

Bioaccumulation of Hg in Rice Leaf Facilitates Selenium Bioaccumulation in Rice (*Oryza sativa* L.) Leaf in the Wanshan Mercury Mine

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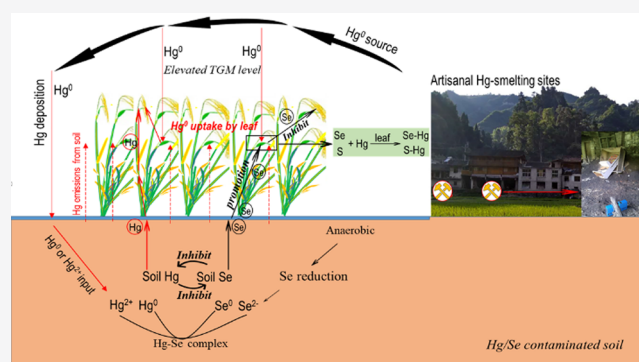
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ABSTRACT: Mercury (Hg) bioaccumulation in rice poses a health issue for rice consumers. In rice paddies, selenium (Se) can decrease the bioavailability of Hg through forming the less bioavailable Hg selenides (HgSe) in soil. Rice leaves can directly uptake a substantial amount of elemental Hg from the atmosphere, however, whether the bioaccumulation of Hg in rice leaves can affect the bioaccumulation of Se in rice plants is not known. Here, we conducted field and controlled studies to investigate the bioaccumulation of Hg and Se in the rice–soil system. In the field study, we observed a significantly positive correlation between Hg concentrations and BAFs of Se in rice leaves ($r^2 = 0.60$, $p < 0.01$) collected from the Wanshan Mercury Mine, SW China, suggesting that the bioaccumulation of atmospheric Hg in rice leaves can facilitate the uptake of soil Se, perhaps through the formation of Hg–Se complex in rice leaves. This conclusion was supported by the controlled study, which observed significantly higher concentrations and BAFs of Se in rice leaf at a high atmospheric Hg site at WMM, compared to a low atmospheric Hg site in Guiyang, SW China.



INTRODUCTION

Mercury (Hg) is a pollutant of global concern due to its long-range transport in the atmosphere, and adverse effects on ecosystems and human health.^{1,2} In aquatic ecosystems, a fraction of mercury can transform into methylmercury (MeHg), a potential neurotoxin that has a strong capacity to bioaccumulate along the food chain.^{3–6} Mercury contamination in Hg mines is receiving special attention due to the extensive release of Hg into the surrounding environment (e.g., atmosphere, water, and soils) during Hg mining activities.^{7–13} Mercury pollution is serious in southwestern China because this area has a number of large Hg mines, including the Wanshan Mercury Mine (WMM) which is the world's third largest Hg mine.¹⁴ To make the situation worse, around these mines, there are many rice paddies that contain a few to hundreds of $\mu\text{g/g}$ Hg in soils^{14,15} and tens to thousands of ng/m^3 Hg in the ambient air.^{16,17} Rice accumulates inorganic Hg through (1) leaf uptake of gaseous elemental Hg (Hg^0) from the atmosphere and (2) root uptake of bioavailable Hg species from the soil.¹⁸ More importantly, rice paddies are hotspots of MeHg production.^{19–21} High levels of MeHg are commonly found in rice near Hg mines.^{14,22–25} At mercury mining sites and in inland China where rice consumption is higher compared to fish consumption, rice is a major MeHg exposure source to local residents.²⁶

Selenium (Se), an essential element and antioxidant, can antagonize the toxicity of Hg and many heavy metals (e.g., Cd and Cr)^{27–35} via the formation of less bioavailable Hg–Se particles in animal and human bodies.^{31,33,36,37} An approximate daily intake of Se of $50 \mu\text{g}/\text{day}$ has been shown to be essential and healthy for the human body.³⁸ While approximately 72% of Chinese land is in a Se-deficient state,³⁹ many Se-rich areas were recently found including WMM. A recent study demonstrated that the soil in WMM contains 0.16 to $36.6 \mu\text{g}/\text{g}$ of Se,⁴⁰ which is 1 to 3 orders of magnitude higher than the abundance of Se in Earth's crust ($50 \text{ ng}/\text{g}$) and comparable with that reported in soils from other seleniferous areas.^{41–44}

At high concentrations, Se has been proven to result in 8–72% of the decrease in the accumulation of Hg in rice grains through the formation of less bioavailable mercury selenides (HgSe) in soil and on the root surface.^{32,45,46} In flooded paddies, the anaerobic and reducing conditions favor the

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interaction between Se and Hg due to the higher affinity constant of Hg to Se (10^{45}) and lower solubility constant of HgSe ($K_{sp} = 1.0 \times 10^{-59}$) than that of Hg sulfides (affinity constant: 10^{39} ; K_{sp} : 1.6×10^{-52} for α -HgS and 4.0×10^{-53} for β -HgS).^{40,47,48} Mercury favors binding to thiol ($-SH$) functional groups over other elements in organisms.^{49,50} However, due to the high-affinity constant of Hg to Se, the complexation between Hg and $-SeH$ has also been found in organisms.^{36,51}

