



# Selenium speciation, distribution, and transport in a river catchment affected by mercury mining and smelting in Wanshan, China



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## ABSTRACT

Selenium (Se) is an important co-existing elemental component of the mineral matrix of mercury (Hg) ore deposits. The hazards associated with Se contamination of the aquatic ecosystems in Hg mining areas; however, are often overlooked by environmental researchers due to a preoccupation with Hg. Selenium may also pose a long-term risk to the local ecosystem, and further complicate the situation as Se may also play an important antagonistic role against Hg. Furthermore, most studies on Se pollution have focused only on total Se, whereas the toxicity, bioavailability, and bioaccumulation of Se in aquatic ecosystems is primarily determined by its site-specific individual species. In this study, the concentrations of total Se, inorganic Se (tetravalent and hexavalent), and organic Se were determined in water samples collected from 41 typical sites selected in rivers, tributaries, and springs in Wanshan, China, where Hg and Se co-occur due to historic Hg mining and retorting activities. Se concentrations were observed to decrease with distance from mine-waste calcines, which indicated that mine-waste calcines may be significant sources of the elevated Se in the rivers, especially in downstream areas within 8 km from the mine-waste calcines. The concentration of total aqueous Se throughout the study area was highly variable ( $3.8 \pm 6.0 \mu\text{g L}^{-1}$ ) and on average was one order of magnitude greater than that in natural river systems worldwide ( $0.1\text{--}0.3 \mu\text{g L}^{-1}$ ). The majority of the Se was hexavalent ( $3.1 \pm 4.9 \mu\text{g L}^{-1}$ ; 65%), followed by tetravalent ( $0.53 \pm 0.86 \mu\text{g L}^{-1}$ ; 15%) and organic forms ( $0.85 \pm 1.5 \mu\text{g L}^{-1}$ ; 20%), possibly due to the generally alkaline conditions. Se concentrations in some sampling sites exceeded certain recommended limit of values. However, the existing criteria for Se in aquatic system are mainly based on total Se and the recommended limit of values in different countries or organizations are inconsistent with one another. Therefore, the need to consider Se speciation rather than only total Se is highlighted for future studies.

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## 1. Introduction

Selenium (Se) is a ubiquitous trace element that was first discovered by Berzelius in 1817. It has recently been proposed by Hu et al. (2009) to be an emerging global metalloid contaminant with potential ecological risk second only to mercury (Hg). In fact, among all trace elements, Se may be one of the most interesting elements due to its unique properties. The occurrence of a well-known cardiomyopathy endemic to China (Keshan disease) has been proposed to be associated with Se deficiency (Tan et al., 2002). Se has the narrowest biological tolerance range of all of the elements, and the toxic levels are only 5–10 times above the bio-essential levels (Fordyce, 2013). With its dual role as an essential micronutrient at physiologically appropriate levels and a toxic substance at higher levels, Se has attracted a great deal of attention from both the scientific community and the public in recent decades (Fordyce, 2013; Rayman, 2012; Zhang et al., 2012).

Se occurs in the supergene environment in the following four oxidation states: –II (selenide), 0 (elemental selenium), +IV (selenite), +VI (selenate), as well as in organic compounds (Se(org)) (Patterson et al., 2010). Every Se species has different characteristics of availability, bioaccumulation, mobility, toxicity, function in nutrition, and other biological/geochemical qualities (Fordyce, 2013; Rayman, 2012; Tan et al., 2002). Therefore, precise knowledge of the chemical speciation of Se in the environment and in food products is essential to a better understanding of the fate and behavior of this element.

Se has been identified as a major contaminant of concern in aquatic ecosystems since the 1980s (May et al., 2008; Patterson et al., 2010). In general, water is not a major exposure pathway for animals and humans due to the extremely low concentrations of Se found in aquatic systems (usually  $<0.2 \mu\text{g L}^{-1}$ ) (Fordyce, 2013). However, in some cases, the bioaccumulation of Se can occur through the food web and can reach levels that are toxic to fish and wildlife (Lemly, 2004). In addition, aquatic life-forms are sensitive to Se intoxication because the soluble forms of selenate and selenite, which have a high bioavailability, are usually the

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dominant species in surface waters (Fordyce, 2013; Patterson et al., 2010; Qin et al., 2013). The impacts of Se contamination in aquatic systems may be rapid and severe and may pose the most serious long-term risks to aquatic habitats and fishery resources and lead to irreversible ecosystem disruption, e.g., teratogenic deformities and the reproductive failure of entire communities of fish (Lemly, 2002, 2007). In addition, previous studies indicate that there may be antagonisms between selenium and mercury which may affect their fate and behavior not only in aquatic ecosystems (Belzile et al., 2009, 2006) but also in terrestrial ecosystems (Zhang et al., 2012).

The Wanshan mercury-mining area, known as the “mercury capital” of China, was the largest mercury industrial base in China, with the greatest reserves and production of Hg in Asia. The mercury mining history in this area dates back more than 2000 years to the Qin Dynasty (221–206 BC), the first imperial dynasty of China, although Hg mining was most intensive during the last half of the 20th century. Large-scale Hg production activities in this area completely ceased in 2001 due to the depletion of mercury resources. The historic large-scale mining and retorting activities over more than 2000 years, especially after the 1950s have produced approximately 22,000 tons of Hg, 6000 tons of cinnabar, and large quantities of mine wastes in Wanshan (Zhang et al., 2012).

Se in the environments can originate from multiple sources, most of which are anthropogenic, e.g., coal mining and combustion, gold/silver/nickel mining; metal smelting (especially pyrometallurgical copper/nickel/zinc production), municipal landfills, oil transport/refining/utilization, and agricultural irrigation, etc. (Lemly, 2004). Hg cinnabar and ores usually contain a considerable amount of Se. In the Wanshan area, the Se content was reported to range from 0.02 to 0.87 wt.% (by weight; w/w) in common cinnabar and the maximum content retained 2.7 wt% in metacinnabar, as the S in the cinnabar ores can be replaced by Se to form an isomorphous series of HgS–HgSe (Zhang et al., 2012). Mining and retorting activities of cinnabar ores can result in the release of large quantities of Se into the surrounding environment. Furthermore, during the retorting processes used to mobilize and separate the desired Hg, Se is readily volatilized and can be emitted into the air (Lemly, 2004). This Se cools and can adhere to atmospheric dust particles, and subsequently accumulated in terrestrial and aquatic systems by either dry or wet deposition (Lemly, 2004). In previous reports, elevated concentrations of both Hg and Se were observed in local soils and foods (Horvat et al., 2003; Zhang et al., 2010a,b, 2012). For instance, Se and Hg concentrations were reported to be up to 36.6 mg kg<sup>-1</sup> and 496 mg kg<sup>-1</sup>, respectively, in local paddy soils (Zhang et al., 2010b, 2012), with corresponding Se and Hg concentration in local rice grain reached 1.06 mg kg<sup>-1</sup> and 0.57 mg kg<sup>-1</sup> (Horvat et al., 2003).

