



## Identification of fractions of mercury in water, soil and sediment from a typical Hg mining area in Wanshan, Guizhou province, China

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### ABSTRACT

Water, sediment and soil in a region with severe Hg contamination resulting from Hg mining and retorting continue to receive anthropogenic Hg loading from discarded tailings and mine waste calcine piles, even after mining has ended. Crucial for potential long-term mobilization and uptake in biota, however, are chemical forms of Hg in the environment. In order to assess potential mobility and bioavailability of Hg in contaminated areas, a refined sequential extraction technique was used for Hg in soil and sediment, allowing identification of the following conceptual Hg fractions: elemental Hg, exchangeable Hg, strongly-bound Hg and organically-bound Hg.

This fractionation scheme was used on stream sediment and rice paddy soil collected from the Wanshan Hg mining area in China. Concentrations of total Hg (THg) were as high as 480 mg kg<sup>-1</sup> in stream sediment samples and reached 130 mg kg<sup>-1</sup> in soil samples. Exchangeable- and strongly-bound Hg constitute 10–30% and 20–40% of the THg, respectively, for most soil and sediment samples. The residual fraction varies considerably (4–82%), with higher Hg concentrations in the sediment samples than in soil samples. Rice paddy soil, which is richer in soil organic matter, also contains a small, but significant amount of organically-bound Hg. Exchangeable-, strongly-bound- and organically-bound Hg fractions are dominantly sorbed to fine particles, which enhances their mobility during high flow in the streams. Elemental Hg is only found in significant proportions proximal to a few artisanal retorts that are still active.

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### 1. Introduction

Mercury as a pollutant has been studied worldwide. Although Hg contamination has been documented in different regions, the processes governing mobilization, transportation and fate in the environment are not well-studied. Mercury is bound to soil and sediment in various forms and to different constituents, representing different fractions of Hg. The potential mobilization and transport of Hg in the environment is determined by these various fractions of Hg. Information on major Hg fractions in soil and sediment is, therefore, required in order to assess efficient and sustainable abatement strategies and to predict the effect of future changes in the environment.

Fractionation studies of Hg in soil and sediment have previously been carried out at the two largest Hg mines worldwide Idriza, Slovenia, and Almadén, Spain (Biestler et al., 2000; Bernaus et al., 2006). These studies revealed that Hg in the local environment is mainly found as cinnabar (HgS), accounting for 5–89% of the THg

in soil samples (Biestler et al., 2000; Bernaus et al., 2006). Acid-soluble Hg is the second most abundant fraction, indicating that Hg may be mobilized under more acidic conditions (Bernaus et al., 2006). A large part of this acid-soluble Hg fraction may be bound to organic matter (Higuera et al., 2003) in soil with high contents of organic matter.

The Wanshan Hg mining area in Guizhou province is situated in the circum-Pacific Hg belt (Gustin et al., 1999; Qiu et al., 2006). Wanshan was at one time the largest conglomeration of Hg mines and refining plants in China. When large-scale Hg mining and retorting were shut down in 2001, approximately 22,000 t of Hg and 6000 t of cinnabar had been produced (Qiu et al., 2005). The Wanshan area is presently suffering from the effects of Hg mining for more than a 1000 years; a large volume of tailings and mine waste calcine from ore processing and retorting have been stockpiled in the valley, typically in the vicinity of headwater streams. Between 1949 and the early 1990s, approximately 130 million t of calcine was discarded and 20 billion m<sup>3</sup> of Hg-containing exhaust gas had been emitted (Feng et al., 2008). Up to 4400 mg kg<sup>-1</sup> of THg has been found in the calcines and mine tailings at Wanshan (Qiu et al., 2005). Mine wastes continue to leach Hg into

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runoff water, causing significant Hg contamination of downstream environments. Several studies have previously documented high concentrations of Hg in the environment in the Wanshan area (Qiu et al., 2005; Horvat et al., 2003), but little research has been done to identify contaminant fractions of Hg in soil and sediment in this area.

The Hg ore at Wanshan is mainly cinnabar and is found in sedimentary bedrock of predominantly Cambrian dolomite, limestone and some sandstone (Zhang et al., 2004). Surface water in the area is generally alkaline due to the presence of carbonate-bearing bedrock and a large number of calcines and tailings. The form of Hg in the calcine is dominantly elemental Hg, metacinnabar, and Hg sulfate and chlorides (Kim et al., 2000, 2004). The concentration of THg in mine waste calcines from various Hg mines varies considerable as it is mainly controlled by the efficiency of the retorting techniques (Gray et al., 2002, 2003, 2004).

Concentrations of THg in surface water collected proximal to calcines were found to be as high as  $11 \mu\text{g L}^{-1}$ , while dissolved Hg concentration was as high as  $0.66 \mu\text{g L}^{-1}$  (Horvat et al., 2003). Another study showed that water draining calcine piles had a pH of about 11 and dissolved Hg concentrations of up to  $1.9 \mu\text{g L}^{-1}$  (Zhang et al., 2004). Water from these streams has been used for irrigation, causing Hg contamination of agricultural soil. Up to  $790 \text{ mg kg}^{-1}$  Hg was found in rice paddy soil in the Wanshan area (Qiu et al., 2005), while the global background Hg concentration is between  $0.01$  and  $0.50 \text{ mg kg}^{-1}$  (Senesi et al., 1999). Large-scale

mining and retorting in the area has now ended, but a few small-scale, illegal, artisanal retorting activities of previously mined ore are presently ongoing (Li et al., 2009; Feng and Qiu, 2008).

A major question regarding long-term management in the region is how soon the Hg contamination of the local environment will decline? In order to assess Hg contamination, a more comprehensive understanding is needed of the long-term future mobilization and leaching of Hg from mine wastes into the local environment, as well as loss of Hg from the local environment through dispersion and downstream leaching. This paper presents data on various Hg fractions in soil and sediment samples and Hg fractions in stream water in the Wanshan area. These new data are then discussed in the context of Hg mobilization, transport and fate, as well as potential bioavailability.