In WMM, which is the “Capital of Mercury in China”, historic large-scale mining activities and ongoing illegal artisanal Hg mining activities have resulted in extremely high Hg levels in the soil and atmosphere.^{15,17} In such a high Hg background, while the inhibition of Hg bioaccumulation in rice by Se has been reported,⁴⁰ the effects of Hg contamination on Se bioaccumulation in rice remains a mystery. As Se may antagonize the toxicity of Hg, understanding the effects of Hg contamination on Se bioaccumulation in rice is critical to evaluate the risk and toxicity of Hg in rice. A laboratory-controlled study demonstrated that adding Hg into the culture solution can promote the translocation of Se to garlic tissues, and suggested that Se can balance the Hg stress by the formation of reduced Se (Se^{2-}) in garlic tissues.⁵² As plant leaves mainly uptake Hg^0 from the atmosphere,¹⁸ the coexistence of the reduction state of Se forms (Se^0 or Se^{2-}) and the oxidation state of Hg (Hg^0 or Hg^{2+}) in leaves provided a possible reaction site where Hg may react with Se. On the basis of the garlic study, there may be an increase in Se translocation in rice plants at regions where soil and atmospheric Hg concentrations are high. In these regions, more Se is possibly needed to antagonize the toxicity of Hg in plant tissues.

Here, we conducted field and controlled studies to investigate the bioaccumulation of Hg and Se in the rice–soil system. In the field study, we investigated the distribution of Hg and Se in rice plants and corresponding rhizosphere soil at both artisanal mining sites and nonartisanal mining sites in WMM. In the controlled study, we conducted pot experiments regarding growing rice plants on a Se-rich soil at high TGM site in the WMM and low TGM site in Guiyang (GY). We aim to (1) test whether the excessive soil Hg could inhibit the uptake of soil Se by roots due to the formation of more HgSe in rhizosphere soil, or (2) test whether atmospheric Hg in rice leaves could facilitate Se bioaccumulation in rice leaves.

MATERIALS AND METHODS

Field Study. To gain a first understanding of the interactions between Hg and Se in the rice–soil system, rice plants and the corresponding rhizosphere soil were collected at 25 sites in the WMM area, SW China (Figure S1 of the Supporting Information, SI), in September 2017. Prior to sample collection, the TGM concentration at each site (~ 0.5 m above ground) was measured three times in July, August, and September, with >30 min each time, using an automated Hg vapor analyzer (LUMEX, RA-915 AM, Russia). The averaged TGM data of each site was used to reflect a long-term TGM concentration. Twelve of the sampling sites were near artisanal Hg smelters (hereafter, artisanal mining sites), while the remainder lacked artisanal Hg smelting activities (hereafter, nonartisanal mining sites). At each site, three 2×2 m plots were established for sample collection. At each plot, three rice plants and corresponding rhizosphere soils (0 to 20 cm depth) were randomly sampled. The rice and soil samples from the

three plots were combined to represent each site. Soil and rice samples were stored in a cooler (-18 °C) and delivered to the laboratory following collection. Soil samples were freeze-dried (-79 °C), crushed, homogenized, and passed through 200 mesh. Rice plants were separated into different tissues (root, stem, leaf, and grain). The hull and bran of grain samples were removed to obtain polished rice. Then, root, stem, leaf, and polished rice samples were washed thoroughly with tap water followed by 18.2 M Ω water (Milli-Q Integral System), freeze-dried (-79 °C), weighed, and powdered using a grinding machine (IKAA11 basic).⁴¹ All soil and rice samples were sealed in polyester plastic bags and stored at room temperature, prior to further analysis.

Controlled Study. To further investigate if the bioaccumulation and translocation of Se can be affected by Hg accumulation in rice leaf, pot experiments regarding growing rice plants on Se-rich soil, were performed at high TGM site in the WMM and low TGM site in Guiyang (GY) in 2018. An active Hg related chemical plant was located nearby the WMM site. According to our study, the TGM concentration at the WMM site during the entire growing season ranges from 24 to 23 842 ng/m³ (geomean: 1556 ng/m³), which are 1–3 magnitudes higher than that at the Guiyang site (range: 5 to 19 ng/m³; geomean: 9.6 ng/m³). The Se-rich soil, containing 7.66 ± 0.16 μ g/g of Se and 389 ± 16 ng/g of Hg, was collected from the Enshi seleniferous area, Hubei province, China. The soil was fully mixed before use in the pot experiment. Storage boxes, $45 \times 34 \times 30$ cm³ in size and each contains ~ 20 kg of the Enshi soil, were used for rice growing. Three boxes at each site and the soil layer is ~ 20 cm deep in each box. Three rice seeds (*Oryza. Sativa L*) were planted in each box. During the growing season, commercial drinking water of the same brand (Long Men drinking water Co., Ltd.) was used for irrigation at the same time-frequency. A transparent plastic cloth was placed ~ 2 m above the box to prevent wet Hg deposition to the box. The TGM concentrations at the Guiyang site and the Wanshan site were measured three times in July, August, and September, with >30 min each time, using the LUMEX automated Hg vapor analyzer. Rice samples were harvested at the end of September 2018. Soil and rice plants were sampled and processed following the method described above.