The river waters in Wanshan that have been impacted by mining and retorting activities are used by the local farmers as the main sources of irrigation for a large quantity of riparian rice paddies, which may cause contamination by Se in addition to mercury in the agriculture system. However, previous studies of rivers in Wanshan have focused only on the ecosystem impacts of Hg contamination (Li et al., 2008; Qiu et al., 2005; Zhang et al., 2010c,d). Until now, the Se status in water (e.g., concentration, speciation and distribution, etc.) from the local rivers has been unclear.

The present study was therefore designed to determine the Se concentration and speciation in the four main rivers and corresponding tributaries downstream of the mine-waste calcines in Wanshan to evaluate the fate and behavior of Se in the local aquatic system affected by historic Hg mining and retorting activities. To the best of our knowledge, this study is the first of its kind in the region.

## 2. Material and methods

### 2.1. Study area

The study area is located in a steep mountain-cliffs zone, which is a typical mountainous and Karst terrain, with elevations ranging from 205 to 1150 m above sea level. This region is a transition from the eastern Yunnan–Guizhou Plateau to the western hill zone of Hunan (Fig. 1). The region has a sub-tropical humid climate characterized by abundant precipitation and a mild temperature. Annual average rainfall is between 1200 and 1400 mm. Annual mean temperature is 17 °C, and the yearly frost-free period is approximately 270 days.

The four main rivers in the territory of the study area include the southwest Gaolouping, southeast Huangdao, northwest Gouxu, and northeastern Aozhai-Xiaxi (or Dashuixi) (Fig. 1). All four streams are mountain rain-fed streams. The annual runoff in the study area is 222 million m<sup>3</sup>. The upstream area of the study area is a typical Karst landscape; hence, the outcrops upstream of the basin are carbonate rocks, including limestone, dolomite, and dolomitic limestone. The downstream area of the study area has a non-Karst landscape with bedrock of sandstone and shale, and developed tributaries.

### 2.2. Sample collection

As shown in Fig. 1, the sampling region was operationally divided into “contaminated area” with distance <8 km from the pollution sources, “less-impacted areas” with distance ≥ 8 km from the pollution source and “control sites” with farthest eight locations from pollution sources which were not included in “less-impacted area”, respectively, to scrutinize the regional difference. This division was identified based on the fact that the Hg contamination in the river waters only occurred within 8 km from mine-waste calcines in our previous studies (Zhang et al., 2010b,c,d).

Water samples were collected from 41 selected sites of mountain streams, tributaries, and springs in the four main rivers in the study area, i.e., Gouxu ( $n = 17$ ), Dashuixi ( $n = 11$ ), Gaolouping ( $n = 8$ ), and Huangdao ( $n = 5$ ) (Fig. 1). At each sampling site, a composite sample was composed of three-five subsamples. The sampling campaign was conducted in a normal flow period (August 2007). Surface water samples were collected from 10 to 15 cm below the surface at all the sampling sites. The water samples were filtered *in situ* with a 0.45 μm polyvinylidene fluoride filter (Millipore) because dissolved Se speciation is important in assessing the adverse biological effects of Se due to the high bioavailability of specific Se species (Cutter and Cutter, 2004). All the Teflon tubing and filter holders were pre-cleaned in acid. During sampling, the filtration equipment and sample bottles were rinsed three times with sample water prior to filling. The sampling started downstream and continued up-stream in order to minimize the risk of cross contamination. The filtered water samples were not acidified. Sample bottles were tightly capped and placed into double plastic bags and stored in clean coolers (4 °C) until processing and analysis. Measurements were conducted within two weeks after sampling to avoid Se loss and speciation transformation. One filtered water sample per site was also analyzed for total organic carbon (DOC) and sulfate.

### 2.3. Analytical methods

For Se(tot) concentration analysis, 3 mL of the filtered water sample was digested in a 15-mL PFA beaker using a mixture of 1 mL concentrated HNO<sub>3</sub> (16 mol L<sup>-1</sup>) and 2 mL H<sub>2</sub>O<sub>2</sub> (30%) (Qin et al., 2013). The volume of the solution was evaporated on a hot