## 2. Materials and methods

### 2.1. Area description

Three stream valleys in Wanshan were selected for study. The Xiaxi and Huangdao watersheds were studied because they contain significant discarded tailings and calcines from large-scale mining and retorts at their headwaters. Tailings were recently covered by concrete as an abatement action to reduce the release of Hg into the surrounding environment. A sedimentation pond below

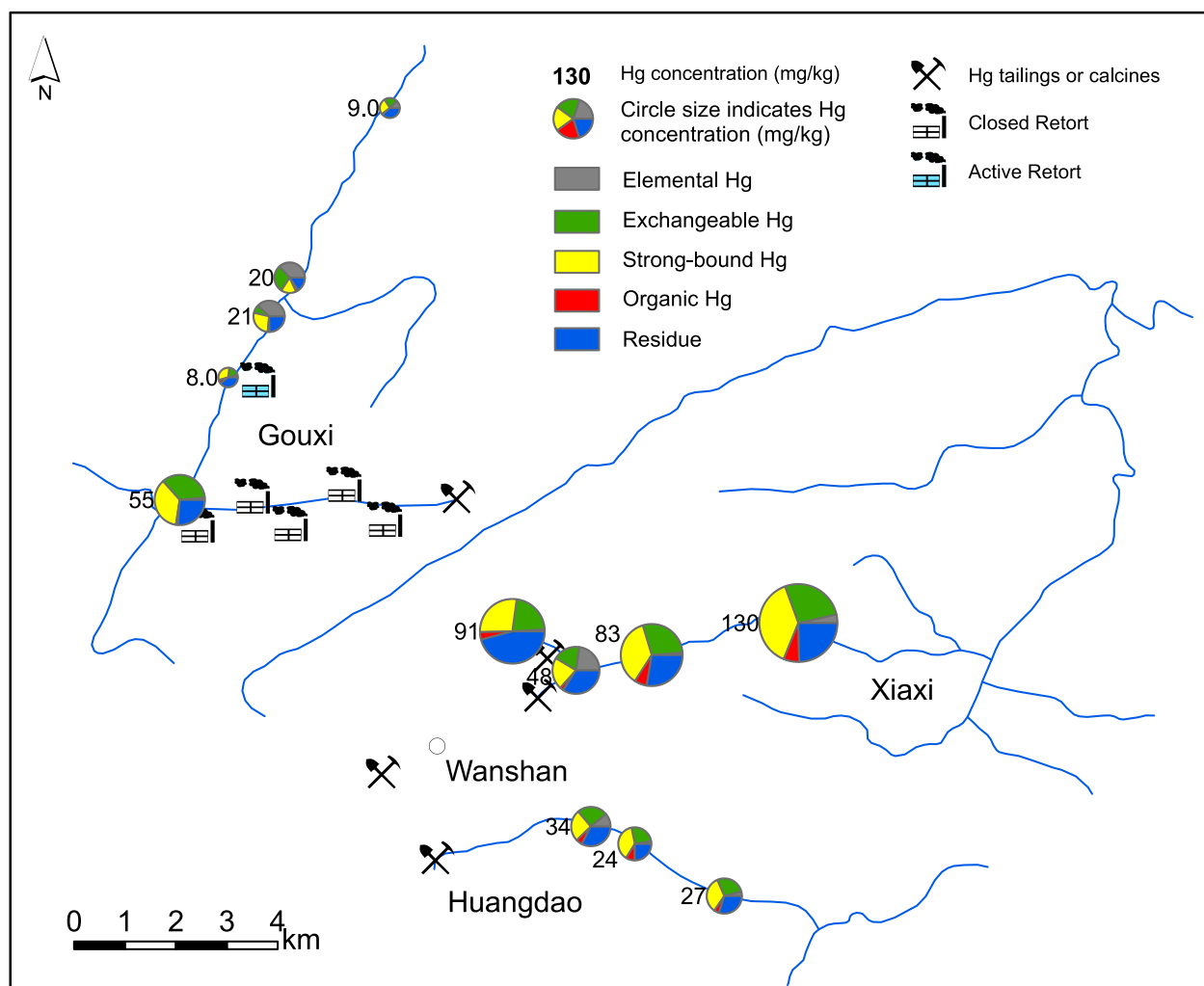


Fig. 1. Distribution and analytical results of sequential extraction of rice paddy soil samples.

each calcine pile captures sediment runoff in seepage water as a measure to further reduce the release of particulate Hg downstream. The Gouxì watershed was studied because there are several retorts in this drainage, a few of which are presently operating, illegal artisanal Hg retorts along its stream banks. Such small retorts lack pollution controls and all wastes from these retorts have been stockpiled in numerous small mine waste piles along the stream banks. A large amount of Hg has also been emitted to the air from the retorts due to poor distillation practices (Li et al., 2009). Since the Gouxì valley is basically a narrow gorge, a considerable fraction of the Hg emitted into air is probably deposited onto the local vegetation and soil, contributing to overall soil contamination. All three of the watersheds studied represent typical conditions for most of the streams in the area.

## 2.2. Sample collection

Soil samples were collected from rice paddy fields receiving irrigation water from the adjacent contaminated streams (Fig. 1). Samples were collected approximately every 3 km along the three streams. The upper 5 cm layer of soil was collected since the majority of roots are found in this layer. There has been a long history of rice cultivation in this area and soil is thoroughly cultivated and ploughed. Sediment samples from the streambed were also collected (Fig. 2), though many locations lacked fine sediment (<2 mm) due to rapid stream flow. A total of 12 soil and 16 sedi-

ment samples were collected and placed in plastic bags that were refrigerated until they were processed and analyzed.

Water samples were also collected. An unfiltered sample was stored in a 200 mL borosilicate glass bottle (for measurements of total Hg), and another sample was filtered *in situ* with a 0.45  $\mu\text{m}$  polyvinylidene fluoride filter (Millipore) (for measurements of dissolved Hg, and major cations and anions). The borosilicate glass bottles were rigorously pre-cleaned including baking for at least 45 min in a muffle furnace at 500 °C. During sampling the filtration equipment and sample bottles were rinsed three times with sample water prior to filling. All water samples, except aliquots for anion analysis, were preserved by adding 0.4% (v/v) of distilled ultrapure HCl within 24 h. The sample bottles were tightly capped and placed into double plastic bags and stored in coolers until further processing and analysis. Collection, storage and preservation techniques of samples followed USEPA Method 1631 (USEPA, 1999). A total of 22 water samples were collected (Fig. 3). Sample sites for soil, sediment and water do not necessarily coincide because of the erratic distribution of rice paddy fields and lack of fine sediment at some sites.

