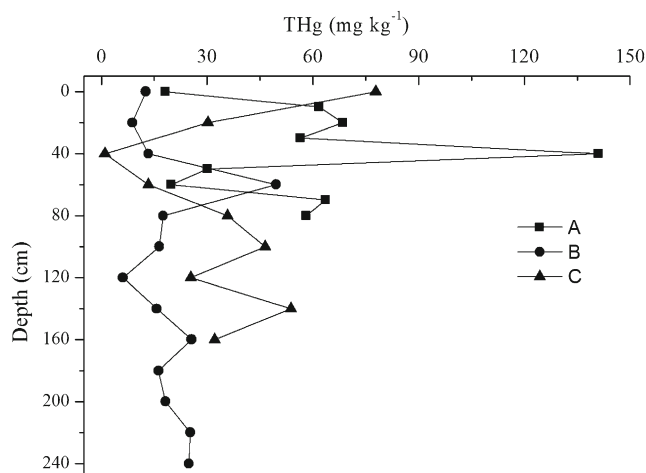


Fig. 3 The THg distribution patterns in mine waste profiles in Wanshan Hg mine. A, C calcines; B waste rocks

high values of $\text{Hg}^{2+}/\text{THg}$ ratio (6.88, 9.30, and 10.6 %) were all observed in the calcines (Fig. 4). There was a significant correlation ($r=0.60$; $p<0.001$) between the Hg^{2+} and THg concentrations in the mine waste samples (Fig. S2a provided in the *ESM*), which indicated the presence of water soluble Hg compounds (Biester et al. 1999; Kim et al. 2000; Gray et al. 2006). By extended X-ray absorption fine structure (EXAFS) approach, Kim et al. (2000) observed the presence of mercuric chloride (HgCl_2) and schuetteite (HgSO_4) in the calcines from California Coast Range Hg mines. Elevated Hg^{2+} concentrations in the mine wastes indicated the mine wasters are significant pollution sources to the surround aquatic ecosystems (Zhang et al. 2010a).

Hg^{2+} concentrations in the mine wastes in this study were much lower than that from Hg mines in Texas, USA (1.5–

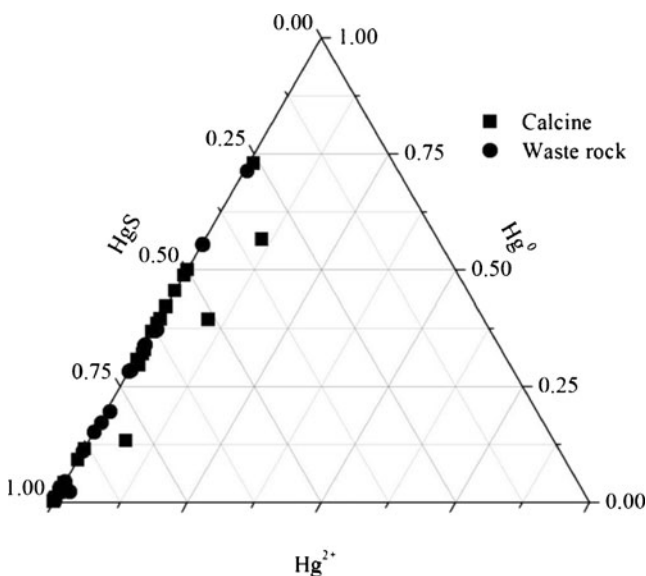


Fig. 4 Triangle diagram showing Hg speciation distributions in mine wastes

2,100 mg kg^{-1} , with a mean of 180 mg kg^{-1} ; Gray et al. 2006). The samples with high Hg^{2+} concentrations were the retort soot and the percentages of Hg as Hg^{2+} averaged at 52.5 % (Gray et al. 2006). This may be attributed to the special hot and dry climate. On the contrary, the study area has a humid subtropical climate characterized by abundant precipitation and mild temperatures; therefore, the abundant rainfall leached out most Hg^{2+} in the mine wastes.