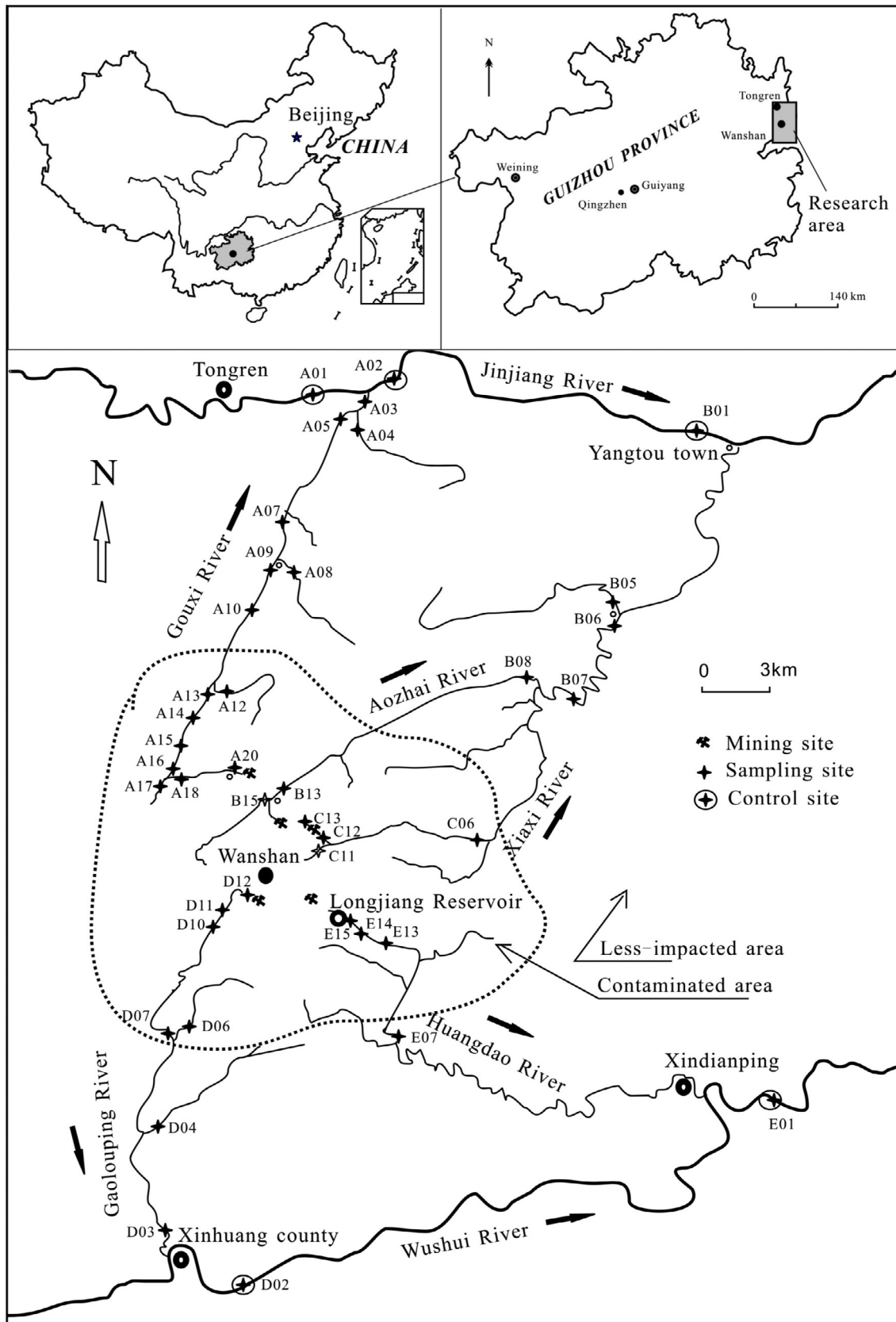


Fig. 1. Map of sampling locations in rivers and tributaries around Wanshan Hg mine and retorting units.

plate to approximately 0.5 mL. At this point, 1 mL H<sub>2</sub>O<sub>2</sub> (30%) and 1 mL HNO<sub>3</sub> were added until the volume of the solution was

evaporated to near dryness. The Se was then transformed into Se(IV) by adding 3 mL of 5 mol/L HCl followed by incubation in a

water bath at 90 °C for 60 min (Zhu et al., 2008). The solution was diluted and Se concentration was determined by hydride generation-atomic fluorescence spectrometry (HG-AFS) (Zhang et al., 2012).

The methods for Se speciation in water samples were partly modified from previous reports (Kulp and Pratt, 2004; Qin et al., 2013). For Se(IV) concentration analysis, 3 mL of the filtered water sample was directly measured by HG-AFS after dilution with 6% HCl (0.72 mol L<sup>-1</sup>). The Se(VI) content was not directly determined, but was calculated as the difference between the content of Se(IV) and the sum of Se(IV) and Se(VI). For the sum of Se(IV) and Se(VI) analysis, 3 mL of the filtered water sample was added to 1.5 mL concentrated HNO<sub>3</sub> (16 mol L<sup>-1</sup>), incubated in a water bath at 90 °C for 90 min, diluted with ultra-pure water to 25 mL (equal to 0.72 mol L<sup>-1</sup> HCl), and then measured by HG-AFS. Similar to Se(VI), the Se(org) content was obtained by subtracting the sum of Se(IV) and Se(VI) from the Se(tot) content.

Hg(tot) was determined with a dual-stage Au amalgamation method and Cold Vapor Atomic Fluorescence Spectrophotometer (CVAFS) detection following BrCl oxidation and SnCl<sub>2</sub> reduction (USEPA, 2002). Detailed procedures for Hg(tot) analysis were reported in our previous study (Zhang et al., 2010d). The pH was measured *in situ* using a pH electrode. Dissolved organic carbon (DOC) was measured with a 1020A TOC Analyzer (OI, USA). Sulfate ions were determined by atomic absorption spectrometry (AAS) and ion chromatography.

All reagents were subdistilled to minimize the blank level. All samples in our data set were measured at least twice. Quality assurance and quality control of Se analysis were conducted using duplicates, method blanks, and matrix spikes. The limit of detection (LOD) of Se concentration in water sample is 0.02 µg L<sup>-1</sup>. The relative standard deviation was less than 8%, and the relative percentage difference of sample duplicates was <6%. The recoveries on matrix spikes of Se in the water samples were in the range of 93–105%.

Data are described in terms of the arithmetic mean ± standard deviation (SD). Correlations between covariant sets of data were subjected to regression analysis. Correlation coefficients (*r*) and significance probabilities (*p*) were computed for linear regression. Significant differences were accepted at *p* < 0.05. Statistical analyses were performed using SPSS 13.

## 3. Results and discussion

### 3.1. Se(tot)

#### 3.1.1. The regional distribution in surface water

The water samples from the Wanshan Hg mining area contained highly variable Se(tot) concentrations ranging from 1.01 to 30.62 µg L<sup>-1</sup> (average: 3.82 µg L<sup>-1</sup>) (Table 1; Figs. 2 and 3). The Se(tot) concentrations in the “contaminated area” (average: 5.95 µg L<sup>-1</sup>) were significantly (ANOVA, *p* < 0.05) higher than those in “less-impacted area” (average: 1.79 µg L<sup>-1</sup>). Of the four rivers, the average Se(tot) concentration in Huangdao (9.53 µg L<sup>-1</sup>) was higher than in the other rivers (Dashuixi: 5.58 µg L<sup>-1</sup>; Gaolouping: 2.54 µg L<sup>-1</sup>; Gouxu: 1.60 µg L<sup>-1</sup>), which may be due to the longer history of large scale of mining and retorting in Huangdao than in the other rivers (Zhang et al., 2010c).

#### 3.1.2. Potential sources

The sample sites with elevated Se(tot) concentrations were all located near the mine-waste calcines, i.e., sites C11, E13, and E14 (Fig. 1). These sites have concentrations of Se(tot) as high as 16–31 µg L<sup>-1</sup> (Fig. 2) and are located at approximately 100–500 m downstream of the calcines. The Se(tot) concentrations rapidly decreased with distance from the calcines to below 3 µg L<sup>-1</sup> at sites

approximately 8 km downstream of the calcines and were relatively stable within the range of 1.1–1.8 µg L<sup>-1</sup> in the downstream area (more than 8 km from the calcines). The correlation between Se(tot) concentrations in water and the distance from the mine-waste calcines was observed to be weak but significant (*r* = -0.37, *p* < 0.05; Fig. 4). These results indicate that in addition to atmospheric deposition and surface runoff (Conde and Alaejos, 1997), the mine-waste heaps containing calcines, may be significant sources of Se in the rivers through leaching and erosion processes (Lemly, 2007).

In addition to the leaching of Se-containing mine-waste upstream, several other sources, including groundwater and surface runoff, leaching and erosion of local high Se-containing bedrock and soils, and atmospheric deposition (Fordyce, 2013; Lemly, 2007), may significantly contribute to the Se content in downstream rivers. Among these sources, groundwater input may be the primary source of Se in the rivers in the downstream area.

Compared with surface water, groundwater usually contains higher Se content due to greater contact times for rock-water interactions (Fordyce, 2013); for example, in the Enshi area of China, Se in well water was observed to reach 8.4–72 mg L<sup>-1</sup> (Wang et al., 1991), which was far beyond the surface water Se content (0.04–0.3 mg L<sup>-1</sup>) (Fordyce et al., 2000). This condition may also be true in downstream areas in Wanshan, as local mineral tiemannite (HgSe) and cinnabar (HgS) are both important Se carriers, as discussed above. Elevated Se levels were observed from two wells representing underground water compared with Se levels in surface water (discussed later in Section 3.3.2: Spring water).