## 2.3. Analytical methods

A sequential extraction technique for soil and sediment samples (Lechler et al., 1997) was modified and employed in this study. This modified procedure produced data on the following fractions of Hg

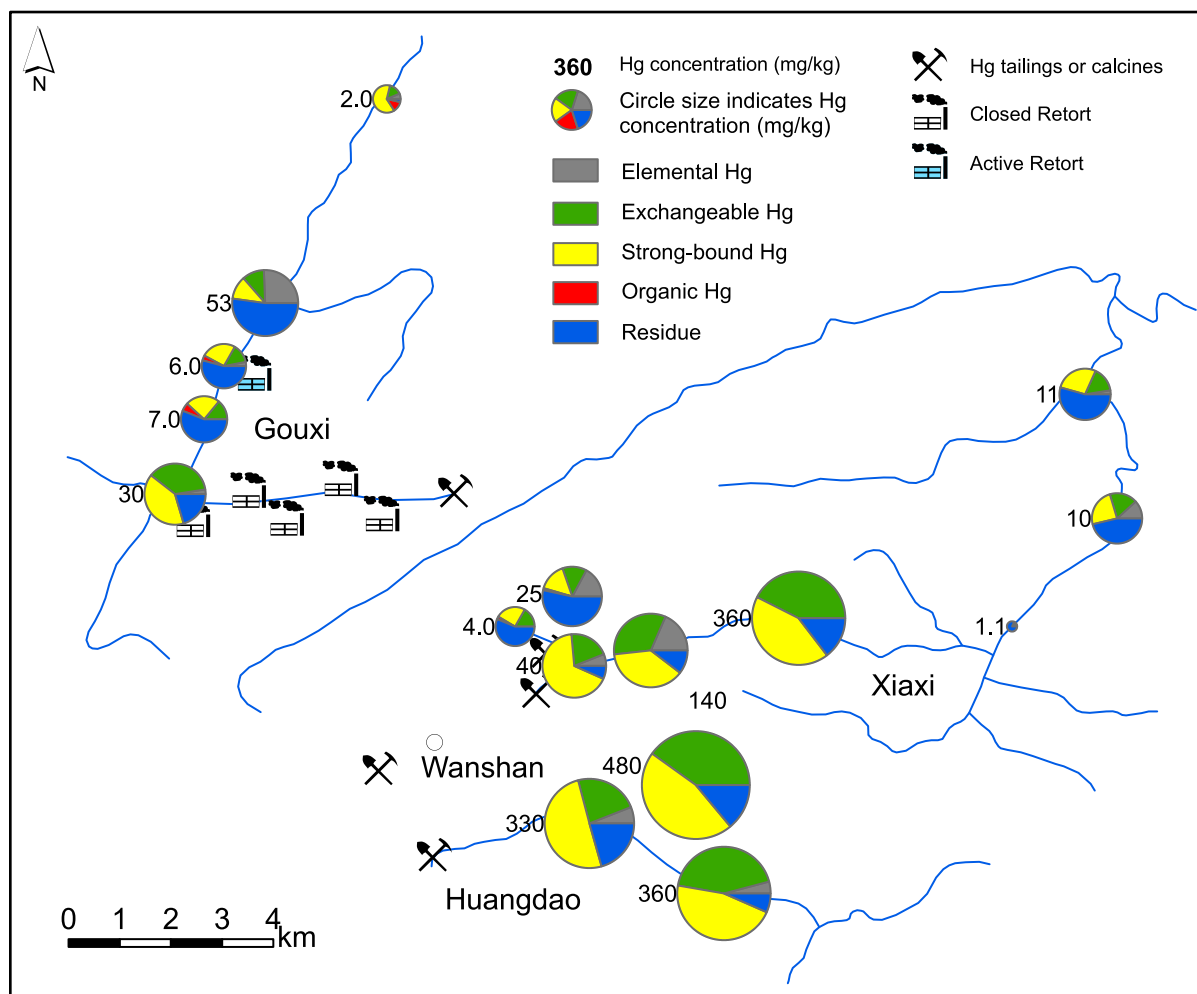


Fig. 2. Distribution and analytical results of sequential extraction of stream sediment samples.

