



Understanding the paradox of selenium contamination in mercury mining areas: High soil content and low accumulation in rice



Hua Zhang^{a,b}, Xinbin Feng^{a,*}, Chengxin Jiang^c, Qihua Li^d, Yi Liu^e, Chunhao Gu^a, Lihai Shang^a, Ping Li^a, Yan Lin^b, Thorjörn Larsen^b

^a State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, 46 Guanshui Road, Guiyang 550002, China

^b Norwegian Institute for Water Research (NIVA), Gaustadalléen 21, 0349 Oslo, Norway

^c Academy of Engineering Institute, China University of Geosciences, Wuhan 430074, China

^d Key Laboratory for Information System of Mountainous Area and Protection of Ecological Environment of Guizhou Province, Guizhou Normal University, Guiyang 550001, China

^e Guizhou Academy of Geological Survey, Guiyang 55005, China

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ABSTRACT

Rice is an important source of Se for billions of people throughout the world. The Wanshan area can be categorized as a seleniferous region due to its high soil Se content, but the Se content in the rice in Wanshan is much lower than that from typical seleniferous regions with an equivalent soil Se level. To investigate why the Se bioaccumulation in Wanshan is low, we measured the soil Se speciation using a sequential partial dissolution technique. The results demonstrated that the bioavailable species only accounted for a small proportion of the total Se in the soils from Wanshan, a much lower quantity than that found in the seleniferous regions. The potential mechanisms may be associated with the existence of Hg contamination, which is likely related to the formation of an inert Hg–Se insoluble precipitate in soils in Wanshan.

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1. Introduction

Selenium (Se) is among the most controversial trace elements because it can be both toxic and nutritional. It is toxic at high levels and essential within a physiologically appropriate margin. Se can have adverse effects on human health in excess or deficiency. Se exists in human and animal selenoproteins as selenocysteine and selenomethionine and is incorporated into the active sites of antioxidant selenoenzymes (Rayman, 2012). For many years, glutathione peroxidase was considered the main selenoprotein; however, later discoveries indicated that glutathione peroxidase is only one of at least 25 genetically encoded selenoproteins (including multiple forms of glutathione peroxidases and thioredoxin reductases) (Reeves and Hoffmann, 2009). Through its incorporation into selenoenzymes, Se is involved in important biological functions that affect such processes as free radical metabolism, immune function, reproductive function and apoptosis (Fordyce, 2013; Rayman, 2012). Severe Se deficiencies (e.g., <10 µg/day) are likely involved in the etiology of a well-known

cardiomyopathy endemic in China (Keshan disease) (KDRG, 1979). Therefore, adequate Se intake is important to maintain normal physiological function in humans. The safe intake range of Se as recommended by the Chinese Nutrition Society is rather narrow: 50–200 µg/day for adults (identical to that recommended by the U.S. National Research Council) (CNS, 1990; Fordyce, 2013).

The distribution of Se is uneven over the Earth's surface. Seleniferous and Se-deficient geo-ecosystems can be formed within limited geographic zones (Tan et al., 2002). Several areas, such as Enshi in Hubei, China; the Great Plains of the USA and Canada; and portions of Ireland, Colombia and Venezuela are known seleniferous areas. However, on a global basis, areas of low-Se or Se-deficient soil are more common than areas of Se-rich soil. Over 40 countries, including China, Denmark, Finland, New Zealand and Russia (eastern and central Siberia), have been designated as low-Se or Se-deficient according to the World Health Organization (WHO) (Combs, 2001; Li et al., 2007a). Globally, between 0.5 and 1 billion people are estimated to suffer from Se deficiency (Combs, 2001).

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

* Corresponding author.

E-mail address: fengxinbin@vip.skleg.cn (X. Feng).

crust. Selenium is often found in association with sulfur-containing minerals. In the natural environment, Se typically exists in four different oxidation states (–II, 0, +IV, +VI) as selenide, elemental Se, dissolved selenates (SeO_4^{2-}) and selenites (SeO_3^{2-}); under normal soil conditions, Se exists as insoluble elemental Se (Se^0), selenides (Se^{2-}) and organo-selenium compounds (containing C–Se–C chemical bonds), such as volatile methyl-selenides, trimethyl-selenonium ions and several seleno-amino acids (Bujdos et al., 2005).

China has abundant Se resources (e.g., Enshi in Hubei province and Ziyang in Shanxi province, where topsoil Se exceeds 1.0 mg kg^{-1}) in some regions and low-Se or Se-deficient soils in others (over two-thirds of the country) (Tan et al., 2002). As shown in Fig. 1, a belt of low-Se soil (the “Se deficiency belt”), primarily composed of brown soil, stretches from the northeast to the southwest across approximately 22 provinces or districts, including Heilongjiang, Jilin, Liaoning, Beijing, Shandong, Inner Mongolia, Gansu, Sichuan, Yunnan, Tibet and Zhejiang (Tan, 1989).

Daily food consumption is typically the primary route for human Se intake. In addition to fish, which is known to accumulate high Se loads, dietary rice is of great significance for maintaining sufficient Se intake for billions of people with a rice-based diet, especially those in Asian countries, including China, where rice is a staple food (Zhang et al., 2012). A recent global survey of rice indicated that approximately 75% of grain samples failed to meet the recommended Se intake quantity for human health (Williams et al., 2009). Although rice grains typically contain much lower Se concentrations than meat and fish (Navarro-Alarcon and Cabrera-Vique, 2008), rice is one of the primary Se sources (40–70%) for rice-eating populations due to their high rice intake (e.g., 300–600 g/day/person) (Williams et al., 2009; Zhang et al., 2012).

Rice can efficiently assimilate inorganic Se into organic forms (Li et al., 2010), which enhances the nutritional efficacy of Se. Organic forms of Se are more bioavailable to humans than inorganic forms are (Rayman et al., 2008). Several studies have revealed that the total Se content in rice is dominated by an organic form, protein-bound selenomethionine, which accounts for more than 80% of the total Se (Fang et al., 2009; Li et al., 2010; Mar et al., 2009).

In addition to serving as a micronutrient, Se can inhibit the harmful effects of Hg exposure, potentially making it the most important micronutrient in rice in regions where rice is the staple food (Khan and Wang, 2009). One good example is a recent study by Li et al. (2012), which indicated that supplementation with organic Se substantially improved Hg excretion in individuals and inhibited the oxidative damage from long-term Hg exposure.

Although usually overlooked by environmental researchers and policy-makers, Se is an important co-existing elemental component of the mineral matrix of Hg ore deposits in mercury mining areas. For instance, tiemannite (mercury selenide, HgSe) has been reported in Wanshan since 1975 (Bao, 1975; Zhang et al., 2012). Wanshan is known as the “mercury capital” of China; it once had the largest reserves and production of Hg in Asia and the third-largest reserves and production in the world (Zhang et al., 2010b, 2012). The chemical composition of the tiemannite from this area was measured as 70–74 wt% Hg and 24–27 wt% Se (Zhang et al., 2012). Selenium often occurs as an isomorphous substituent of sulfur in sulfide crystal lattices. Sulfur atoms in cinnabar ore can be replaced by Se atoms to form an isomorphous series of HgS–HgSe because the extremely high binding affinity between Se and Hg for mercury selenide (HgSe) is much greater than that for mercury sulfide (HgS) (Zhang et al., 2012). Therefore, cinnabar and ores in mercury mining areas typically contain considerable Se contents.