#### 3.1.3. The local background concentrations of Se(tot) in surface water

There was no significant difference in Se(tot) content in downstream sites (exceeding 8 km) caused by dilution effect areas (Fig. 4); however, several sites farther downstream (e.g., A5, B6, and B7; Fig. 1), i.e., more than 20 km away from the mine-waste calcines, still showed Se(tot) concentrations over 2 µg L<sup>-1</sup>. In general, net flows downstream of the main rivers in Wanshan receive inputs from a large number of riparian tributaries (Fig. 1). The Se(tot) from tributaries (1.01–1.71 µg L<sup>-1</sup>) was quite similar to that in the downstream main areas more than 8 km from mine-waste calcines (1.10–1.83 µg L<sup>-1</sup>). These values may represent the local background Se(tot) content in surface water in Wanshan.

#### 3.1.4. Comparison with other regions

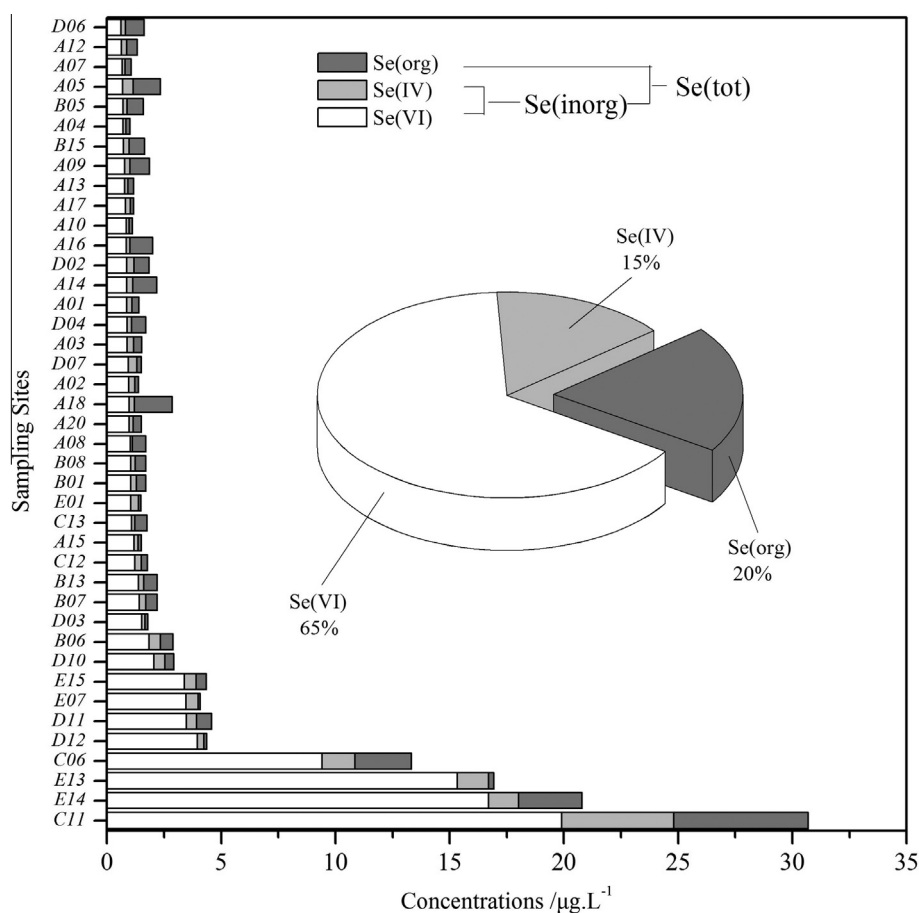
Se concentrations in natural, unpolluted rivers are primarily influenced by the geology of the region and can vary greatly. A comparison of Se concentrations in river water in national and international regions is summarized in Table 2. Although the monitoring of contaminants in water bodies reflects only information under the specific hydrological conditions during the sampling period (Horvat et al., 2003), such a comparison is still of great significance, at least to some extent, for reflecting the regional distribution and difference. The dissolved total Se content for global natural waters rarely exceeds the standard limit of 10 µg L<sup>-1</sup> set by the United States Environmental Protection Agency (USEPA) (Fordyce, 2013) and is generally less than 0.8 µg L<sup>-1</sup>. The concentrations of majority rivers range 0.1–0.3 µg L<sup>-1</sup> (Bujdos et al., 2005), with an average of 0.2 µg L<sup>-1</sup> (Wang and Gao, 2001). This level was similar to that in Chinese rivers (0.01–0.80 µg L<sup>-1</sup>), which exhibit an average concentration of 0.25 µg L<sup>-1</sup> (Wang et al., 1991). Thus, the dissolved Se(tot) concentration in the rivers in the study area (3.82 µg L<sup>-1</sup>) were approximately one order of magnitude higher than those in national or global natural waters.

Comparing the Se concentrations in river water in Wanshan with published levels from elsewhere (Table 2), the Se concentrations in the river water in the Wanshan area is far beyond that of natural river systems, and the highest concentrations (31 µg L<sup>-1</sup>)

**Table 1**

Concentrations of total Se, component Se species, and their ratios to total Se, total Hg, dissolved organic carbon,  $\text{SO}_4^{2-}$ , and pH in four main streams around the Wanshan Hg-mining area.