Mercury Concentration Analysis. For THg analysis, approximately 0.1 g of soil samples were digested in a water bath (95 °C, 6 h) using 5 mL of aqua regia ($HCl/HNO_3 = 3/1$, v/v), and measured by F732–VJ cold vapor atomic absorption spectrometry (detection limit: 0.05 ng/mL Hg) following a previous method.^{18,53} Approximately 0.2 g of rice tissues were digested with 5 mL of HNO_3 and H_2SO_4 (4/1, v/v) and measured by Tekran 2500 cold vapor atomic fluorescence spectroscopy (detection limit: 0.1 pg Hg) following the US EPA Method 1631.⁵⁴

Se Concentration Analysis. TSe concentrations of soil and rice samples were measured following a previous method.⁴¹ Briefly, approximately 0.1 g of soil samples and approximately 0.2 g of rice samples were weighed into 15 mL Teflon bombs. Soil samples were digested by 2.5 mL HNO_3 and 0.5 mL of HF, and rice samples were digested by 2.9 mL HNO_3 and 0.1 mL of HF. The Teflon bomb was placed in a steel can and heated in an oven (155 °C) for 36 and 18 h, respectively, for soil and rice samples. The bombs were then screwed open and supplemented with 1 mL of 30% (v/v) H_2O_2 and heated on a hot plate (90 °C) until the solution was evaporated to near dryness. The residual solution was added to

Table 1. Concentrations and BAFs of Hg and Se in Soil and Rice Tissues at Non-artisanal Mining Sites ($n = 13$) and Artisanal Mining Sites ($n = 12$)

	nonartisanal mining sites				artisanal mining sites			
	THg ($\mu\text{g/g}$)		Hg BAFs		THg ($\mu\text{g/g}$)		Hg BAFs	
	range	mean	range	mean	range	mean	range	mean
TGM (ng/m^3)	13–113	38.8			64–1287	369		
soil	0.35–833.7	13.5			12.5–115	36.8		
root	0.12–20.1	1.13	0.02–0.69	0.08	0.96–20.6	2.94	0.04–0.20	0.08
stem	0.018–0.64	0.058	$1 \times 10^{-4} \sim 0.06$	0.0043	0.09–1.50	0.34	0.002–0.02	0.0093
leaf	0.24–3.16	0.65	0.004–0.87	0.048	2.31–7.19	4.09	0.029–0.27	0.11
polished rice	0.015–0.081	0.031	$2.04 \times 10^{-5} \sim 0.12$	0.0023	0.065–0.45	0.14	0.0007–0.0081	0.0038
	TSe ($\mu\text{g/g}$)		Se BAFs		TSe ($\mu\text{g/g}$)		Se BAFs	
	range	mean	range	mean	range	mean	range	mean
	soil	0.43–21.7	2.13			0.63–4.20	1.65	
root	0.19–5.79	0.99	0.04–2.02	0.40	0.18–3.58	1.02	0.23–1.11	0.62
stem	0.022–0.56	0.11	0.02–0.22	0.05	0.023–0.82	0.16	0.03–0.20	0.10
leaf	0.065–0.98	0.24	0.04–0.46	0.12	0.077–1.53	0.39	0.10–0.55	0.24
polished rice	0.029–0.91	0.12	0.016–0.18	0.055	0.026–0.68	0.15	0.032–0.19	0.091

3 mL of 6 mol/L HCl and heated in a water bath (95 °C) for 2 h, and then diluted to 15 mL with 18.2 M Ω water for hydride generation atomic fluorescence spectrometry analysis (HG-AFS 9700, BJHG, China).

Quality Control. The standard reference materials GBW07405 (yellow-red soil), GBW10020 (citrus leaf), and BCR-482 (lichen), and sample replicates were included during both THg and TSe analysis. The recoveries of Hg for GBW07405, GBW10020 and BCR-482 are $109 \pm 6\%$ ($n = 6$), $101 \pm 7\%$ ($n = 6$), and $88 \pm 2\%$ ($n = 3$), respectively, and the recoveries of Se for GBW07405 and GBW10020 are $106 \pm 5\%$ ($n = 5$) and $93 \pm 4\%$ ($n = 9$), respectively. Duplicate analysis of soil and rice plant tissue samples were conducted in every ten samples, and the relative standard deviations of THg and TSe of all duplicate samples were all within 5% ($n = 22$).