b. Hg^0

— Hg^0 concentrations in the calcines and waste rocks ranged from 0.22 to 79 mg kg^{-1} and from 0.14 to 15 mg kg^{-1} , respectively (Table 2). Among the selected samples, 37.5 % (12/32) exceeded the screening level of Hg^0 for residential soil set by US Environmental Protection Agency (2011) (10 mg kg^{-1}); 6.3 % (2/32) exceeded that for industrial soil recommended by US Environmental Protection Agency (2011) (43 mg kg^{-1}). The calcines showed significantly higher Hg^0 concentrations (with a mean of 16 mg kg^{-1}) than the waste rocks (with a mean of 6.2 mg kg^{-1} ; $p<0.05$). During the retorting process, most Hg compounds are converted to Hg^0 at high temperatures. But Hg^0 in the gas phase may reabsorb to the matrices when the materials cooled down. There was a significant correlation ($r=0.43$; $p<0.05$) between Hg^0 and THg concentrations in the mine wastes (Fig. S2b provided in the *ESM*).

Mine wastes can continuously release Hg^0 to the atmosphere under environmental conditions. Many studies confirmed that mine wastes were significant Hg emission sources to the atmosphere. The Hg emission fluxes from calcines reached 5,724 $\text{ng m}^{-2} \text{h}^{-1}$ in Wanshan Hg mine and the annual emission achieved 1.0–5.0 kg (Wang et al. 2007). Hg emission fluxes ranged from 30 to 1,000 $\text{ng m}^{-2} \text{h}^{-1}$, and mine wastes contributed several kilogrammes annually to the atmosphere in Nevada and California Hg mines, USA (Gustin et al. 2003). The highest Hg flux above the calcines in Almadén Hg mine varied from 100 to 400 $\mu\text{g m}^{-2} \text{h}^{-1}$ and the annual emission ranged from 263 to 1,050 kg (Ferrara et al. 1998). The average emission flux from soils in Idrija Hg mine reached 1,600 $\text{ng m}^{-2} \text{h}^{-1}$, and the annual emission estimated at 51 kg (Kocman and Horvat 2011). Hg^0 released from soils and mine wastes originated mainly from Hg^0 bound to the matrices and partly from photoreduction of Hg^{2+} (Schroeder and Munthe 1998). Hg^0 concentrations in mine wastes correlate with Hg fluxes released during light and dark exposure, with higher evasion ratios from samples with higher Hg^0 concentrations (Jew et al. 2011). In summary, high Hg^0 concentrations in the mine wastes are significant Hg emission sources to the atmosphere. It not only poses a threat to the local environment, but also contributes to the global Hg cycle in the atmosphere.

Hg^0 concentrations were relatively low in mine wastes from Texas Hg mine and mostly were below the detection

limit (0.005 mg kg⁻¹). This may be due to the special hot and dry climate since high temperature will result in evaporation of Hg⁰ from the mine wastes (Gray et al. 2006). The means of Hg⁰/THg ratios in the mine wastes in this study (34.5 % for calcines and 24.3 % for waste rocks, respectively) were comparable with those in contaminated soils in Wanshan Hg mine (10.1–76.4 %; Wang et al. 2011b), Idrija Hg mine (about 10 %; Kocman et al. 2004), Oak Ridge in the USA (10–30 %; Liu et al. 2006), and sediments of Haihe River, China (23.7–65.8 %; Shi et al. 2005).

c. HgS

HgS concentrations in the calcines and waste rocks ranged from 0.31 to 185 and 0.23 to 500 mg kg⁻¹, respectively (Table 2). The waste rocks showed significantly higher concentrations (with a mean of 83.7 mg kg⁻¹) than the calcines (with a mean of 32.1 mg kg⁻¹; *p*<0.05). Ratios of HgS/THg averaged at 63.7 and 75.3 % for calcines and waste rocks, respectively. HgS is the dominant form of Hg in the calcines and waste rocks in this study (Fig. 4). This indicated that calcines and waste rocks both contain a significant amount of unconverted HgS. The results were comparable to the mean ratio of HgS/THg (86 and 48–100 %) in calcines from California Coast Range Hg mines (Kim et al. 2000, 2004).

Leaching experiment

The leachates of the mine wastes showed variable TSHg concentrations (Table 2). The mean of TSHg concentrations was 0.45 μg L⁻¹ (with a range of 0.012–2.8 μg L⁻¹). Three values exceeded Grade V (1 μg L⁻¹) according to National Surface Water Quality Standard of China (GB3838-2002; MEP 2002). TSHg only accounted for a small portion

(0.0020–0.61 %) of THg in the mine wastes. There was no significant difference of TSHg concentration between the leachates of calcines and waste rocks (Table 2). However, a significant correlation (*r*=0.72; *p*<0.001) between TSHg in the leachates and THg in the mine wastes was observed (Fig. S2c provided in the *ESM*).