River	Se(tot) $\mu\text{g L}^{-1}$	Se(inorg) $\mu\text{g L}^{-1}$	Se(IV) $\mu\text{g L}^{-1}$	Se(VI) $\mu\text{g L}^{-1}$	Se(org) $\mu\text{g L}^{-1}$	Se(IV)/Se(VI) %	Se(IV)/Se(tot) %	Se(VI)/Se(tot) %	Se(org)/Se(tot) %	Hg(tot) $\text{ng L}^{-1}$	DOC $\text{mg L}^{-1}$	Sulfate $\text{mg L}^{-1}$	pH
<i>Gouxu, n = 17</i>													
Mean	1.60	1.06	0.24	0.85	0.63	0.30	15.91	53.19	33.40	15.59	1.09	20.53	8.25
STD	0.51	0.15	0.09	0.12	0.48	0.15	9.55	12.44	15.95	17.55	0.57	6.09	0.48
Min	1.01	0.79	0.08	0.64	0.14	0.08	4.60	33.90	11.10	1.00	0.60	11.45	7.10
Max	2.85	1.36	0.46	1.03	1.65	0.67	40.26	69.90	58.00	64.50	3.00	35.91	8.70
<i>Dashuixi, n = 11</i>													
Mean	5.58	4.41	0.92	4.23	1.46	0.22	13.94	64.57	27.02	41.57	1.04	160.16	8.00
STD	8.99	7.35	1.55	6.48	2.53	0.07	3.35	10.11	8.89	108.50	0.25	331.93	0.54
Min	1.59	0.89	0.15	0.73	0.28	0.14	8.40	44.20	15.90	1.30	0.69	9.55	6.80
Max	30.62	24.82	4.92	19.90	4.80	0.34	17.50	82.51	44.05	368.00	1.58	1102.12	8.70
<i>Gaolouping, n = 8</i>													
Mean	2.54	2.10	0.30	1.79	0.45	0.23	13.63	67.99	21.51	12.93	1.92	40.19	8.03
STD	1.27	1.33	0.12	1.28	0.27	0.13	5.75	21.61	16.66	12.32	0.40	25.87	0.57
Min	1.50	0.82	0.15	0.61	0.13	0.07	6.40	37.70	3.17	2.70	1.16	18.59	7.10
Max	4.58	4.23	0.48	3.96	0.81	0.39	24.70	93.60	49.40	41.80	2.44	82.98	8.50
<i>Huangdao, n = 5</i>													
Mean	9.53	8.80	0.82	7.99	0.73	0.16	13.01	85.03	6.64	17.68	1.12	148.19	8.12
STD	8.71	7.89	0.49	7.41	1.15	0.10	6.30	8.62	5.08	12.66	0.26	145.22	0.11
Min	1.48	1.39	0.34	1.05	0.09	0.08	7.31	70.70	1.40	4.30	0.84	21.63	8.00
Max	20.80	18.02	1.37	16.70	2.78	0.32	23.10	92.69	13.35	33.70	1.49	330.85	8.30
<i>Whole area, n = 41</i>													
Mean	3.82	3.10	0.53	3.08	0.85	0.24	14.38	64.70	25.32	22.30	1.24	80.31	8.12
STD	5.96	5.15	0.86	4.90	1.48	0.12	6.69	17.27	15.48	57.01	0.54	188.55	0.48
Min	1.01	0.79	0.08	0.61	0.09	0.07	4.60	33.90	1.40	1.00	0.60	9.55	6.80
Max	30.62	24.82	4.92	19.90	4.80	0.67	40.26	93.60	58.00	368.00	3.00	1102.12	8.70



**Fig. 2.** Concentrations of different species and their corresponding ratios to Se(tot) in water samples from selected sites in Wanshan. The pie chart illustrates the average distribution of species for all samples.

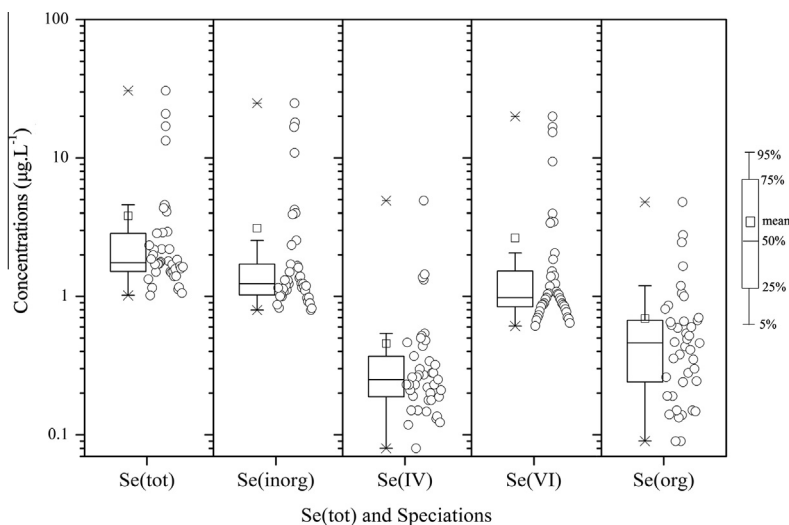


Fig. 3. Statistical chart of concentrations of Se(tot) and component species in water samples collected from Wanshan.

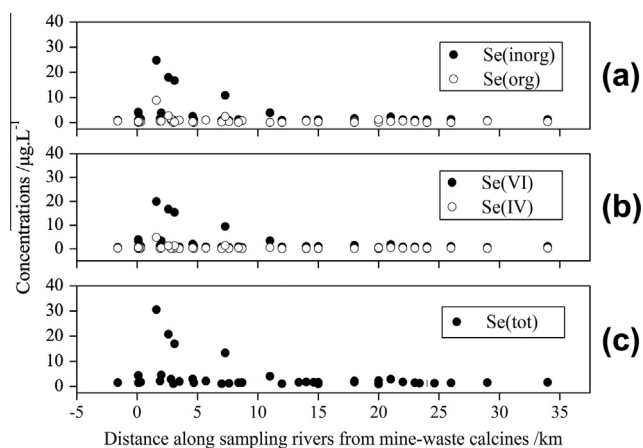


Fig. 4. Distribution of Se(tot) and Se species in water samples along sampling rivers from mine-waste calcines (Negative distances are locations upstream of the pollution sources).

at sites near mine-waste calcines approached the levels in surface water in the world-famous Se-rich Enshi region in China (Fordyce

et al., 2000). This result indicates that the mining and retorting activities of Hg ores have resulted in the release of a large quantity of not only Hg (Zhang et al., 2010c,d), but also Se in the rivers, especially downstream close to the mine-waste calcines.

### 3.1.5. Relationship with sulfate, pH, and DOC

It is well-known that selenium and sulfur have similar chemical behavior (Wang et al., 1994). On the periodic table, Se belongs to the same group of elements as sulfur. Consequently, its biogeochemical properties are analogous to those of sulfur, one of the most common elements in Earth's crust. In the present study, a significant positive correlation ( $r^2 = 0.88$ ,  $p < 0.01$ ) between sulfate ion content and Se(tot) concentrations in river water samples was observed (Fig. 5a). Similar to selenium, the concentrations of sulfate in rivers in this area were also highly elevated just downstream of the mine waste sites (Zhang et al., 2010c,d). The correlation between these two elements might be, therefore, just a co-variation.

Generally, as the solubility of Se in an alkaline environment is higher than that in an acidic environment, water bodies with high pH values contain higher amounts of dissolved Se compared with low-pH water bodies. For instance, in an Se- and iron-enriched area in Colorado, U.S., surface water with a pH value below 7 generally contained Se content lower than  $1 \mu\text{g L}^{-1}$ , but when the pH

Table 2  
Se concentrations ( $\mu\text{g L}^{-1}$ ) in river waters in Wanshan in the present study compared with other domestic and worldwide regions.