Bioaccumulation Factors of Hg and Se in Rice Tissues. Bioaccumulation factors (BAFs) of Hg and Se in rice tissues were calculated using the following equation:

$$\text{BAF}_{\text{tissue}} = C_{\text{tissue}}/C_{\text{soil}} \quad (1)$$

where C_{tissue} is the THg (or TSe) concentration of rice tissue and C_{soil} is the THg (or TSe) of the corresponding rhizosphere soil.

Statistical Analysis. Correlation analyses and t test were performed using IBM SPSS 22.0 software. Correlation coefficients (r^2) and significance probabilities ($p > 0.05$ is insignificant; $p < 0.05$ is significant; $p < 0.01$ is very significant) were computed for regression fits. A t test was performed to compare whether Hg or Se concentrations and BAFs in rice tissues differed significantly between artisanal and nonartisanal mining sites. Graphical analyses were performed by Origin 2019 and Microsoft Office 365.

RESULTS

Mercury and Selenium Distribution in the Field Study. THg and TSe concentrations in the field study are summarized in Table 1 and described in detail in Text S1. Briefly, artisanal mining sites show significantly higher TGM levels (geomean: 369 ng/m^3) and soil THg concentrations (geomean: 36.8 $\mu\text{g/g}$) than nonartisanal mining sites (geomean TGM: 38.8 ng/m^3 ; geomean soil THg: 13.5 $\mu\text{g/g}$), as shown in Figure 1. Slightly lower soil TSe can be found at

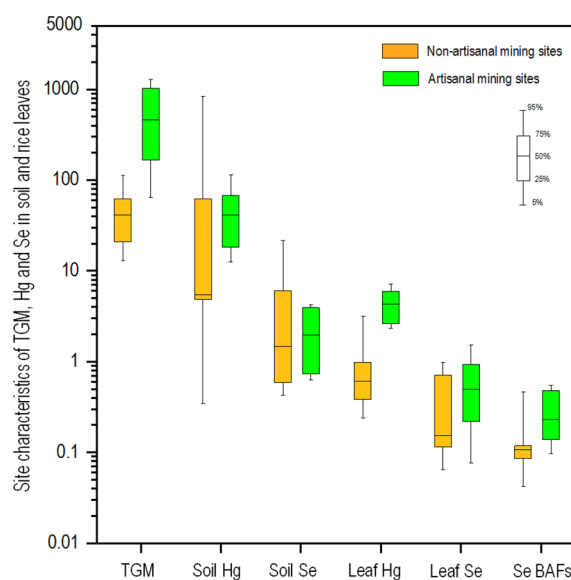


Figure 1. Site characteristics of TGM, Hg, and Se in soil and rice leaves in artisanal mining sites and nonartisanal mining site (TGM: ng/m^3 ; Hg and Se in soil and rice leaves: $\mu\text{g/g}$).

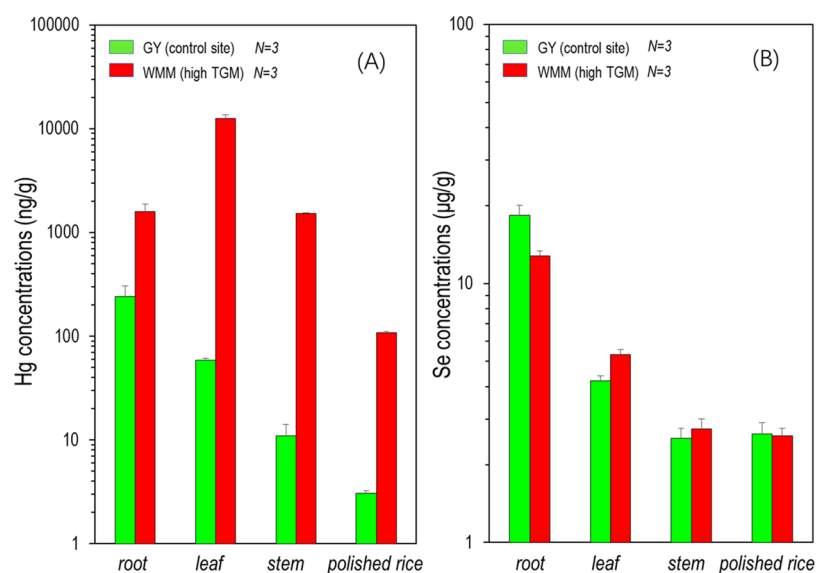
artisanal mining sites (geomean: 1.65 $\mu\text{g/g}$) over nonartisanal mining sites (geomean: 2.13 $\mu\text{g/g}$). Significantly positive correlations between soil THg and soil TSe can be observed at nonartisanal mining sites ($r^2 = 0.32$, $p < 0.01$) and at artisanal mining sites ($r^2 = 0.35$, $p < 0.05$), suggesting Hg and Se may share a similar source.