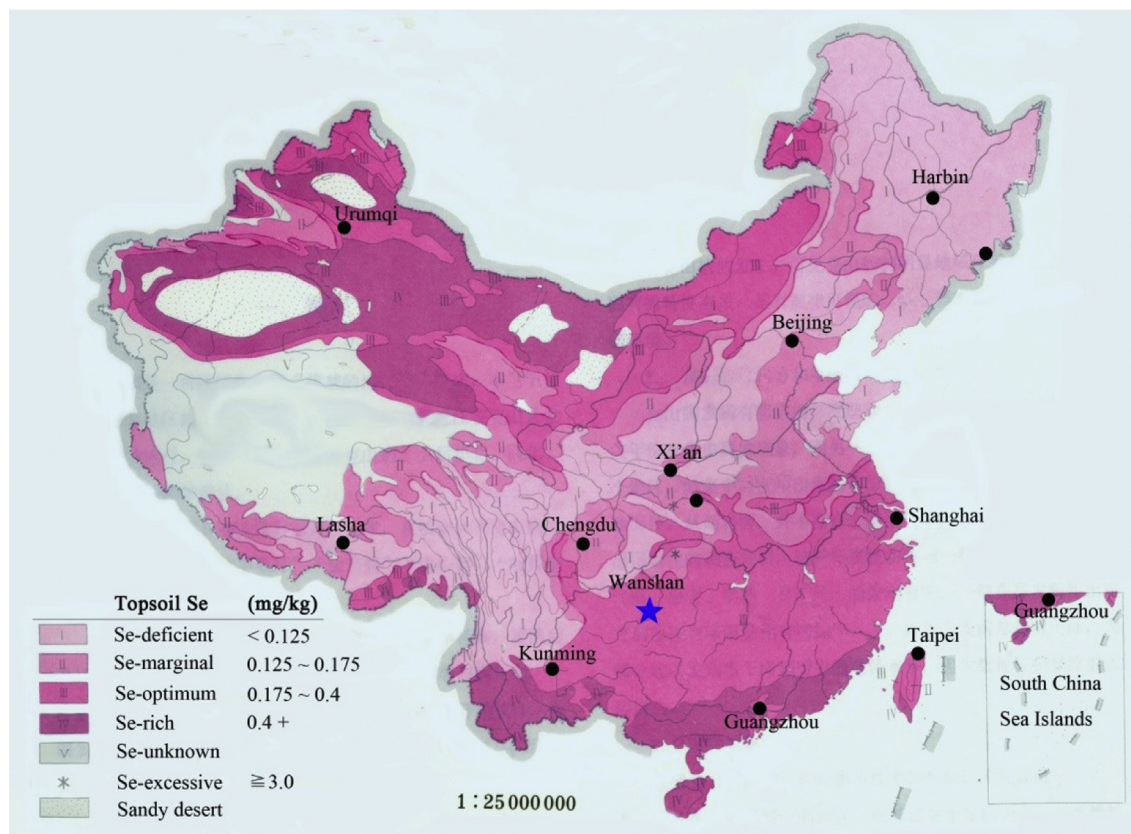


Fig. 1. Soil selenium distribution in China and the location of the study area (modified from that found in the literature; Tan, 1989).

However, the majority of the Se in Hg-mining areas is typically distributed in cinnabar (the natural ore of mercuric sulfide), with small quantities found in tiemannite and metacinnabar. In the Wanshan area, the Se content in common cinnabar was observed to range from 0.02 to 0.87 wt%, with a maximum Se content in metacinnabar of approximately 2.7 wt% (Zhang et al., 2012).

The historic large-scale mining and retorting activities of cinnabar and other Se-rich ores can result in the release of large quantities of Se and Hg into the surrounding environment. The average (range) paddy soil Se content in Wanshan is 2.1 (0.16–36.6) mg kg⁻¹ (Horvat et al., 2003; Zhang et al., 2010b), which is comparable to the soil content of 6.5 (0.41–47.7) mg kg⁻¹ reported from the well-known seleniferous area of Enshi, China (known as the “world capital of selenium”) (Fordyce et al., 2000; Sun et al., 2010; Zhu et al., 2008). However, contrary to expectations, the Se concentration in the rice grains from Wanshan, 0.10 (0.02–0.67) mg kg⁻¹, is approximately 27 times lower than that in Enshi, 2.73 (0.08–9.67) mg kg⁻¹ (Sun et al., 2010). A comparison of the Se concentrations in soil and rice among different countries and regions of China (Table 1) has further revealed that an obvious discrepancy exists in the Se contamination in Wanshan: unlike other areas, in Wanshan, high-Se soils produce low-Se rice.

Several plant studies have indicated that the presence of Hg in the environment plays an important antagonistic role against Se, influencing its bioavailability, uptake and translocation in aerial

plants (Afton and Caruso, 2009; McNear et al., 2012; Mounicou et al., 2006a, 2006b; Yathavakilla and Caruso, 2007). However, our previous field study in the Wanshan area indicated that the antagonistic effects of Hg on Se uptake by rice plants may only significantly occur when Se exposure exceeds a certain threshold (Zhang et al., 2012). A recent study on garlic (*Allium sativum*) in laboratory experiments has also indicated that an increase in Hg levels surrounding the root environment seems to have no inhibitive effects on the plant's uptake of Se into the aerial tissues when the Se levels surrounding the root are low. On the contrary, it even significantly enhanced the plant's Se uptake (Zhao et al., 2013a). A possible explanation of this phenomenon is that the plant may have a special biological function to protect against the toxicity of Hg exposure through enhanced Se uptake from the soil. However, when exposed Se and Hg are both high, there is a common phenomenon of antagonism between the two elements (Zhang et al., 2012; Zhao et al., 2013b), although the processes of uptake and translocation of Se versus Hg by plants are inconsistent (Zhang et al., 2012; Zhao et al., 2013b). A significantly negative correlation between rice Se content and soil Hg content was not observed in Wanshan's Hg-mining area (Horvat et al., 2003; Zhang et al., 2012). Therefore, the Se cycling, flux and balance in the soil–plant system is complicated and is associated with the Se levels, bioavailable fractions, interactions with Hg and other complex processes.

Table 1

Comparison of the Se concentrations in soil and rice among different countries and regions of China (mg kg⁻¹).