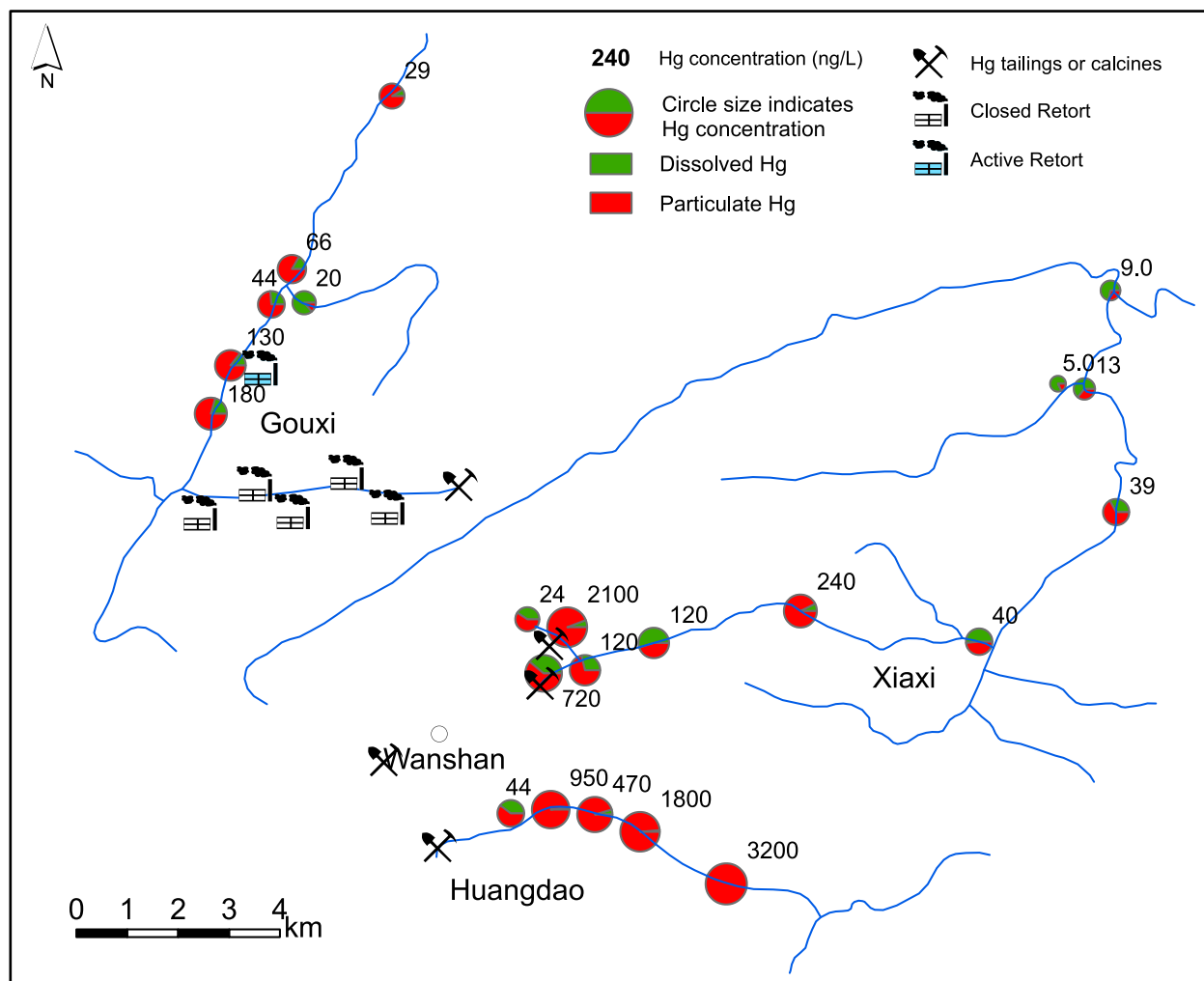


Fig. 3. Distribution and analytical results of Hg concentration of water samples.

in soil: THg, elemental Hg, exchangeable Hg, strongly-bound Hg and organically-bound Hg. The different fractions of Hg are operationally defined and each fraction may consist of several specific Hg compounds. The following procedure was used for the sequential extraction (Fig. 4):

1. A DMA-80 direct Hg analyzer was used to measure the THg concentration in all the soil and sediment samples. In the DMA-80, the sample material was run through an initial drying step at 300 °C and then decomposed at 850 °C. The resulting Hg vapor was trapped onto a Au amalgamator and then subsequently released as Hg<sup>0</sup> by heating. The released Hg vapor was measured in an atomic absorption spectrophotometer at wavelength ( $\lambda$ ) 253.65 nm.
2. Two 1 g samples were placed in 2–150 mL conical beakers in an oven for 8 h at 80 °C. Studies have shown that heating at 80 °C will effectively remove Hg<sup>0</sup> from samples, while avoiding significant decomposition of other forms of Hg (Sladek and Gustin, 2003; Feng et al., 2004). This was the major modification of the Lechler et al. (1997) technique, which was made in order to avoid excessive decomposition of Hg. The concentration of Hg in one of the heat-treated samples was then measured by DMA-80 following step 1. The difference in the Hg concentrations of the two samples is defined as elemental Hg.
3. To the second heated sample from step 2 was added 50 mL of 0.5 M MgCl<sub>2</sub>, it was mixed at room temperature for 2 h, and then let to settle for another 2 h, before 10 mL of the upper clear solution was extracted. This extract was analyzed by cold vapor atomic fluorescence spectrometry (CVAFS) for exchangeable Hg. The rest of the solution was decanted off the soil before the conical beaker containing the soil sample was placed back in the oven for 2 h at 75 °C, dried, and then weighed again.
4. To the sample from step 3 was added 50 mL of 0.5 N HCl, it was mixed at room temperature for 2 h, and the pH was then adjusted to about 3. The sample was then allowed to rest for another 2 h before removing 10 mL of the upper clear solution. This extract was analyzed by CVAFS for strongly-bound Hg. The rest of the solution was decanted before the conical beaker was put back in the oven for 2 h at 75 °C, dried, and then weighed again. Strongly-bound Hg consists of that from several acid soluble soil and sediment compounds such as carbonates, hydroxides and Hg adsorbed to Fe and Mn oxyhydroxides. The organically-bound Hg is released by the acid treatment and measured in this fraction.
5. To the sample from step 4 was added 25 mL of 0.2 N NaOH, it was mixed at room temperature for 2 h, and then 25 mL 4% (v/v) of CH<sub>3</sub>COOH (acetic acid) was added, it was mixed at room temperature for another 2 h, and then 10 mL of the upper clear solution was removed. This extract was then analyzed by CVAFS for organically-bound Hg.
6. Elemental Hg, exchangeable Hg, strongly-bound Hg and organically-bound Hg was subtracted from the THg concentration,

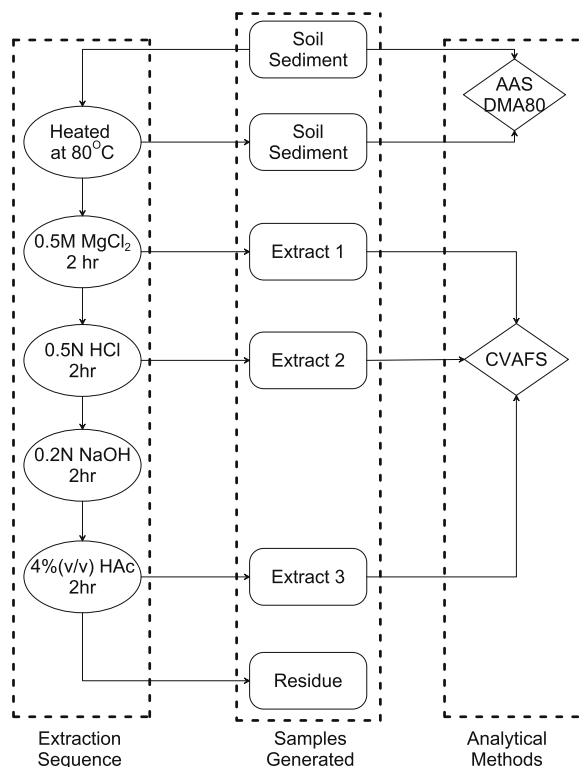


Fig. 4. Flowchart of sequential extraction.

providing a calculation for residual Hg. Residual Hg was defined as Hg bound to silica or Hg sulfide.