The concentrations and BAFs of Hg and Se in rice tissues in the field study are summarized in Table 1. Briefly, significantly higher geomean values of THg and TSe were observed at artisanal sites, compared to nonartisanal mining sites (Table 1). At all studied sites, root and leaf have higher THg concentrations and Hg BAFs than grain and stem (Figure S2). Similarly, at all studied sites, higher TSe concentrations and Se BAFs were also observed in root and leaf, compared to grain and stem (Figure S3).

Mercury and Selenium Distribution in the Controlled Study. THg and TSe concentrations of rice tissues in the controlled site are shown in Table 2 and Figure 2. During the

Table 2. Hg and Se Concentrations and BAFs of Pot Rice Plants Grown in GY (Low TGM, $n = 3$) and WMM (High TGM, $n = 3$)

sites	GY				WMM			
	THg ($\mu\text{g/g}$)		Hg BAFs		THg ($\mu\text{g/g}$)		Hg BAFs	
	range	mean	range	mean	range	mean	range	mean
TGM (ng/m^3)	5–19	9.6			24–23842	1556		
soil	0.37–0.42	0.40			0.44–0.59	0.54		
root	0.17–0.30	0.24	0.45–0.71	0.60	1.26–1.86	1.58	2.13–3.68	3.02
stem	0.009–0.012	0.011	0.02–0.03	0.028	1.51–1.53	1.53	2.60–3.41	2.89
leaf	0.056–0.062	0.059	0.14–0.16	0.15	11.8–13.7	12.54	21.1–26.7	23.7
polished rice	0.003–0.003	0.003	0.007–0.009	0.0078	0.095–0.12	0.11	0.17–0.24	0.20
	TSe ($\mu\text{g/g}$)		Se BAFs		TSe ($\mu\text{g/g}$)		Se BAFs	
	range	mean	range	mean	range	mean	range	mean
	soil	7.42–7.70	7.54			7.73–7.81	7.77	
root	16.4–19.5	18.3	2.14–2.55	2.40	12.1–13.4	12.8	1.58–1.74	1.67
stem	2.21–2.87	2.53	0.29–0.37	0.33	2.34–3.37	2.74	0.31–0.44	0.36
leaf	3.83–4.60	4.22	0.50–0.60	0.55	4.78–5.59	5.33	0.62–0.73	0.70
polished rice	2.40–2.92	2.63	0.31–0.38	0.34	2.40–2.75	2.58	0.31–0.36	0.34

**Figure 2.** Distribution of Hg (A) and Se (B) of pot rice plants placed in GY and WMM.

growing season, the THg of soil placed at the Wanshan site increased from 389 ng/g to 535 ng/g, whereas soil placed at the Guiyang site showed consistent THg concentration (395 ± 24 ng/g). The increase of soil THg at the Wanshan site is thought to be caused by the intensive release of Hg from the nearby artisanal Hg sites. Soil Se showed no significant variation at both sites (Wanshan: 7.77 ± 0.04 $\mu\text{g/g}$; Guiyang: 7.54 ± 0.14 $\mu\text{g/g}$) during the growing season.

The concentrations and BAFs of Hg in rice tissues at the Wanshan site decrease in the following order: leaf > root > stem > grain (Figure 2A, Table 2). However, at the Guiyang site, the concentrations and BAFs of Hg decrease as follows: root > leaf > stem > grain. The concentrations and BAFs of Se at both sites show a consistently decreasing order: root > leaf > grain > stem (Figure 2B, Table 2).

DISCUSSION

Hg Distribution in Rice Plants in the Field Study. At both artisanal and nonartisanal mining sites, roots and leaves showed much higher THg concentrations and Hg BAFs than

other tissues (Table 1, Figure S2). Meanwhile, THg concentrations of leaf and stem showed significantly positive linear correlations with TGM, whereas root THg was positively correlated with soil THg (Table S1). As discussed in Text S2, these correlations are consistent with previous studies that demonstrated that rice takes up Hg by root and leaf from the soil and ambient air,¹⁸ respectively, and Hg is not readily translocated among plant tissues.^{55,56}

The bioaccumulation of Hg in rice tissues may be inhibited by elevated soil TSe concentrations.⁴⁰ Such a hypothesis can be supported by the negative correlations ($p < 0.01$) between soil TSe and BAFs of Hg in rice tissues at nonartisanal mining sites (Figure 3A). At nonartisanal mining sites, a positive correlation between TGM and soil THg can be observed ($r^2 = 0.82$, $p < 0.01$), suggesting that TGM mainly originated from the in situ emission of Hg^0 from the soil. It is likely the elevated soil TSe at nonartisanal mining sites can reduce the bioavailability of soil Hg or the emission of Hg^0 from the soil, through the formation of less soluble HgSe in soil.^{57–60} At artisanal mining sites, however, we did not observe any clear