Area	Soil Se	Soil water-soluble Se	Reference	Rice Se	Reference
Earth's crust	0.05		Fordyce, 2013		
Global	0.2 (0.1–2)		Swaine, 1995	0.095	Williams et al., 2009
U.S.	0.39 (<0.1–4.3)	0.05–0.39	Shacklette and Boerngen, 1984	0.319	Nazemi et al., 2012
England/Wales (general)	<0.01–16		Fordyce, 2013		
Scotland (general)	0.12–0.88	0.007–0.027	Fordyce, 2013		
Northern Ireland (general)	<0.02–7.8		Fordyce, 2013		
Finland (general)	0.005–1.24		Fordyce, 2013		
Iran (general)	0.23 (0.04–0.45)		Nazemi et al., 2012		
India (Se-deficient)	0.025–0.71	0.019–0.066	Fordyce, 2013		
India (seleniferous)	1–19.5	0.05–0.62	Fordyce, 2013		
Sri Lanka (Se-deficient)	0.11–5.24	0.005–0.043	Fordyce, 2013		
Norway	3–6		Fordyce, 2013		
New Zealand (general)	0.1–4		Fordyce, 2013		
China (general)	0.29 (0.05–0.99)	0.010 (0.0025–0.018)	CNEMC, 1990; Wu et al., 1997	0.032	Wang, 1991
China (Se-deficient)	<0.125	<0.003	Tan et al., 2000	<0.025	Tan et al., 2000
China (Se-marginal)	0.125–0.175	0.003–0.006	Tan et al., 2000	0.025–0.04	Tan et al., 2000
China (Se-optimum)	0.175–0.40	0.006–0.008	Tan et al., 2000	0.04–0.07	Tan et al., 2000
China (Se-rich)	0.175–3	0.008–0.02	Tan et al., 2000	0.07–1	Tan et al., 2000
China (Se-excessive)	>3	>0.02	Tan et al., 2000	>1	Tan et al., 2000
Beijing, China	0.28	0.039 ± 0.005	Yang et al., 1983		
Beijing (Zhoukoudian), China	0.21 ± 0.013		Li et al., 2007a	0.034 ± 0.002	Li et al., 2007a
Ganshu, China	0.16 (0.045–0.40)		Zhu and Jia, 1991		
Guangdong, China	0.23 (0.03–1.42)		Zhang et al., 2008		
Guangxi, China	0.55		Ban and Ding, 1992		
Guizhou, China	0.37 (0.064–1.33)		Wang et al., 2008	0.025 (0.011–0.055)	Li et al., 2005
Guizhou (Kaiyang), China	0.59 (0.21–2.36)	0.013 (0.0075–0.024)	Li et al., 2005	0.081 (0.039–0.134)	Li et al., 2005
Hainan, China	0.765 (0.055–2.23)		Xu et al., 2010		
Heilongjiang, China	0.21 (0.035–0.36)	0.0033 ± 0.0003	Shao and Guan, 1993; Yang et al., 1983		
Hong Kong, China	0.76 (0.07–2.26)		Zhang et al., 2005		
Hunan, China	0.43 (0.08–2.78)		Wang et al., 2008		
Jiangsu (Rugao), China	0.13 ± 0.02	0.0023 ± 0.0011	Sun et al., 2008	0.097 (0.016–0.40)	Sun et al., 2008
Northeast China	0.11 (0.015–0.54)		Wang et al., 2008		
Shanxi, China	0.12 (0.018–17.62)		Wang et al., 2008		
Tibet, China	0.15 (0.049–0.37)		Wang et al., 2008		
Yangtze River Delta, China	(0.035) 0.022–0.050	0.0095 (0.0067–0.012)	Cao et al., 2001	0.029 (0.02–0.036)	Cao et al., 2001
Zhejiang, China	0.29 ± 0.061		Li et al., 2007b		
Enshi, Hubei, China ^a	6.5 (0.41–9.67)	0.354 ± 0.045	Sun et al., 2010; Yang et al., 1983	2.73 (0.08–9.67)	Sun et al., 2010
Wanshan, Guizhou, China ^b	2.1 (0.16–36.6)	0.019 (0.0058–0.046)	Zhang et al., 2012 ^b	0.10 (0.02–0.67)	Zhang et al., 2012

^a Enshi seleniferous areas versus Wanshan mercury mining areas.

^b Present study.

The present study was designed (1) to test the hypothesis that the inhibition of Se uptake by rice plants is associated with the Se speciation in the soil using a sequential partial dissolution method and (2) to explore the possible mechanisms behind the low bioavailability of Se in the soil from the Hg-mining areas. We suspected that the bioavailability was related to Hg contamination.

2. Materials and methods

2.1. Study area

The Wanshan area is a typical mountainous and karstic terrain with elevations ranging from 205 to 1149 m above sea level. The region has a sub-tropical humid climate characterized by abundant precipitation and mild temperatures. The annual average rainfall is 1200–1400 mm, and the annual mean temperature is 17 °C. The upstream portion of the study area is a typical karstic landscape; hence, the outcrops upstream of the basin are carbonate rocks, including limestone, dolomite and dolomitic limestone. The area downstream of the study area features a non-karstic landscape with a bedrock of sandstone and shale and developed tributaries.

2.2. Sample collection and preparation

Building upon our previous studies, 16 typical soil samples were selected from 59 sampling sites in the Wanshan area, for which the total Se in the soil and rice samples has been previously reported (Zhang et al., 2012). The soil samples were used to measure the Se speciation. Typical soil samples were identified according to the total Se content, with a gradient varying widely from 0.65 to 12.2 mg kg⁻¹. We selected soil samples with Se contents (0.65 mg kg⁻¹ minimum) over six times greater than the average for the area (0.1 mg kg⁻¹) to ensure the success of the extraction and the analysis of different Se fractions.

The soil samples were collected from the rice roots (approximately 5–10 cm top depth). At each sampling site, a composite sample was composed of five subsamples. All soil samples were individually sealed in three successive polyethylene bags to avoid cross-contamination and transferred to the laboratory on the day of sampling (stored and transferred with ice packs). A detailed description of the sample collection and preparation is provided in our previous reports (Zhang et al., 2010b, 2012).

2.3. Analytical methods

There is no standard method for soil Se speciation analysis that is commonly accepted by researchers. For better comparison with the data of previous reports in other regions in China (Table 1), in the present study, selenium speciation analyses of the 16 selected typical soil samples were conducted according to a sequential partial dissolution (SPD) method, which was modified from a previous study (Zhang et al., 1997). The SPD procedure extracts soil Se into six operationally defined

fractions (Fig. 2): water-soluble (Milli-Q water); ligand-exchangeable (0.1 mol L⁻¹ KH₂PO₄); organic-bound (0.1 mol L⁻¹ NaP₂O₇); Fe/Mn/Al oxide-, amorphous material-, hydrate- and carbonate-bound (4.0 mol L⁻¹ HCl); sulfide-bound (KClO₃ + HCl); and residual Se (HF + HNO₃ + HClO₄). To ensure the extraction efficiency, the procedure for each fraction established by Zhang et al. (1997) was repeated by dividing the extraction agent into two parts. The procedures are described in detail in Table 2.

The Se fractions were determined via hydride generation atomic fluorescence spectrometry (HG-AFS). Measurements of the total Se in the soils and rice grains were reported in detail in our recent paper (Zhang et al., 2012). The total Se in the six species accounted for 92% (81–105%) of the measured total Se content; furthermore, the total Se in the soils was significantly correlated with all species ($r^2 = 0.25–0.92$, $p < 0.01$ for all; Fig. 3). The results indicate that the SPD technique used in the present study is suitable for meeting the study objectives.