Concentrations of THg in water samples were determined using a PSA Merlin Hg analyzer based on atomic fluorescence spectroscopy. Dissolved Hg was also analyzed by filtering samples through a 0.45  $\mu\text{m}$  filter. The difference between THg and dissolved Hg is termed particulate Hg.

Suspended solids in water collected by filtering through 0.45  $\mu\text{m}$  filter were analyzed by scanning electron microscopy

(SEM), to semiquantatively estimate element compositions of particulates.

Particle size distribution of the sediment and soil samples was determined by a combination of sieving and coulter counter analysis. All soil and sediment samples were first sequentially sieved by using sieves with aperture size of 600  $\mu\text{m}$ , 212  $\mu\text{m}$  and 70  $\mu\text{m}$ . For particles smaller than 70  $\mu\text{m}$  a coulter counter was used to quantify the size distribution.

Water pH was determined *in situ* during sampling. Major dissolved ions were analyzed by using inductively coupled plasma-atomic emission spectrometry (ICP-AES) for cations and ion chromatography (IC) for anions. Organic C (OC) and total C (TC) were determined in solution by a wet-dry combustion method (Bisutti et al., 2004).

The relative percent difference (RPD) on analyses of Hg on the CVAFS was assessed by analyzing blind duplicates. Furthermore, each sample was analyzed three times on each run to achieve an estimate of standard deviation (RSD). Both RSD and RPD were found to be below 8%. Matrix spikes were used to calculate the percent recovery, which ranged from 92% to 110%. The limit of determination was found to be 0.1  $\text{ng L}^{-1}$ . For DMA-80 analysis the RSD and RPD were below 15%. Samples with high Hg concentration were diluted using graphite; the upper limit for this method was 600  $\text{ng Hg}$ . The lower limit of determination on the DMA-80 was 0.05  $\text{ng Hg}$ .

### 3. Results and discussion

#### 3.1. Hg in rice paddy soil

The THg concentration in the rice paddy soil samples ranged from 8.0 to 130  $\text{mg kg}^{-1}$  (Fig. 1). Sequential extraction results showed that exchangeable (11–35%), strongly-bound (18–38%) and residual Hg (25–46%) were the main Hg fractions (Fig. 1). In most soil samples, elemental Hg accounted for <10% of the THg, but was significant in some samples collected close to the source of contaminants (tailings and retorts). The fraction of organically-bound Hg was 1–9% of the THg in soil.

The concentration of THg in rice paddy soil was higher than the limit set by the Chinese national standard for farmland

Table 1  
Concentration of major ions.

Name of valley	Sample number	Conductivity ( $\mu\text{S cm}^{-1}$ )	pH	$\text{Mg}^{2+}$ ( $\text{mg L}^{-1}$ )	$\text{Ca}^{2+}$ ( $\text{mg L}^{-1}$ )	$\text{SO}_4^{2-}$ ( $\text{mg L}^{-1}$ )	$\text{NO}_3^-$ ( $\text{mg L}^{-1}$ )	$\text{Cl}^-$ ( $\text{mg L}^{-1}$ )	Alkalinity ( $\text{mmol L}^{-1}$ )	THg ( $\text{ng L}^{-1}$ )	Comments
Xiayi	070201w	310	8.3	21	43	60	4.0	2.5	2.3	24	Mountain stream, before tailings
	070202w	360	7.9	17	42	76	5.0	2.5	2.0	2100	Tailings seepage
	070203w	530	11	<DL	50	86	6.0	3.2	1.5	720	Drainage from sediment pond
	070204w	3100	5.0	110	350	2300	110	26	0.070	110	Tributary, Mn contamination observed
	070209w	2700	5.1	93	320	1900	110	24	0.090	120	Main stream
	070210w	1800	4.9	30	130	1500	130	22	0.080	230	Main stream
	070211w	1200	5.4	16	100	1000	140	20	0.080	40	Main stream
	070214w	880	6.6	52	310	460	83	11	0.35	39	Main stream
	070215w	690	7.1	3.0	19	16	2.0	3.6	0.55	4.5	Tributary, clear
	070216w	680	7.1	51	270	390	72	11	0.75	13	Main stream
070217w	660	6.6	46	220	300	54	8.0	0.95	9.3	Main stream	
Guangdao	070301w	710	7.6	95	160	280	56	7.3	2.2	3200	Main stream
	070302w	530	7.6	94	150	270	58	7.4	2.2	1800	Main stream
	070303w	540	7.4	94	150	270	60	6.9	2.1	460	Main stream
	070304w	390	7.4	58	120	160	36	6.6	2.6	44	Drainage from reservoir
	070305w	720	7.3	48	74	290	63	7.1	2.1	950	Main stream
Gouxi	070406w	280	8.2	24	39	25	5.0	4.8	3.9	29	Main stream
	070407w	230	8.3	21	31	25	3.0	4.5	3.4	20	Tributary
	070408w	270	8.1	26	43	27	5.0	5.0	4.0	66	Main stream
	070409w	260	8.2	26	44	28	5.0	4.9	4.1	44	Main stream
	070410w	270	8.2	26	42	27	4.0	5.0	4.0	130	Artisanal retorts in operation
	070411w	280	8.2	26	38	27	5.0	5.1	3.8	180	Demolished artisanal retorts

(1.0 mg kg<sup>-1</sup>). The maximum THg concentration (130 mg kg<sup>-1</sup>) in Wanshan soil (Table 2) was lower than the highest concentrations found in soil at both Almadén, Spain (2700 mg kg<sup>-1</sup>) and Idrija, Slovenia (420 mg kg<sup>-1</sup>) (Molina et al., 2006; Kocman et al., 2004). The highest concentration of Hg in Wanshan soil was found 4 km downstream from a major tailings pile at Xiaksi. In addition, the highest THg concentrations in soil samples were along all four streams found immediately downstream from major tailings or retorts. The level of Hg contamination found in this study was generally lower than that documented in a previous study (Qiu et al., 2005). During the past few years many mine tailings have been covered and artisanal retorting has been strictly regulated, which may explain the lower concentrations of THg in soil collected in this study.