The pH of the leachates ranged from 4.94 to 9.86 (with a mean of 8.80). Most of the leachates are alkaline, which were related to the special mineral components. The mine wastes are dominantly composed of alkali minerals, such as CaCO₃, CaO, and MgO (Zhang et al. 2004). In addition, acid mine drainage-producing minerals, such as pyrite and other metal sulfides, are rare in the studied Hg mines (Qiu et al. 2005). There was a significantly negative correlation (*r*=-0.56; *p*<0.001) between the pH of the leachates and Hg²⁺ concentrations in mine wastes. The most soluble inorganic species are Hg²⁺ at low pH and oxic environments (Navarro et al. 2009), which can explain this negative correlation.

TSHg concentrations in the leachates in this study were comparable to THg concentrations in the surface water collected from different Hg mines worldwide (Fig. 5). However, high TSHg concentrations were reported in leachates from Tongren artisanal Hg mining area (130 μg L⁻¹; Li et al. 2008) and Idrija Hg mine (475 μg L⁻¹; Biester et al. 1999). The calcines collected from Tongren were derived from abandoned catalysts with extremely high THg concentrations (Li et al. 2008) while humic substances may increase the solubility of matrix-bound Hg⁰ in Idrija Hg mine (Biester et al. 1999). Coupling hydrology and aquatic Hg simulation models, Lin et al. (2011) estimated annual Hg emission from mine wastes to be 8.8 kg in one stream of Wanshan Hg mine. The results confirmed mine wastes were significant Hg pollution sources to the aquatic ecosystem.

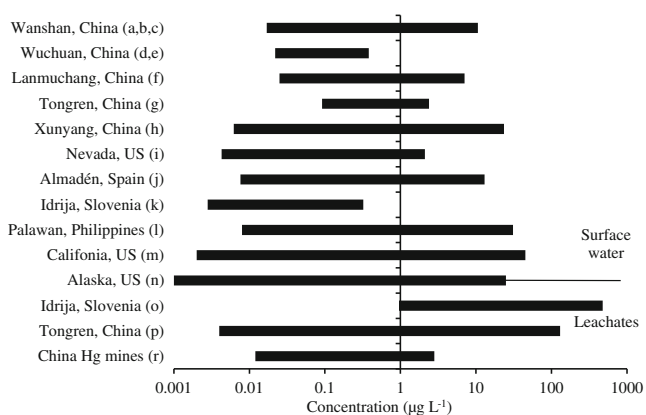


Fig. 5 Comparison of TSHg in the leachates of mine wastes and THg in surface water from different Hg mines worldwide. *a* Horvat et al. (2003), *b* Qiu et al. (2005), *c* Zhang et al. (2010a), *d* Qiu et al. (2006a, b), *e* Li et al. (2012), *f* Qiu et al. (2006b), *g* Li et al. (2008), *h* Zhang et al. (2009), *i* Bonzongo et al. (1996), *j* Gray et al. (2004), *k* Hines et al. (2000), *l* Gray et al. (2003), *m* Ganguli et al. (2000), *n* Gray et al. (2000), *o* Biester et al. (1999), *q* Li et al. (2008), and *r* this study

Conclusions

THg concentrations and Hg speciation in the mine wastes varied widely in different Hg mines. HgS is the dominant form of Hg in the mine wastes. However, the calcines showed significantly higher Hg²⁺ and Hg⁰ concentrations than the waste rocks, which indicated the presence of reabsorbed Hg⁰ and secondary Hg compounds in the calcines. Nearly half of the mine waste samples exceeded the screening level of inorganic Hg and one-third exceeded that of Hg⁰ for residential soil use recommended by USEPA. TSHg concentrations in three leachate samples of mine wastes exceeded Grade V according to National Surface Water Quality Standard of China. The results confirmed mine wastes are significant Hg sources to the local aquatic ecosystem and the atmosphere. Proper treatments and remediation techniques should be utilized to reduce Hg release to the local environments.

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