3. Results and discussion

3.1. Total Se in soil and rice

A comparison of the Se concentrations in soil and rice among counties and regions of China (including the Wanshan area in the present study) is shown in Table 1.

Total Se in soil. The overall average soil Se content in the Wanshan area (2.1 mg kg⁻¹) is five times greater than that of all of Guizhou province, which contains the Wanshan area (0.39 mg kg⁻¹) (Wang et al., 2008); seven times greater than that of China (0.29 mg kg⁻¹) (CNEMC, 1990; Wu et al., 1997); and 40 times greater than that of the Earth's upper crust (0.05 mg kg⁻¹) (Fordyce, 2013). In addition, the soil Se content in Wanshan (0.16–36.6) is greater than that in not only many other provinces of China, e.g., Heilongjiang, Shanxi, Gansu, Guangxi, Hainan and Hong Kong (0.11–0.77 mg kg⁻¹) (Table 1), but also many other countries, e.g., the US (<0.1–4.3 mg kg⁻¹), the UK (<0.01–18 mg kg⁻¹), Finland (0.005–1.24 mg kg⁻¹), Iran (0.04–0.45 mg kg⁻¹), India (0.025–19.5 mg kg⁻¹), Sri Lanka (0.11–5.24 mg kg⁻¹), Norway (3–6) and New Zealand (0.1–4 mg kg⁻¹) (Fordyce, 2013; Nazemi et al., 2012; Shacklette and Boerngen, 1984). Furthermore, as previously mentioned, the average (range) paddy soil Se value in Wanshan (2.1 (0.16–36.6 mg kg⁻¹)) is comparable to that reported for the well-

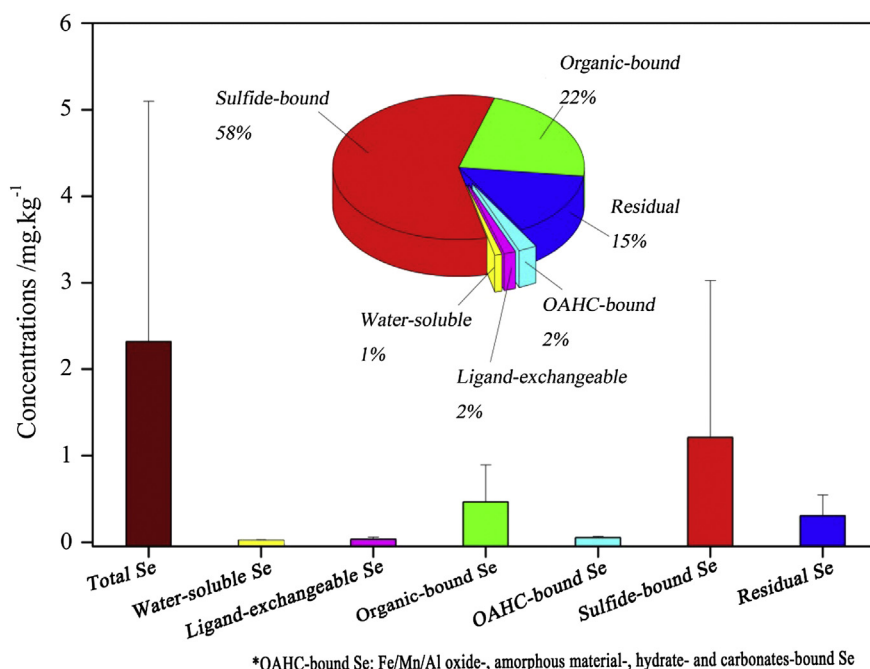


Fig. 2. Averages and standard deviations of the concentrations of each speciation and their ratios to total Se in all selected soil samples.

Table 2
Sequential partial dissolution procedures for Se fractionation in soil (modified from Zhang et al., 1997).

ID.	Se fractionation	Method description
1	Water-soluble (Milli-Q water)	A 0.5–1.0-g soil sample was transferred into a 50-mL centrifuge tube. Next, 10 mL of Milli-Q water at room temperature was added, and the mixture was shaken for 2 h using a reciprocal laboratory shaker (150/min). The suspension was then centrifuged at 3500 rpm at 25 °C for 30 min, and the extracted solution was removed into another tube. An additional 10 mL of Milli-Q water was then added to the residue, and the procedure was repeated. The extracted 20-mL solution was mixed for final analysis.
2	Ligand-exchangeable (0.1 mol L ⁻¹ KH ₂ PO ₄)	K ₂ HPO ₄ (10 mL, 0.1 mol/L) was added to the tube containing the residual solids from step (1). The other steps were identical to those in (1). When the extracted solution was transferred, another 10 mL of K ₂ HPO ₄ was added to the residual solids, and the procedure was repeated. The extracted 20-mL solution was mixed for final analysis.
3	Organic-bound (0.1 mol L ⁻¹ NaP ₂ O ₇)	The tube containing the residual solids from step (2) was treated with 20 mL of 0.1 mol/L Na ₄ P ₂ O ₇ (pH = 10) and shaken for 4 h using a reciprocal laboratory shaker (150/min). The suspension was then centrifuged at 3500 rpm and 25 °C for 30 min, and the extracted solution was removed into a 50-mL PFA beaker. Next, 5 mL of Milli-Q water was added to the residual solids, which were shaken for 30 min and centrifuged for 20 min. The extracted solution was transferred into the PFA beaker containing the previous solution. After adding 5 mL of 16 mol/L HNO ₃ , the PFA beaker was placed on an electric hotplate. The solution was evaporated and reduced to approximately 5 mL. An additional 5 mL of 16 mol/L HNO ₃ and 2 mL of HClO ₄ were added, and the solution was re-evaporated until the volume reached approximately 1–2 mL. After cooling, the solution was added to 18 mL of HCl (6 mol/L), heated until near ebullition (which was maintained for 10 min), and then diluted to 25 mL with 6 mol/L HCl for final analysis.
4	Fe/Mn/Al oxide-, amorphous material-, hydrate- and carbonate-bound Se (4.0 mol L ⁻¹ HCl)	The tube containing the residual solids from (3) received 20 mL of 4 mol/L HCl and was heated in a water bath at 95 °C for 45 min, followed by centrifugation for 30 min. Afterwards, the extracted solution was removed into a 50-mL PFA beaker, and 2 mL of 0.5 g/L FeCl ₃ was added and heated until slight ebullition (which was maintained for 10 min). Once cooled, the solution was diluted to 25 mL with 4 mol/L HCl for final analysis.
5	Sulfide-bound (KClO ₃ + HCl)	The tube containing the residual solids from (4) was mixed with 0.5 g of KClO ₃ . Next, 10 mL of 12 mol/L HCl was added. After stirring for 45 min, the tube received 10 mL of Milli-Q water and was centrifuged for 30 min. The extracted solution was transferred into a 50-mL PFA beaker, heated for 45 min at 50 °C, and then diluted to 25 mL with 4 mol/L HCl for final analysis.
6	Residual (HF + HNO ₃ + HClO ₄)	The residual solids from (5) were removed into a PFA beaker containing 10 mL of 16 mol/L HNO ₃ . Next, 5 mL of HF and 2 mL of HClO ₄ were added, and the beaker was heated on an electric hotplate until the volume was reduced to 1–2 mL. After cooling, the beaker received 18 mL of 6 mol/L HCl and 2 mL of 0.5 g/L FeCl ₃ and was heated close to ebullition for 10 min. The solution was diluted to 25 mL with 4 mol/L HCl for final analysis.

known seleniferous areas in Enshi, China (6.5 (0.41–47.7) mg kg⁻¹) (Sun et al., 2010; Yang et al., 1983).