Region	Se(tot)	Se(IV)	Se(VI)	Se(org)	Reference
World freshwater	0.02				Fordyce (2013)
Amazon River, Brazil	0.21				Fordyce (2013)
Michigan River, US	0.8–10				Robberecht et al. (1982)
Mississippi River, US	0.14				Fordyce (2013)
Seleniferous Regions, US	50–300				Fordyce (2013)
Scheldt River, Belgium	0.23–1.78	0.13–1.45	<0.05–0.3		Robberecht et al. (1982)
Rhone River, France	0.15–10				Robberecht et al. (1982)
Rhine River, Germany	0.14–5	0.065	0.1		Robberecht et al. (1982)
Ticino River, Italy	29.1–32.7	7.5	3.2–5.8	7.8–9.2	Robberecht et al. (1982)
Asahi River, Japan	0.016–2	0.002–0.017	0.005–2		Robberecht et al. (1982)
Low Se, Keshan disease, villages, Enshi, China	0.168 (0.1–0.44)				Fordyce et al. (2000)
High Se, No toxicity, villages, Enshi, China	7.7 (0.46–44)				Fordyce et al. (2000)
High Se, Toxic, villages, Enshi, China	32.6 (7.3–275)				Fordyce et al. (2000)
Kaschin–Beck disease area, Tebitan area, China	0.10 (0.03–0.24)				Zhang et al. (2011)
Yangzi River, China	0.28 (0.17–0.44)				Yao et al. (2007)
Zhoukoudian Se-deficient area, China, drinking water	0.017 ± 0.002				Li et al. (2007)
Zhangjiakou district, Keshan disease belt of China	0.17 (0.005–1.15)				Johnson et al. (2000)
Cixian area, Hebei, China, drinking water	0.72 (0.1–2.43)				Appleton et al. (2006)
Wanshan Hg mining area, Guizhou, China	3.82 (1.01–30.6)	0.53 (0.08–4.92)	3.08 (0.61–19.9)	0.85 (0.09–4.80)	This study

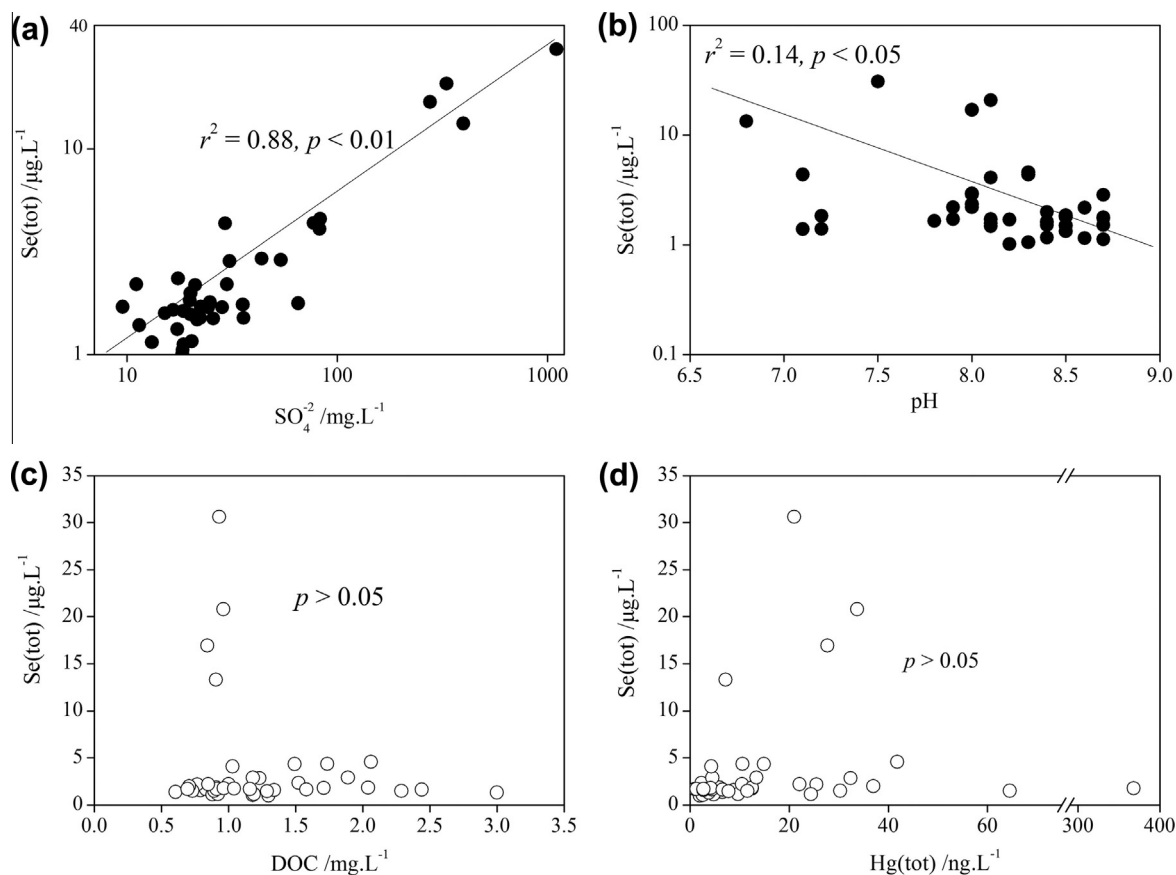


Fig. 5. Relationship between Se(tot) and sulfate, pH, DOC, and Hg in filtered (0.45  $\mu\text{m}$ ) water samples collected from rivers in Wanshan.

increased to 7.8–8.2, the Se content increased and exceeded  $1 \mu\text{g L}^{-1}$ , rising as high as  $400 \mu\text{g L}^{-1}$  because the selenite may be oxidized into the more soluble selenate in a high-pH environment with high loading of Se (Lakin, 1973). In the Wanshan area, the pH of the surface water is generally greater than 7, with an average of 8.1, meaning that the alkaline environment is likely to result in the enhancement of the dissolved Se content in the water to a certain extent. This concept was supported by the negative correlation observed between Se concentration and pH values ( $r^2 = 0.14$ ,  $p < 0.05$ ; Fig. 5b).

No significant correlation was observed between the Se(tot) concentrations and DOC concentrations in the river waters ( $p > 0.05$ ; Fig. 5c), suggesting that the Se in the dissolved phase in the rivers may not be influenced by the DOC.

### 3.1.6. Relationship with Hg

Although mine-waste calcines were also observed to be sources of Se in the downstream areas, similar to Hg (Zhang et al., 2010c,d), the correlation between Se and Hg in the dissolved phase in river water was not significant ( $p > 0.05$ ; Fig. 5d). This result was likely affected by the enhanced Se content in the downstream area contributed by the Se-enriched groundwater, as discussed above. The Se content in river water affected by mining and retorting activities in Wanshan was controlled by multiple dynamic factors, e.g., combined point-source pollution (primarily mine-waste calcines) and non-point-source pollution (surface run-off and groundwater, etc.); therefore, the precipitation of possible interactions between Hg and Se, if present, may be hidden behind the detectable phenomena.

In present study, based only on the Hg and Se in the dissolved phase of river waters, we cannot draw any conclusion regarding

the potential interactions of Se and Hg in river waters. However, it appears that the elevated selenate and selenite (80%) are controlled by the alkaline conditions and the formation of a considerable amount of Hg–Se insoluble complexes is likely to be insignificant, if it exists. Therefore, a negligible influence from the formation of inert Hg–Se complexes on the transport of Se or Hg in the river systems may be expected.