Concentrations of THg in soil collected in rice paddy fields did not show a consistent spatial trend downstream from the main Hg mine tailings. Irrigation practices may explain this inconsistency; local farmers do not use water from Hg contaminated tributaries during periods of high precipitation because they have access to other water sources and they are aware of the high Hg loadings in the main stream. During dry periods, however, they are dependent on the water from the Hg contaminated streams, but Hg loading in the stream is usually lower due to less particle transport. The long history of varying cultivation (over 1 ka) and sporadic mining also add to inconsistent trends of the spatial Hg distribution in the Wanshan area.

The exchangeable Hg fraction in soil increased downstream from the large tailings in both Xiaksi and Huangdao. Conversely, in the Gouxu valley where many artisanal retorts are found, the fraction of exchangeable Hg decreased downstream and decreased even more below a few operating retorts. This difference in the exchangeable Hg fraction may be due to the sedimentation ponds below tailings at both Xiaksi and Huangdao, where coarser Hg-bearing particulates are deposited in the pond. Smaller particles may preferentially absorb Hg as a result of larger surface area and higher exchange capacity. Such smaller suspended particulates probably pass through the ponds and generate a larger fraction of exchangeable Hg downstream. In Gouxu, there are no sedimentation ponds catching the large particles from the numerous tailings along the stream banks, which lead to a more diverse flux of Hg forms to be eroded and released into the stream.

The fraction of strongly-bound Hg in the rice paddy soil samples was determined by extraction using strong acid. The main compounds in this fraction are Hg(II) bound to carbonates and crystalline Fe- and Mn oxyhydroxides. This fraction could be leached by a change in water chemistry (especially pH), and therefore, may be of great importance in terms of bioavailability.

The remains of a large number of small retorts, closed less than a year prior to sampling, were found in the Gouxu valley proximal

to the stream. During sampling, only a few of these retorts were operating. Along the stream banks close to these retorts were numerous tailings and calcine. Both THg and elemental Hg (up to 48%) was found to be especially high in this area. The generally low efficiency of these primitive artisanal retorts probably results in a release of considerable elemental Hg during operation as well as from calcines discarded in this area and such elemental Hg is then deposited along the stream banks. The fraction of elemental Hg in rice paddy soil along the other valley streams was not as high as in the Gouxu area.

The organic content of the soil samples was relatively low and results showed that the fraction of organically-bound Hg was of less importance compared to the exchangeable and strongly-bound Hg fractions. No significant correlation between the fraction of organically-bound Hg and the organic content of the soil was found (Fig. 5). The low organic matter content is likely the main reason that the organically-bound Hg fraction was small and that no clear correlation was found.

Most of the residual Hg in the soil samples is cinnabar that has entered the stream as particulates due to erosion from the calcines and mine tailings. The residual Hg fraction (cinnabar in the Wanshan soil samples) is stable in the environment and is not considered to be bioavailable.

### 3.2. Hg in stream sediment

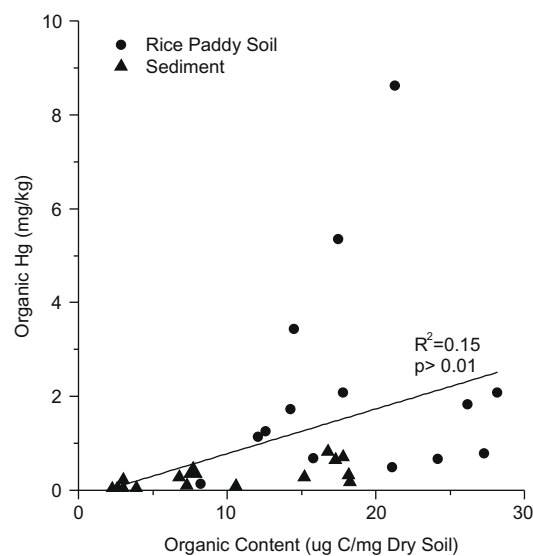
Concentrations of THg in stream sediment samples ranged from 1.1 to 480 mg kg<sup>-1</sup>, with a strong spatial correlation to the location of large tailings piles (Fig. 2). Sequential extraction results showed that exchangeable (9–43%), strongly-bound (11–67%) and residual Hg (4–82%) were the main Hg fractions in most sediment samples (Fig. 2). The sediment THg data was similar to that found for the rice paddy soil samples collected in the Wanshan area. The elemental Hg fraction in the stream sediment samples generally accounted for <6% of the THg. The fraction of organically-bound Hg was <5% of the THg in sediment, except for one sample, where 12% of the THg was bound to organic matter.

The concentration of THg found in all stream sediment was higher than the probable effect concentration (1.06 mg kg<sup>-1</sup>), the Hg concentration above which harmful effects are likely to be observed in sediment dwelling organisms (MacDonald et al., 2000). However, the maximum THg concentration (480 mg kg<sup>-1</sup>) in these

**Table 2**

Comparison of total Hg concentration in water, soil and sediment from several important Hg mining areas.

Location	THg	References
Water	ng L <sup>-1</sup>	
Idrija, Slovenia	6–320	Hines et al. (2000)
Almadén, Spain	7.6–20,000	Berzas Nevado et al. (2003)
Wanshan, Guizhou, China	4.5–3200	This study
Soil	mg kg <sup>-1</sup>	
Idrija, Slovenia	8.4–420	Kocman et al. (2004)
Almadén, Spain	0.13–2700	Molina et al. (2006)
Wanshan, Guizhou, China	8.0–130	This study
Sediment	mg kg <sup>-1</sup>	
Idrija, Slovenia	5.0–1000	Gosar et al. (1997)
Almadén, Spain	5.5–1000	Berzas Nevado et al. (2003)
Wanshan, Guizhou, China	1.1–480	This study