There was a weak but significantly negative correlation between soil pH and soil Se in the present study ($r^2 = 0.17$, $p < 0.05$, log-transformed; Fig. 4a), suggesting that acidic soils may have enhanced stability for Se relative to alkaline soils. However, no significant correlations ($p > 0.05$) were observed between the Se content and the organic matter content in the paddy soils (Fig. 4d) despite the well-known strong association between the Se in soil and organic matter, which may indicate that the Se content in local soils was not dominated by organic matter. However, the total Se concentrations in soils decrease significantly with the distance from the mine-waste calcines ($r^2 = 0.38$, $p < 0.01$; Fig. 5), which indicated that the mine-waste calcines are significant sources of Se in soil in the downstream areas.

In previous studies, the total Se content has been used to classify soil type. As shown in the map in Fig. 1, according to the spatial coupling between the total soil Se content and its endemic distribution throughout China, soils with different Se contents can be categorized into five different soil types: Se-deficient (<0.175 mg kg⁻¹), Se-marginal (0.125–0.175 mg kg⁻¹), Se-sufficient (0.175–0.4 mg kg⁻¹), Se-rich (0.4–3.0 mg kg⁻¹) and Se-excessive (>3.0 mg kg⁻¹) (Tan, 1989). Based on this classification, 95% of the soils in Wanshan are Se-adequate/rich areas, and approximately 5% are Se-excessive soils (>3.0 mg kg⁻¹) (Zhang et al., 2012). However, the total Se content may not be a good indicator of soil type. Previous studies have demonstrated that the total Se contents in soils from some Keshan areas were equal to or greater than those from non-endemic areas (Johnson et al., 2000), which indicates that the total Se cannot represent all bio-available soil Se.

Total Se in rice. Due to the high soil Se content, the average Se content in rice in Wanshan (0.10 mg kg⁻¹) is three to four times

greater than that in China (0.032 mg kg⁻¹) (Wang, 1991); Guizhou province (0.025 mg kg⁻¹) (Li et al., 2005), which includes the Wanshan area; Zhoukoudian, Beijing (0.034 mg kg⁻¹) (Li et al., 2007a); and the Yangtze River Delta (0.029 mg kg⁻¹) (Cao et al., 2001). The rice Se in Wanshan is generally higher than the value of 0.040–0.070 mg kg⁻¹ recommended for agricultural products by the Chinese Nutrition Society (Tan et al., 1982). It is comparable with the rice Se for Se-rich regions, e.g., Rugao county, Jiangsu (0.097 mg kg⁻¹) (Sun et al., 2008) and Kaiyang county, Guizhou (0.081 mg kg⁻¹) (Li et al., 2005), and similar to the average global rice Se content (0.095 mg kg⁻¹) (Williams et al., 2009). However, the Se content in Wanshan rice (0.10 mg kg⁻¹) is approximately 27 times lower than that from the Enshi seleniferous region, a Se-excessive area (2.73 mg kg⁻¹), although the corresponding soil Se values in the two areas are comparable (2.1 and 6.5 mg kg⁻¹, respectively) (Sun et al., 2010; Zhang et al., 2012). A simple estimate of the translocation factors (TFs) for Se (grains/soil) demonstrates that the average TF of the Se in Wanshan (0.047) is approximately one-tenth of that in Enshi (0.42), suggesting that the bioavailability of the Se in the Wanshan soils may be much lower than that in Enshi.

Previous studies in the study area indicated that the correlation between the total Se in rice grains and the total Se in soils is weak ($r^2 = 0.31$, $p < 0.01$, log-transformed) (Zhang et al., 2012), which indicates that the total Se content in soil is not a good indicator of the total Se absorbed in rice grains. Therefore, the total Se in soil should not be used for environmental Se risk assessment. In addition, the pH values in the soils in the present study were positively ($r^2 = 0.25$, $p < 0.05$) correlated with the TFs of Se (grain/soil) (Fig. 4b), although the correlation between the soil pH and grain Se levels was poor ($p > 0.05$) (Fig. 4c). These results indicate that high soil pH may facilitate Se uptake by rice plants. In general, neutral-to-alkaline soils might enhance the availability of Se more than

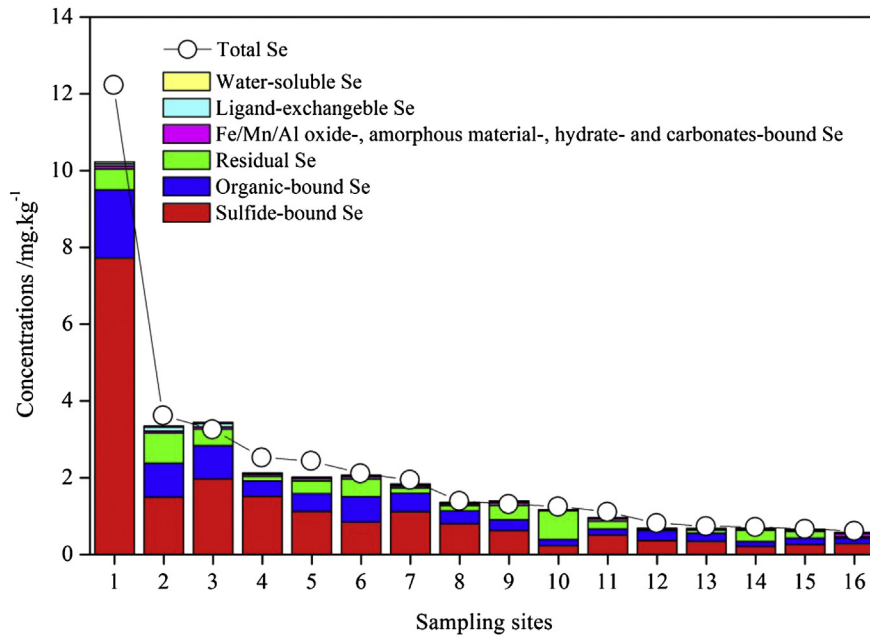


Fig. 3. Total Se concentrations and speciation of Se in the soil samples from the selected sites.

acidic soils. In neutral-to-acidic soils, Se is mainly present as selenite (SeO_3^{2-}), which has very low solubility and plant availability, whereas in neutral-to-alkaline soils, Se is oxidized to selenate (SeO_4^{2-}), which is more soluble and better assimilated by crops than selenite (Navarro-Alarcon and Lopez-Martinez, 2000). Furthermore, the organic matter content in the soils was negatively related to both the TFs of Se ($r^2 = 0.20$, $p < 0.01$, log-transformed; Fig. 4e) and the grain Se levels ($r^2 = 0.13$, $p < 0.05$, log-transformed; Fig. 4f), which is easily attributed to greater association of Se with soil organic matter being unfavorable for Se absorption by the plant (see Section 3.2: Organic-bound Se for a more detailed discussion).