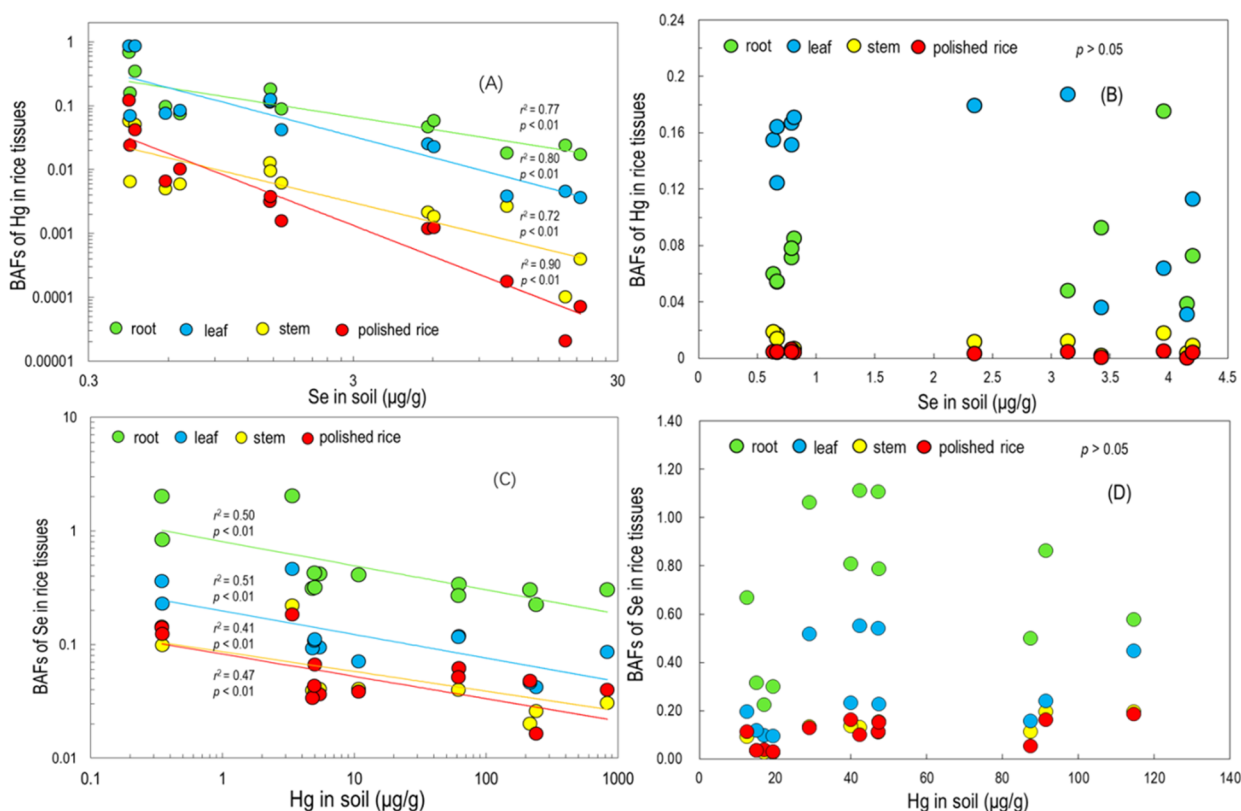


Figure 3. (A) Correlations between soil TSe and BAFs of Hg in rice tissues collected from nonartisanal mining sites of the Wanshan Mercury Mine; (B) correlations between soil TSe and BAFs of Hg in rice tissues collected from artisanal mining sites of the Wanshan Mercury Mine; (C) correlations between soil THg and BAFs of Se in rice tissues collected from nonartisanal mining sites of the Wanshan Mercury Mine; and (D) correlations between soil THg and BAFs of Se in rice tissues collected from artisanal mining sites of the Wanshan Mercury Mine.

correlation between soil TSe and BAFs of Hg in rice tissues (Figure 3B). Unlike nonartisanal mining sites, no significant correlation between TGM and soil THg was observed at artisanal mining sites, suggesting that the TGM was not mainly emitted from soil, but directly from artisanal mining activities. Therefore, soil Se seems not to significantly limit the bioaccumulation of Hg in rice tissues at artisanal mining sites, because of the fact that atmospheric Hg (mainly emitted from the Hg smelters) was directly uptaken by rice leaves, and there is little chance for soil Se to complex with atmospheric Hg.