Elemental Se and selenide are the most typical stable forms under flooded soil conditions (Elrashidi et al., 1987). Under highly reduced paddy soil conditions with prolonged flooding, selenate is expected to be reduced to selenite, elemental Se or even selenide-metal complexes (Zhang et al., 2012). Then, in the presence of Hg in almost any form, HgSe formation (according to the equations  $\text{Hg}^0 + \text{Se}^0 \rightarrow \text{Hg} - \text{Se}$  and/or  $\text{Hg}^{2+} + \text{Se}^{2-} \rightarrow \text{Hg} - \text{Se}$ ) is likely as the exceptionally high binding affinity between Se and Hg ( $10^{45}$ ) that is one-million times greater than the binding affinity between sulfur and Hg ( $10^{39}$ ) for the production of mercury sulfide (Hg–S) (Björnberg et al., 1988; Dyrssen and Wedborg, 1991).

According to our recent study on the local paddy soil and rice plants (Zhang et al., 2012), Se may exert a very important role in limiting the bioaccumulation of Hg in the rice–soil system, which is likely related to the formation of an inert insoluble Hg–Se complex in the soil or on the root surface. The independent mineral form of mercury selenide (HgSe) has been discovered in the Wanshan's Hg mining area as early as forty years ago (Zhang et al., 2012). Recently, studies using X-ray absorption near-edge structure (XANES) analysis of marine mammals and seabirds by Arai et al. (2004) have unambiguously confirmed the existence of inert, insoluble Hg–Se complexes even *in vivo*. It is therefore reasonable to speculate that the same condition may occur in the river sediments, contributing to the stabilization of Hg and Se. Although

these investigations were not included in present study, they deserve attention in future studies.

### 3.2. Se speciation

#### 3.2.1. Se(VI)

The concentrations of Se(VI) in river waters in the Wanshan area varied from 0.61 to 20  $\mu\text{g L}^{-1}$ , with an average of 2.65  $\mu\text{g L}^{-1}$  (Fig. 3; Table 1). The average concentrations of Se(VI) in the “contaminated-” and “less-impacted” areas were 3.97 and 1.12  $\mu\text{g L}^{-1}$ , respectively, but the difference was not significant ( $p > 0.05$ , ANOVA). The relative Se(VI) concentrations in river waters among the four rivers was similar to that of Se(tot), i.e., Huangdao 7.99 > Dashuixi 4.23 > Gaolouping 1.79 > Gouxu 0.85 (all units  $\mu\text{g L}^{-1}$ ) (Table 1). The Se(VI) concentrations (0.61–20  $\mu\text{g L}^{-1}$ ) in river in Wanshan area in the present study was far greater than that in the Scheldt River, Belgium (<0.05–0.03  $\mu\text{g L}^{-1}$ ); Rhine River, Germany (average 0.1  $\mu\text{g L}^{-1}$ ); and Asahi River, Japan (0.005–0.2  $\mu\text{g L}^{-1}$ ), but relatively lower than that in the Ticino River, Italy (3.2–5.8  $\mu\text{g L}^{-1}$ ) (Table 2).

Se(VI) was the primary Se species in Wanshan (65%), and there was no significant difference in the ratios of (Se(VI)/Se(tot)) between the “contaminated-” and “less-impacted” areas (average of 64% and 66%, respectively); therefore, Se(VI) was positively and significantly correlated with Se(tot) ( $r^2 = 0.98$ ,  $p < 0.01$ ; Figs. 2 and 4). In the surface water of the southern region of Manitoba, Canada, where the alkaline water environment is similar to that in the Wanshan area, the ratio of Se(VI) to Se(tot) reaches 85.5% (Hu et al., 2009). Although there are some exceptions, under alkaline and oxidized conditions, Se(VI) has been primarily found to be the major fraction of Se in river waters and groundwater in areas with either high or low Se(tot) concentrations (Conde and Alaejos, 1997; Fordyce, 2013). Alkaline and oxidizing environments have been reported to be in favor of the formation and stabilization of selenate, and selenate are usually very soluble and do not form stable complexes (Saiki and Lowe, 1987). Moreover, the process of converting selenate into the less soluble selenite or elemental Se is very slow, resulting in commonly elevated levels of Se(VI).

#### 3.2.2. Se(IV)

The concentrations of Se(IV) in river water in the Wanshan area ranged from 0.08 to 4.92  $\mu\text{g L}^{-1}$ , with an average of 0.46  $\mu\text{g L}^{-1}$  (Fig. 3; Table 1). Concentrations of Se(IV) in water in the “contaminated area” closed to calcines/tailings (average: 0.63  $\mu\text{g L}^{-1}$ ) were significantly higher than those of the “less-impacted area” far from the calcines/tailings (0.26  $\mu\text{g L}^{-1}$ ) (ANOVA,  $p < 0.01$ ). The regional difference in Se(IV) concentrations among the four rivers was Dashuixi (0.92) > Huangdao (0.82) > Gaolouping (0.30) > Gouxu (0.24), all in units of  $\mu\text{g L}^{-1}$  (Table 1). These differences may be primarily affected by the regional differences in the redox potential in waters, in addition to Se(tot) concentrations. Se(IV)/Se(VI) has been proposed to be a proxy for the redox potential of waters (Conde and Alaejos, 1997), but in the present study, the Se(IV) was not significantly ( $p > 0.05$ ) correlated with Se(IV)/Se(VI). The Se(IV)/Se(VI) in the rivers in the Wanshan area was low ( $0.21 \pm 0.12$ ) and varied within a small range, which is consistent with the generally alkaline and oxidizing environment of the surface water in the study area.

Se(IV) species accounted for only approximately 15% of Se(tot), which was much less than that of Se(VI) (65%) (Table 1). The lower amount of selenite compared to selenate in the dissolved phase in river waters may be explained by several reasons. For instance, the stronger and more rapid adsorption and precipitation of selenite than selenate onto sediments and sand particles, resulting in selenite becoming relatively less mobile (Zhang and Sparks, 1990). Besides, selenite is the most bioavailable Se form for aquatic

organisms (e.g., algae) (Wang et al., 1994). In addition, in aerobic and alkaline water environments, Se(IV) can easily be oxidized to Se(VI) due to the small difference of redox electric coupling (0.4 V) between  $\text{SeO}_3^{2-}/\text{SeO}_4^{2-}$  and  $\text{H}_2\text{O}/\text{O}_2$  (Yao, 2005).