However, the weak relationship ($r^2 = 0.13$ – 0.31 , all log-transformed) between grain Se content (or Se TFs) and soil total Se (or soil pH or organic matter) mentioned above further indicates

that the Se content in plant or agricultural products is not directly dependent on the total Se content, pH and organic matter content of the soils in which they are grown and may instead be dominated by the bioavailable speciation of the soil Se.

3.2. Fractionation of the Se in soil

Water-soluble Se. The concentrations of different Se fractions and the corresponding ratios to total Se in soils are shown in Figs. 2 and 3. The water-soluble Se content ranged from 0.0058 to 0.046 mg kg^{-1} , with an average of $0.019 \pm 0.011 \text{ mg kg}^{-1}$. Its proportion of the total Se ranged from 0.45% to 2.70% , with an average of $1.0\% \pm 0.6\%$. The water-soluble Se primarily included Se(VI), with some Se(IV) and soluble organic Se (e.g., Se amino acids, proteins,

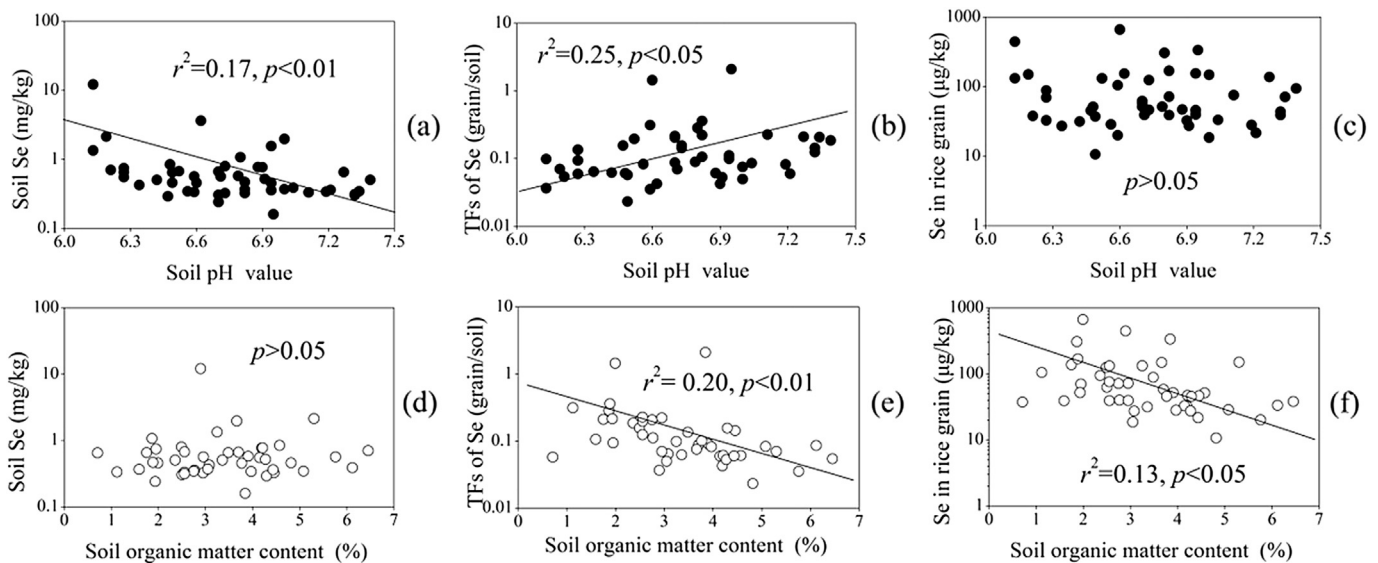


Fig. 4. Translocation factors (TFs) of Se (seed/soil) and Se in soil and seeds by OM (a–c) and pH (d–e) in the soil (total Se reported elsewhere (Zhang et al., 2012), soil pH and organic matter content reported elsewhere (Zhang et al., 2010b)).

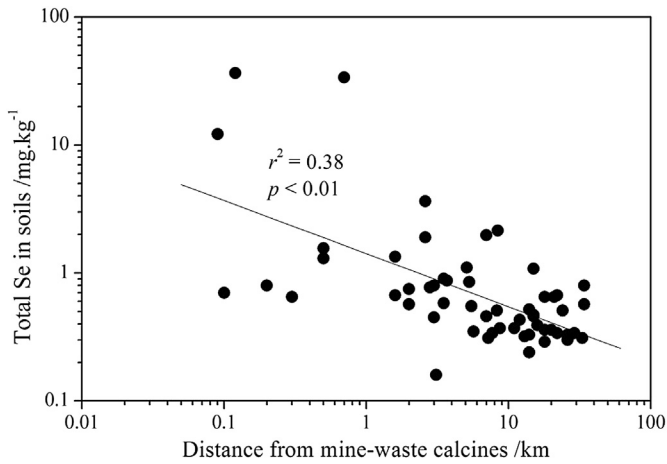


Fig. 5. Relationship between total Se concentration in soil (Zhang et al., 2012) and distance from mine-waste calcines.

etc.). Water-soluble Se is the Se species most easily absorbed by plants and, in agriculture, is considered bioavailable Se (Ge et al., 2000; Olson and Moxon, 1939).

A multiple regression analysis (by IBM SPSS Statistics 21) of the total Se in the rice grains (as the dependent variable) by total Se and the corresponding six operationally defined Se fractions (i.e., water-soluble Se; ligand-exchangeable Se; organic-bound Se; Fe/Mn/Al oxide-, amorphous material-, hydrate- and carbonate-bound Se; sulfide-bound Se; and residual Se) in the soils (as independent

variables) was conducted. The adjusted R^2 is 0.87, which indicates that all seven variables together could predict the value of approximately 87% of the total Se found in the rice. However, the results indicate that among the seven variables, water-soluble Se is the only factor significantly ($p < 0.01$) controlling the total Se content in the rice, with the ability to predict the value of approximately 77% of the total Se found in the rice ($r^2 = 0.81$, or adjusted $r^2 = 0.77$, $p < 0.01$; Fig. 6a). These results indicate that, compared with total Se and other Se fractions in soils, the water-soluble Se in soils is very important in determining the Se levels in rice and can be used as an efficient proxy to evaluate the bioavailability of soil Se.