Se Distribution in Rice Plants in the Field Study. The distribution patterns of TSe and Se BAFs in rice tissues in the field study, as illustrated in Table 1 and Figure S3. At nonartisanal and artisanal mining sites, the TSe concentrations of rice tissues are all positively correlated with soil TSe concentrations ($p < 0.01$ for all), consistent with the fact that rice plant uptakes Se mainly from soil.^{41,44}

As shown in Figure 3C, the BAFs of Se in rice tissues are all negatively correlated with soil THg concentrations at nonartisanal mining sites ($p < 0.01$ for all). Hence, we hypothesized that the uptake of soil Se by rice plant may be inhibited by high soil THg concentrations, although other mechanisms may exist. This can be explained by the formation of less soluble HgSe in paddy soil. Indeed, previous studies have demonstrated that Hg–Se interaction can occur in the rhizosphere by detecting a proportion of Hg–Se in root surface.^{45,46} Under flooded conditions, oxidized Se species (SeO_4^{2-} , SeO_3^{2-}) can transform to reduced Se species (Se^{2-} or Se^0).⁴⁰ Reduced Se species can react with dissolved Hg^{2+} or

Hg^0 in soil solutions, forming Hg–Se complex in soil and rice rhizosphere. HgSe has much lower mobility and bioavailability compared to Hg-sulfides, due to their much lower K_{sp} than HgS .^{40,47,48}

At artisanal mining sites, however, we observed no clear correlation between soil THg and BAFs of Se in rice tissues (Figure 3D). However, compared to nonartisanal mining sites, relatively higher TSe concentrations and higher BAFs of Se were observed in rice leaves at artisanal sites ($p = 0.039$, $t = -2.193$). This is contradicting with the slightly lower soil TSe concentrations at artisanal mining sites, indicating that environmental conditions in the regions of artisanal Hg mining activities facilitated the bioaccumulation of Se in rice leaves. As mentioned above, soil Hg tends to decrease the bioavailability of Se in soils, therefore it should not be the reason for the higher BAFs of Se in rice leaves at nonartisanal mining sites. For rice leaf, significantly positive correlations were observed between Hg concentrations and Se BAFs (Figure 4A) and between TGM and Se BAFs (Figure 4B), which implies that the bioaccumulation of Hg facilitated the uptake of soil Se by leaf.

Artisanal Hg mining activities significantly increased the TGM levels at artisanal Hg mining sites, which resulted in elevated THg levels in rice leaves, perhaps forming Hg–Se complex in rice leaf. A substantial amount of atmospheric Hg^0 can pass through stomata, and be oxidized to Hg^{2+} and accumulated by leaf of plant tissue.^{49,61} In leaf and other tissues, a substantial amount of Hg^{2+} binds with sulfur-containing groups (e.g., $-\text{SH}$) to form less soluble Hg sulfides (e.g., $\beta\text{-HgS}$), which combat the toxicity of Hg.⁴⁹ It should be

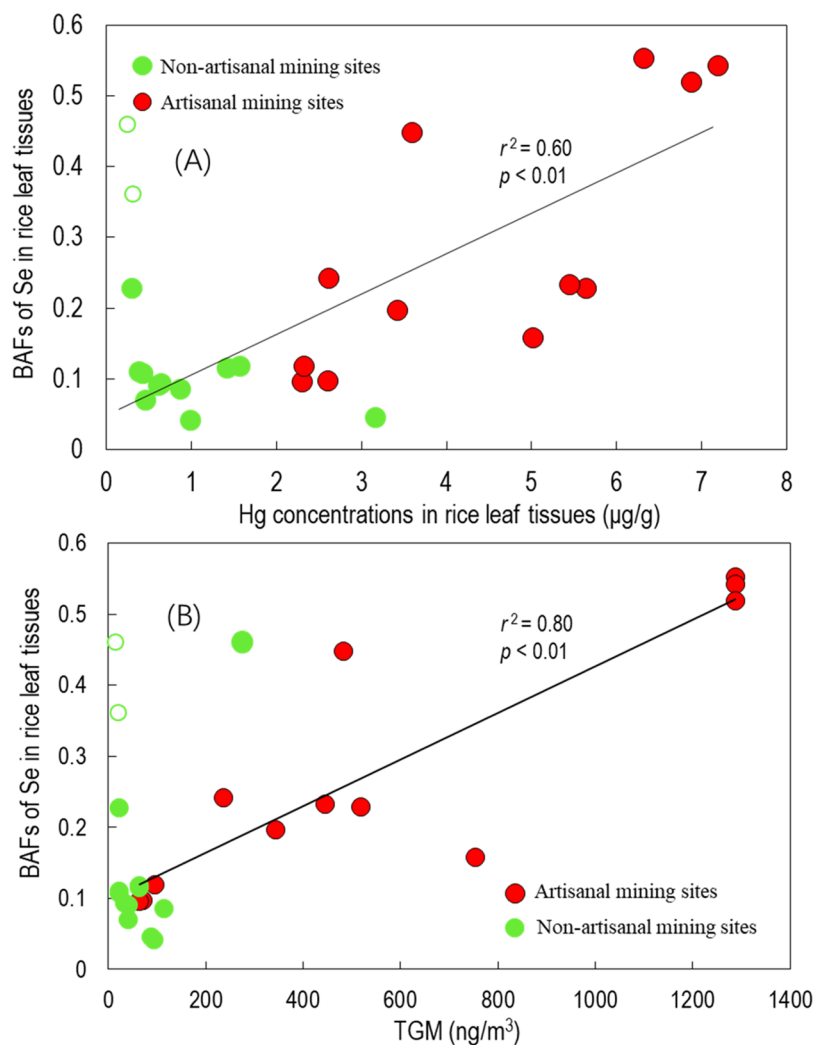


Figure 4. (A) Correlation between Hg concentrations and BAFs of Se in rice leaves collected from the Wanshan Mercury Mine; and (B) correlation between TGM and BAFs of Se in rice leaves collected from the Wanshan Mercury Mine.