#### 3.2.3. Se(org)

The Se(org) concentrations in water samples in the Wanshan area ranged from 0.09 to 4.80  $\mu\text{g L}^{-1}$ , with an average of 0.85  $\mu\text{g L}^{-1}$  (Figs. 2 and 5). Similar to Se(tot), Se(VI) and Se(IV), the Se(org) concentrations in “contaminated area” (an average of 1.1  $\mu\text{g L}^{-1}$ ) were significantly higher than those in the “less-impacted area” (an average of 0.43  $\mu\text{g L}^{-1}$ ). The regional difference in Se(org) concentrations among the four rivers was as follows: Dashuixi 1.46 > Huangdao 0.73 > Gouxu 0.63 > Gaolouping 0.45, all in units of  $\mu\text{g L}^{-1}$ . For the entire region, Se(org) species accounted for 20% of Se(tot), which was only one-third that of Se(VI) (65%) but accounted for a slightly higher proportion than Se(IV) (15%) (Fig. 2). In Antarctic surface water and Pacific seawater, Se(org) was observed to be 37% and 26% of Se(tot), respectively (Xia et al., 1996). However, a ratio of Se(org) to Se(tot) over 60% has also been reported (Cooke and Bruland, 1987).

### 3.3. Risk considerations

#### 3.3.1. River water

In the present study, approximately 10% of the sampling sites exceeded Se levels of 5  $\mu\text{g L}^{-1}$ , the water-quality criterion set by the USEPA for protecting wildlife and aquatic life (Vinceti et al., 2000); however, many aquatic biologists have proposed that this criterion should be lower at 2  $\mu\text{g L}^{-1}$  given the potential of Se for bioaccumulation in the food chains of fish and avian populations (Vinceti et al., 2000). There were 40% of selected sampling sites in the study area showed total Se concentrations exceeding the recommended limit value of 2  $\mu\text{g L}^{-1}$ . In a previous study, the concentrations of total Se in local fish were observed to be higher than 3  $\text{mg kg}^{-1}$  (Ji et al., 2006), which exceeded the maximum food standard limit of 1  $\text{mg kg}^{-1}$  Se in fish set by the Standardization Administration of the People's Republic of China (SAC, 2005).

Over the entire study area, only two sites exceed the 20  $\mu\text{g L}^{-1}$  limit for irrigation sources set by the WHO (Qin et al., 2013). Surface water bodies are important carriers of Se migration and sites of species transformation. Selenium released near sites of Hg mining and smelting can be steadily transported by the river to the downstream regions. In addition, irrigation with river water containing a considerable amount of bioavailable inorganic Se in paddy soils over time may be a significant contributor to the elevated Se observed in local paddy soil (0.16–36.6  $\text{mg kg}^{-1}$ ) and bioaccumulation in rice grains (0.02–0.67  $\text{mg kg}^{-1}$ ) (Zhang et al., 2012). The mercury concentrations in the river water more than 8 km from the mine-waste calcines are generally lower than 0.050  $\mu\text{g L}^{-1}$ , the standard limit for the protection of freshwater set by the USEPA (Zhang et al., 2010c,d). Therefore, from the perspective of the antagonistic effects of Se on the mobility, bioaccumulation, and toxicity of mercury (see recently published two excellent reviews, e.g., Khan and Wang, 2009; Yang et al., 2008), Se input in the paddy soils through irrigation in downstream areas may play a naturally beneficial role in the environmental remediation of mercury contamination in this area (Zhang et al., 2012). The formation of inert and insoluble HgSe precipitates due to the extremely high binding affinity between Se and Hg as mentioned earlier may result in a reduction of available inorganic Hg in the paddy soils, thereby indirectly inhibit the Hg methylation, thus there is less methylmercury released into surface water (Zhang et al., 2012). However, the long-term adverse influences of Se contamination on the local environment and ecosystem still deserve attention, as the release of Se in water affected by mine-waste



calcines into the downstream river system over time may result in Se accumulation and, if thresholds are exceeded, subsequent adverse effects on sensitive species such as fish in the downstream rivers.

### 3.3.2. Spring water

There are no consistent standards and guidelines on Se concentrations for water quality worldwide. For instance, the standard limit for Se(tot) to protect surface water as drinking water sources are currently set to be 40 and 50  $\mu\text{g L}^{-1}$ , respectively, by the WHO and USEPA. However, 10  $\mu\text{g L}^{-1}$  is the standard set by China, the European Union, Canada, Australia, Japan, Thailand, and New Zealand (Vinceti et al., 2013). Russia has had the unusually low standard limit of 1  $\mu\text{g L}^{-1}$  since 1970 (Vinceti et al., 2013). Obviously, the same data assessed with different standards may show conflicting results regarding health risk, which can be misleading to the public.

It is commonly recognized that even in high-Se areas, the relative contribution of Se from drinking water is likely to be negligible in comparison with that from locally produced food (Qin et al., 2013). However, inorganic Se (selenate), commonly found in drinking water, has a much higher toxicity than that of organic Se (Vinceti et al., 2010a), and several epidemiological studies have indicated that human toxicity may occur at 10  $\mu\text{g L}^{-1}$ , far below the level previously suggested to be hazardous (e.g., 50  $\mu\text{g L}^{-1}$  by the WHO) (Vinceti et al., 2013; Xiao et al., 2006).

In the Wanshan area, most of the sites where surface water samples were collected are not usually used as drinking water sources by the local residents. However, two well-water sites (D10 and D12; Fig. 1) were still in use as drinking water sources for the local residents when we collected the samples. The Se concentrations in drinking water from the two wells were 2.93 and 4.37  $\mu\text{g L}^{-1}$ , respectively, both of which with inorganic fraction (>90%) exceeded the 1  $\mu\text{g L}^{-1}$  level that was recently proposed as the standard limit of Se in drinking water (Vinceti et al., 2013). As the exposed Se by drinking water are dominated by inorganic fraction which are much toxic than organic species, This result suggest that some health risks may exist for the local residents near the two wells. Previous studies indicated that inorganic Se in drinking water greater than 1  $\mu\text{g L}^{-1}$  may result in increased health risks (e.g., amyotrophic lateral sclerosis) (Vinceti et al., 2010b).

## 4. Conclusion and perspectives

Elevated Se concentrations in river water were observed in Wanshan, China, compared with other natural river systems. Mine-waste calcines were likely the primary pollution sources for the Se in river waters, especially upstream (“contaminated area”). However, in downstream (“less-impacted area”) far from the calcines, groundwater may also contribute significantly to the water Se content. The Se(tot) in the river waters was dominated by Se(VI), followed by Se(org) and Se(IV). Two wells used as drinking water sources also contained elevated Se, which may pose health risks to the nearby residents because the dominant species of the spring water in the wells is inorganic species.

Currently existing environmental quality standards and guidelines for Se in water are based on total Se concentrations, which are not appropriate for all ecosystems because the biogeochemical behavior and toxicity of Se depend on the site-specific forms. Hence, there is an urgent need to establish new standard limits for water based on individual Se species. However, available data of Se species in aquatic system are lacking, although the measurement methods and techniques for Se species have greatly improved in recent decades. At present, Se species analyses can be widely promoted and finally undergo routine testing at many

environmental monitoring stations at national or district levels. Updating the traditional standard limits from total Se to Se species will provide great benefits and support for policy-making on related regulatory and control of water quality issues.

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