As shown in Table 1, the water-soluble Se content in Wanshan mercury mining areas (0.019 mg kg^{-1}) is higher than that in many other regions in China (e.g., $0.0095 \text{ mg kg}^{-1}$ in the Yangtze River Delta, $0.0023 \text{ mg kg}^{-1}$ in Rugao, Jiangsu, and $0.0033 \text{ mg kg}^{-1}$ in Heilongjiang) and comparable with that in Kiayang, Guizhou (0.013 mg kg^{-1}) and Beijing (0.039 mg kg^{-1}). However, the water-soluble Se content in Wanshan (0.019 mg kg^{-1}) is approximately 18 times less than that in Enshi seleniferous areas (3.54 mg kg^{-1}), although the total Se content in the soils from Wanshan is comparable to those in the Enshi areas. The water-soluble Se, which represents the bioavailable species, can clearly aid in understanding the elevated total Se content in soils and the reduced total Se in rice grains in Wanshan compared with those in Enshi. Furthermore, the measures taken to prevent Keshan disease and Kashin–Beck disease and related studies on the formation of the “Se-deficiency belt” in China have confirmed that bioavailable Se is primarily represented by water-soluble Se (Tan, 1989; Tan, 1996; Tan et al., 1982; Tan et al., 2002). Therefore, water-soluble Se is a key factor

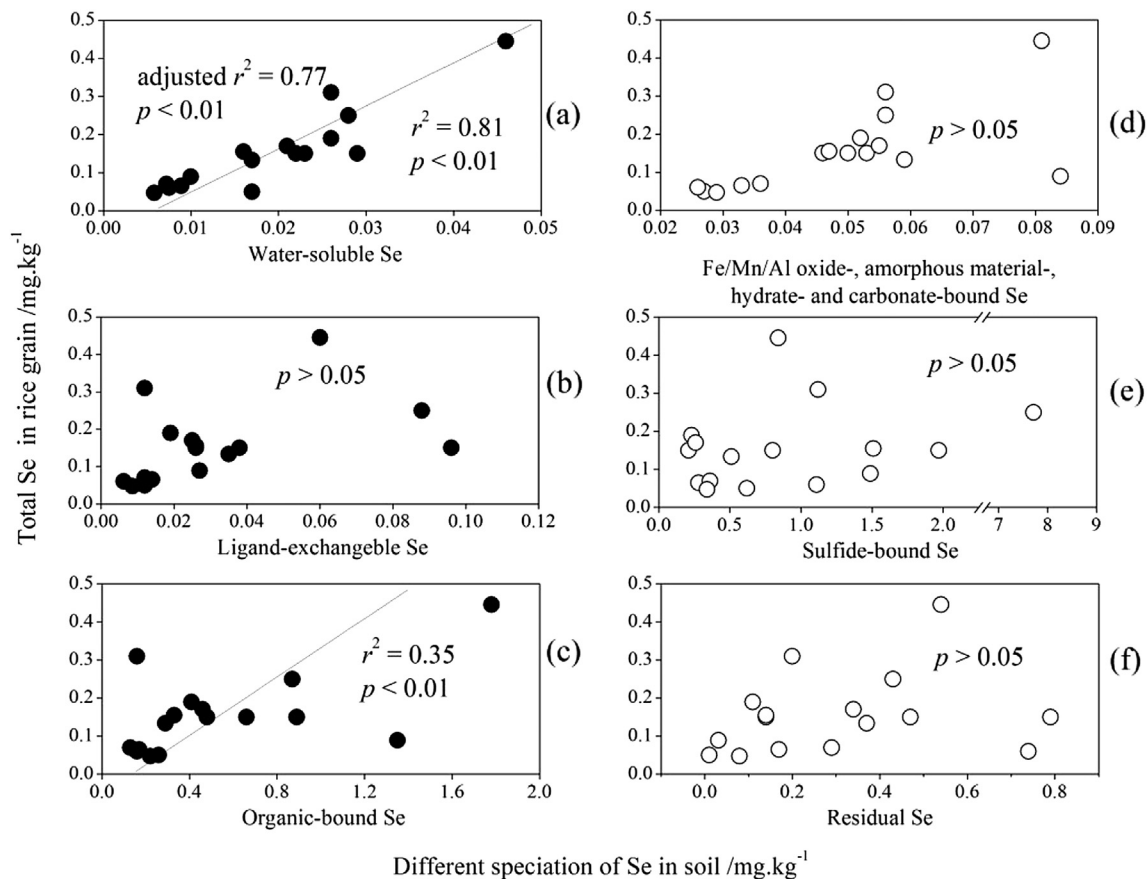


Fig. 6. Relationship between total Se in rice and Se species in soil.

in determining the nutrients levels of Se in the local food chain. In addition to total Se, water-soluble Se can also be used for soil Se classification in terms of environmental risk assessment. Previous studies have indicated that the background thresholds of soil Se for Keshan disease or Kashin–Beck disease in endemic and non-endemic areas are 0.11 mg kg⁻¹ for total Se and 0.0024 mg kg⁻¹ for water-soluble Se (Wei et al., 1991), providing a more reasonable scientific basis for Se endemic research.

Ligand-exchangeable Se. The average (range) of the ligand-exchangeable Se content was 0.032 ± 0.027 (0.0062–0.096) mg kg⁻¹, and the corresponding ratio to the total Se in the soils was 1.83 ± 1.02% (0.53–4.64%) (Figs. 2 and 3). Ligand-exchangeable Se primarily refers to the tetravalent selenite ion (SeO₃²⁻) associated with hydrous oxides and surface adsorption by clay and humus. Loss of this Se species due to leaching primarily occurs through ligand exchange or anion competition (Zhang et al., 1997). Although much less bioavailable than selenate, selenite can also be absorbed by plants (depending on soil conditions). However, in the present study, no significant correlation was observed between the ligand-exchangeable Se content and total Se content in rice grains ($p > 0.05$; Fig. 6b), suggesting that the total Se in rice grains is not dominated by ligand-exchangeable Se in the soil.

Organic-bound Se. The average (range) of organic-bound Se and the corresponding ratio to the total Se in the soils were 0.46 ± 0.43 (0.13–1.78) mg kg⁻¹ and 24% ± 6.36% (13.68–37.90%), respectively (Figs. 2 and 3). Organic-bound Se primarily originates from plant decomposition, with a small contribution from rainfall. Se is a pro-biological element that exists and bio-accumulates as organic compounds in plants or organisms (Fang et al., 2009; Li et al., 2010; Mar et al., 2009). In soil organic matter, especially in soils in which Se-rich plants are grown, Se-enriched organic residues remain in the soil after the plant decays. Organic Se primarily occurs in soil humus (humic acid and fulvic acid). Humic acid is a polymer with a stable structure; thus, plants have difficulty absorbing the Se bound by humic acid (Ge et al., 2000). In comparison, the structure of fulvic acid is relatively simple, and the fulvic-acid-bound Se can be easily mineralized and decomposed into inorganic forms and low-molecular-weight organic compounds, such as Se amino acids, for easy absorption by plants (Ge et al., 2000). In the present study, a positive correlation ($r^2 = 0.35$, $p < 0.05$) was observed between the organic-bound Se and the total Se in rice grains (Fig. 6c). This correlation, however, may be only an indirect reflection of a co-variation between the water-soluble Se and the organic-bound Se (Fig. 3), as a negative correlation was observed between the translocation factors of Se (grain/soil) and the organic matter content in the soils ($r^2 = 0.20$, $p < 0.01$, log-transformed; Fig. 4e), suggesting that an increase in soil organic matter may inhibit the uptake of Se by a rice plant due to the strong binding affinity of Se by humic acid in the organic matter. Typically, 85–90% of the soil organic matter is humic acid substance (Ge et al., 2000).