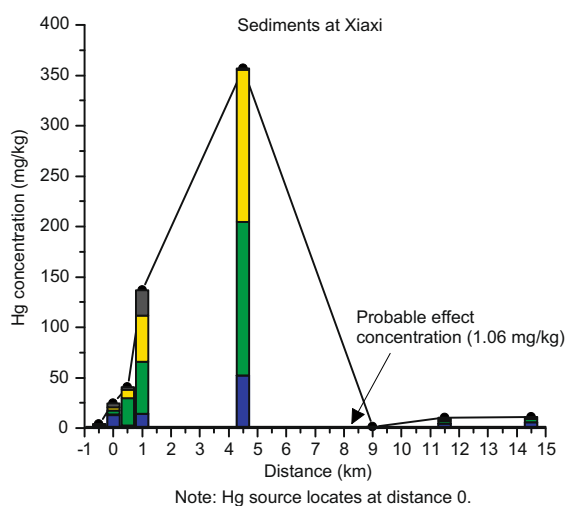
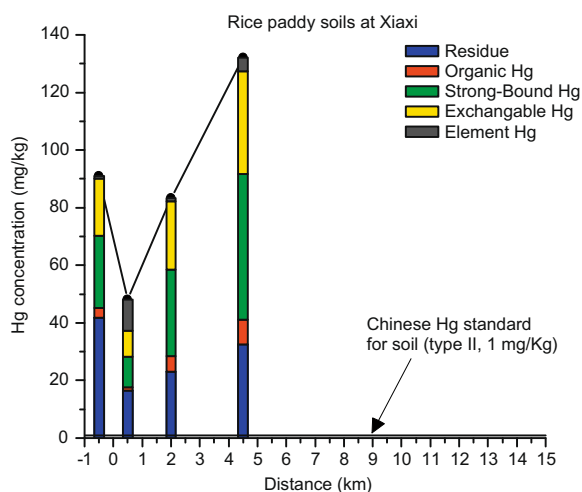


**Fig. 5.** Relationship between organic content and organically-bound Hg.

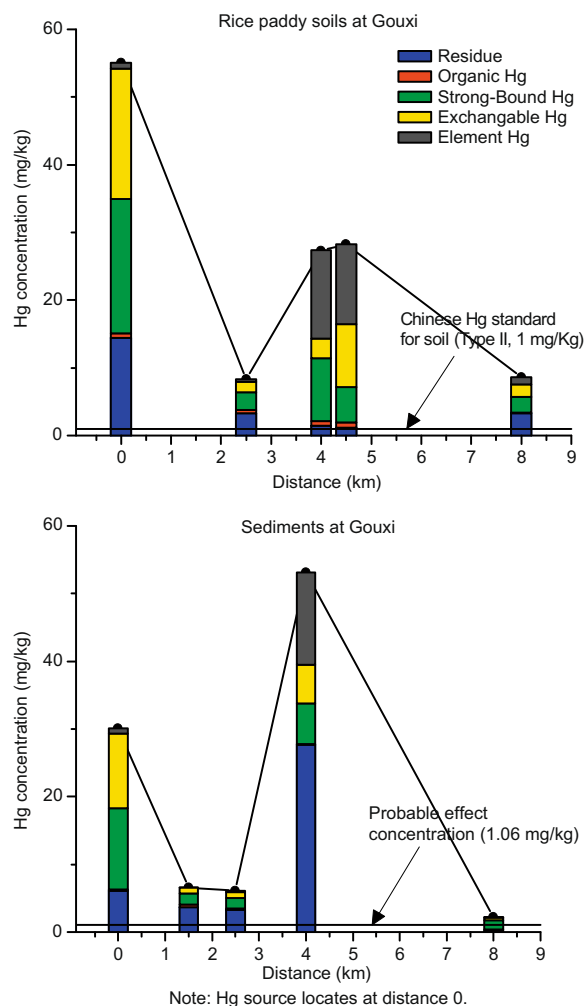
streambed sediment samples (Table 2) was lower than that reported for Hg mine studies at both Almadén, Spain ( $1000 \text{ mg kg}^{-1}$ ) and Idrija, Slovenia ( $1000 \text{ mg kg}^{-1}$ ) (Table 2, Berzas Nevado et al., 2003; Gosar et al., 1997). The concentration of THg in Wanshan area streambed sediment was generally found to be higher than that found in rice paddy soil at corresponding locations (Figs. 1 and 2), which is similar to findings at Almadén and Idrija (Table 2). The reason for the higher concentrations of THg in stream sediment samples is probably because sediment runoff is derived directly from upstream calcines and tailings (Figs. 6 and 7). Especially high concentrations of THg were found in stream sediment collected downstream from mine waste calcines and tailings at Huangdao (Fig. 2).

Similar to soil samples, the exchangeable and strongly-bound Hg fractions in stream sediment were the dominant Hg fractions. Those Hg fractions are more easily mobilized and transported downstream and, thus, potentially more bioavailability.

The elemental Hg fraction was generally found to be low, except for stream sediment collected close to retorts and tailings at Xiaxi and Gouxu, and was similar to that found for rice paddy soil (Figs. 1 and 2). The elemental Hg fraction found in stream sediment was usually lower than that in soil, which may be due to rapid stream flow transporting abundant HgS, increasing the residual Hg fraction.



**Fig. 6.** Results of sequential extraction at Xiaxi. Note: Chinese environmental quality standard for soils (GB15618-1995), type II represents farmland with soil pH higher than 7.5. Probable effect concentration ( $1.06 \text{ mg kg}^{-1}$ ) represents Hg concentration above which harmful effects are likely to be observed in sediment dwelling organisms.

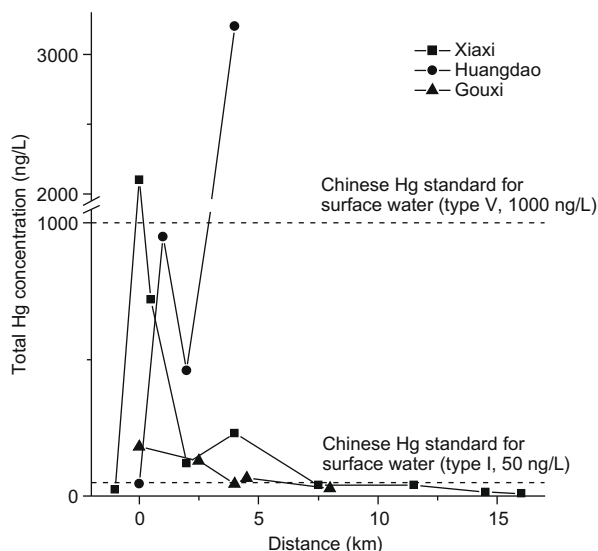


**Fig. 7.** Results of sequential extraction at Gouxu. Note: Chinese environmental quality standard for soils (GB15618-1995), type II represents farmland with soil pH higher than 7.5. Probable effect concentration ( $1.06 \text{ mg kg}^{-1}$ ) represents Hg concentration above which harmful effects are likely to be observed in sediment dwelling organisms.