Fe/Mn/Al oxide-, amorphous material-, hydrate- and carbonate-bound Se. The average (range) of the Fe/Mn/Al oxide-, amorphous material-, hydrate- and carbonate-bound Se content was 0.049 ± 0.017 (0.026–0.084) mg kg⁻¹, and its corresponding ratio to total Se in the soil was 3.9 ± 3.2% (0.8–14%) (Figs. 2 and 3). The Fe/Mn/Al oxide-, amorphous material-, hydrate- and carbonate-bound Se in the present study primarily refers to the Se fraction bound with Fe/Mn/Al oxides, amorphous materials, hydrate and carbonates, which is difficult for plants to take up and is thus easily lost into solution due to mineral decomposition (Ge et al., 2000). This phenomenon is reflected in the poor correlation ($p > 0.05$; Fig. 6d) found between the soil Fe/Mn/Al oxide-, amorphous material-, hydrate- and carbonate-bound Se content and the grain Se content.

Sulfide-bound Se. The average (range) of the sulfide-bound Se content in soils was 1.21 ± 1.82 (0.21–7.72) mg kg⁻¹, and its corresponding ratio to the total Se was 50.1 ± 14.0% (19.7–75.5%) (Figs. 2 and 3). The sulfide-bound Se is the dominant Se species in the Wanshan soils. In a study from the Keshan disease belt of Zhangjiakou in Hubei, China, which used methods similar to those in the present study, the sulfide-bound Se generally accounted for 32% of the total Se in soil (Ge et al., 2000). Under reducing conditions, sulfide is a stable mineral, although strong oxidizing conditions enable decomposition via leaching. Therefore, under normal circumstances, the sulfide-bound Se is not readily absorbed by plants, as reflected in the poor correlation ($p > 0.05$; Fig. 6e) found between the sulfide-bound Se and the total Se in the rice grains.

Residual-bound Se. The average (range) of the residual Se content in soils was 0.30 ± 0.24 (0.011–0.79) mg kg⁻¹, and its corresponding ratio to the total Se was 18.8 ± 16.0% (1.5–63.3%) (Figs. 2 and 3). No significant correlation ($p > 0.05$; Fig. 6f) was observed between the residual Se in the soils and the total Se in the rice grains. Residual Se primarily occurs in silicate minerals (e.g., feldspar, quartz, mica, etc.) and cannot be easily damaged by acid–base reactions (Ge et al., 2000). Obviously, such forms of Se are unavailable to plants.

3.3. Impact of Hg on Se bioavailability in paddy soil

Previous studies have overlooked the impact of Hg on the biogeochemical properties of Se in ecosystems due to a preoccupation with Hg (Zhang et al., 2010a, 2010b). Intuitively, the low bioavailability of Se in Wanshan's Hg-mining area is likely affected by the high Hg levels in the soils, especially compared with those in the Enshi seleniferous area, which has no known Hg contamination (Sun et al., 2010; Zhang et al., 2012). The Hg content and the Hg species and fractions in the paddy soils in the Wanshan area have been reported in our previous studies (Lin et al., 2010; Zhang et al., 2010b). The translocation of both inorganic Hg and organic Hg in the soil–rice system was observed to decrease with increasing soil Se concentrations, which may be associated with the formation of an Hg–Se insoluble complex in the rhizospheres and/or roots, as mentioned earlier (Zhang et al., 2012).

The inorganic Se species most frequently found in soils are selenite and selenate. Selenate is more available for plant uptake than selenite because selenate behaves largely as a non-absorbing solute; however, solid-phase selenite can be strongly adsorbed by soil (e.g., iron oxides/hydroxides), thus resulting in a reduced availability in the soil solution (Li et al., 2010). Under highly reduced paddy soil conditions with prolonged flooding (rice plants typically grow in flooded paddy soils), selenate is expected to be reduced to selenite, elemental Se or even selenide–metal complexes (Zhang et al., 2012). Elemental Se and selenide with low availability for plants are the most typical stable forms under flooded soil conditions (Elrashidi et al., 1987). Similarly, mercuric chloride and mercuric hydroxide are likely to reduce to elemental Hg. Anaerobic flooded paddies are different from aerobic bulk soil, which provides enhanced microbial activity, lower pH and a release of carbon-rich root exudates that can facilitate the reduction of SeO₄²⁻ and SeO₃²⁻ into Se⁰ or Se²⁻ (or Hg²⁺Cl₂ and Hg²⁺[OH]₂ into Hg⁰) (McNear et al., 2012). Selenium has an exceptionally high binding affinity with Hg, with a constant of 10⁴⁵, which is one million times greater than the binding affinity between sulfur and Hg (10³⁹) for the production of mercury sulfide (Hg–S). Therefore, Se should readily bond with Hg to form inert Hg–Se precipitates (according to the equations Hg⁰ + Se⁰ → Hg–Se and/or Hg²⁺ + Se²⁻ → Hg–Se), which have extremely low solubility product constants (10⁻⁵⁸–10⁻⁶⁵) compared with those of Hg–S precipitates (10⁻⁵²) (Björnberg et al., 1988; Dyrssen and Wedborg, 1991). The extensive formation of

unavailable, inert, insoluble Hg–Se precipitates due to Se's extremely high binding affinity for Hg could compromise the availability of Se in the soil, thereby resulting in a low Se content in local rice. In our previous study (Zhang et al., 2012), a positive correlation was observed between Hg concentrations and Se concentrations in paddy soils ($r^2 = 0.88$, $p < 0.01$; log-transformed) and in rice roots ($r^2 = 0.99$, $p < 0.01$; log-transformed) in Wanshan, and the latter showed a pattern similar to a 1:1 (Hg:Se) molar ratio, indicating the formation of an Hg–Se insoluble complex in the rhizospheres and/or roots. The independent mineral form of mercury selenide (HgSe) was discovered in Wanshan as early as forty years ago (Bao, 1975; Zhang et al., 2012), as mentioned earlier. 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*. These results indicate that the antagonistic effects of Hg exposure on Se may be a ubiquitous phenomenon, although the mechanisms in mammals should be different from those under natural environmental conditions, a topic that requires further study. In addition, it has been revealed that the risk considerations of Hg exposure or Se intake should take into account the interactions between Hg and Se. More detailed information on this issue can be found in our recently published article (Zhang et al., 2014).

4. Conclusion

Elevated total Se content and low water-soluble Se content were observed in the paddy soil in Wanshan mercury mining areas relative to those in seleniferous regions with an equivalent soil Se level. The leaching of Se-containing Hg-mining waste may be a significant source of Se released into the local paddy soils. The Se level in rice grain is significantly correlated with water-soluble Se, suggesting that water-soluble Se may play an important role in Se uptake by rice plants and that water-soluble Se can be used as an important proxy for reflecting bioavailable Se in soils in high-Se and high-Hg areas of Wanshan. The low bioavailable Se content in paddy soil in Wanshan may be associated with the co-existing high Hg content in the local soil. A possible mechanism explaining the paradox of high soil Se content and low rice accumulation in Wanshan likely involves the formation of inert and insoluble HgSe precipitates in paddy soil due to the extremely high binding affinity between Se and Hg.

Acknowledgments

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