The organically-bound Hg in sediment samples was lower than that found in soil samples. The reason for this is likely the slightly higher organic matter in rice paddy soil samples (Fig. 5), but there was no significant correlation between organically-bound Hg and the amount of organic matter in soil.

### 3.3. Hg in surface water

Concentrations of THg in stream water samples were as high as  $3200 \text{ ng L}^{-1}$  (Table 1) just downstream from mine tailings, although THg decreases significantly further downstream (Figs. 3 and 8). For most streams, THg concentrations were  $<50 \text{ ng L}^{-1}$  at distances of  $>10 \text{ km}$  downstream from the main Hg contamination source. The maximum THg concentration ( $3200 \text{ ng L}^{-1}$ ) in Wanshan stream water was significantly lower than that observed at Almadén ( $20,000 \text{ ng L}^{-1}$ ), but higher than that found at Idrija ( $320 \text{ ng L}^{-1}$ ) (Table 2; Berzas Nevado et al., 2003; Hines et al., 2000). The downstream decrease in Hg concentration in stream water is more complex than simple dilution from uncontaminated tributaries. Settling of particles is probably an important process in the removal of Hg. Particulate bound Hg was the dominant fraction in the water samples, accounting for between 60% and 90% of



**Fig. 8.** Hg concentration of water samples Note: Chinese environmental quality standard for surface water (GB3838-2002), type I represents natural reserve and water sources; type V represents water bodies for agricultural purposes.

**Table 3**  
Main element composition of suspended solids.

Sample number	Al (%)	Si (%)	Fe (%)	Mn (%)	Cu (%)	Ba (%)	Na (%)	K (%)	Mg (%)	Ca (%)
070201w	20	18	13	10	0.5	1.5	0.5	2.3	17	17
070202w	16	11	16	18	0.1	1.0	2.6	4.1	18	13
070203w	33	21	21	1.3	0.5	0.9	1.7	2.9	5.8	12
070205w	23	21	19	3.2	1.4	1.5	2.5	4.1	12	12
070209w	27	17	12	15	2.7	0.6	0.8	5.6	5.1	14
070210w	29	8.4	19	7.2	3.9	0.3	0.5	6.8	7.8	16
070211w	29	12	21	6.3	0.0	0.5	1.2	6.8	9.0	14
070214w	27	11	30	3.0	0.0	0.1	1.2	7.2	5.3	15
070215w	21	11	32	3.1	0.0	0.1	1.2	7.6	8.7	15
070216w	13	18	10	7.2	0.1	0.1	0.4	6.1	7.6	37

the THg concentration in most of samples (Fig. 3). Furthermore, transport of particulate Hg in water is an important mechanism that leads to increased Hg in streambed sediment and the rice paddy fields (irrigated by local stream water).

The stream water was mostly alkaline, with a pH of about 8 and  $\text{HCO}_3^-$  was the dominant anion (Table 1). Such alkaline stream water in the area is due to water interaction with sedimentary bedrock of dolomite and limestone. Leaching of calcines produced local, strongly alkaline water just downstream from discharge points. The Xiaxi stream was a special case as it originates from two smaller streams; one flowing through a large calcine pile with a high pH (11), while the other was water derived from a Mn-bearing mine tailings pile having low pH (5.0). The pH of the merged stream was acidic until joining another new tributary further downstream (Table 1).

Sulfate was found to be the second most dominant anion. Sulfate production is likely due to release of S from the tailings; during retorting, oxidization of sulfide in cinnabar ore produced  $\text{SO}_4^{2-}$ , which was subsequently deposited as gypsum in the calcines and was later leached into streams. Chloride and  $\text{NO}_3^-$  were also found in significant amounts in most water samples, though the concentration of these constituents were apparently not directly related to release from mine tailings (Table 1). Due to the presence of limestone and dolomite in the area,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  were the major cations in local streams.

Ten samples of suspended particles were collected on filters during water collection and analyzed by SEM to identify major elements. The three most abundant major elements were Si, Ca and Al (oxygen not considered), followed by Mn and Fe (Table 3). Adsorption of Hg onto particulates such as Fe- and Mn oxyhydroxides is well known (Holmstrom and Ohlander, 2001), and furthermore, Bernaus et al. (2006) found significant Fe–Hg and Mn–Hg correlations using  $\mu$ -XRF analysis. Waterborne particulate capture and transport of Hg in the Wanshan area is an important mechanism during leaching and runoff from mine waste sources.

#### 4. Conclusions

The concentration of THg in soil, sediment and water in the local environment of Wanshan were generally high due to long-term release from mining-related Hg contaminant sources. Concentrations of THg in stream sediment were much higher than that of rice paddy soil due to direct runoff from calcines and tailings.

Fractions of Hg in soil and sediment, determined by a sequential extraction method, indicated that the main fractions of Hg in contaminated soil were exchangeable-, strongly-bound- and residual Hg. The exchangeable- and strongly-bound fractions are related to the presence of more soluble Hg compounds, and therefore, pose a greater potential for Hg mobilization. These fractions are also more important in terms of bioavailability. The same fractions seem to accumulate more Hg onto fine particles, which enhanced Hg mobility during high flow seasons. The amount of elemental Hg was only significant at sites with recent or active artisanal retorts, due to locally high amounts of  $\text{Hg}_{(g)}^0$  emitted to air from the retorts, and  $\text{Hg}_{(l)}^0$  remaining in the calcines in the vicinity. Such elemental Hg is of significant concern in terms of bioavailability. The organically-bound fraction of Hg was generally low for most samples. Rice paddy soil samples contained a higher organically-bound Hg fraction than that of sediment samples.

Concentrations of THg were highly elevated (as high as 3200 ng/L) in water samples collected proximal to calcine and tailings, but THg in water decreased rapidly downstream. A large fraction of dissolved Hg was adsorbed to suspended solids in water samples, which is an important mechanism leading to the rapid decrease in THg in water downstream from Hg contaminant sources in the Wanshan area.

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