noted that the leaf is also the site where the transformation of inorganic Se (e.g., Se^{6+} and Se^{4+}) to organic Se species occurs. Inorganic Se^{6+} and Se^{4+} are transported from the root to leaf by sulfate and phosphate transporters and are transformed to organic Se (Se-Met, Se-Cys, Se-MeSeCys, DMSe, DMDSe, etc.) and reduced Se (Se^{2-} or Se^0) species, with the involvement of many enzymes.^{62–64} Here, we speculate that the formation of Hg–Se may occur in rice leaf due to the presence of reduced Se (Se^{2-} or Se^0) species, considering the stronger chemical bonding ability of Se–Hg (10^{45}) than of S–Hg (10^{39}). The free functional groups of –SeH are preferentially bound with Hg^{2+} over –SH,^{36,37} even capturing the Hg that has formed $\text{Hg}(\text{SR})_2$ by ligand exchange reaction.⁶⁵ The sulfur in β -HgS is readily replaced by Se through isomorphism.⁶⁶ To test our hypothesis, more studies are needed in the future.

Se Distribution in Rice Plants in the Controlled Study. Compared to the field study, significantly higher Se BAFs were observed in the controlled study. This is due to the use of Enshi soil in the controlled study. The Enshi soil has previously been shown to have high Se bioavailability, as indicated by the high concentrations of bioavailable Se species such as water-soluble Se (0.008–0.175 $\mu\text{g/g}$), ligand-exchangeable Se (0.10–1.45 $\mu\text{g/g}$), and organically bound Se

(0.61–8.11 $\mu\text{g/g}$).⁴¹ The controlled study further supported our hypothesis that the high TGM, which is the major source of Hg in rice leaves, facilitates the uptake of soil Se by rice leaves. As shown in Figure 2B, the concentrations and BAFs of Se in root at the Wanshan site was much lower ($p = 0.006$, $t = 5.274$) than that at the Guiyang site, which may be due to intensive Hg deposition that decreased Se bioavailability by forming less bioavailable HgSe species in soil. However, the concentrations and BAFs of Se in rice leaves at the Wanshan site were surprisingly higher than those at the Guiyang site. In particular, statistic tests suggested the concentrations and BAFs of Se in leaf at the Wanshan site are significantly higher ($p = 0.035$, $t = -3.148$) than that at the Guiyang site. Rice leaves receive the majority of Hg from the atmosphere.¹⁸ As the same soil and water were used throughout the controlled study at both sites, we suggest that the high TGM is an important driver for the relatively higher concentrations and BAFs of Se in leaves at the Wanshan site.

Environmental Implications. The Hg–Se interaction in the rice–soil system, as demonstrated in this study, provided some new insights into the biogeochemical cycling of both Hg and Se in the environment. As a toxin, the bioaccumulation of Hg in plants is a critical step for Hg entering the food web.⁶⁷ Selenium in soil has great potential to limit the bioavailability

of Hg in soil, through the formation of less soluble HgSe, especially in Se-rich regions.^{40,53} In highly Hg-polluted regions, mercury, in turn, has an undeniable effect on the biogeochemical fate of Se. According to our study, elevated Hg concentrations could decrease the mobility of Se in soil, due to the formation of HgSe. Meanwhile, plants receive a substantial amount of Hg⁰ from ambient air, and the uptake of atmospheric Hg by plant leaves can facilitate the uptake of Se by rice, especially in areas associated with high TGM levels. Although the mechanism behind this phenomenon remains not well explained by this study, we hypothesized that interactions between Hg and Se may readily form HgSe in leaf, where atmospheric Hg⁰ and soil Se are transformed to oxidation and reduction states, respectively. The formation of less soluble HgSe exhausts the available Se species (Se⁶⁺ and Se⁴⁺) in rice leaves, which, in turn, facilitates the uptake of soil Se by leaves. The complex of Hg to Se has been observed in many animal tissues, and such kind of complex has been assumed to prevent negative effects of Hg in animals.⁶⁸ The present study implies the same mechanism may also occur in plant leaves that exposed in a high TGM environment. However, it is worth mentioning that this study failed to detect the in situ presence of HgSe. To verify the possibility of HgSe formation in rice plant and other plant species, we encourage researchers to conduct further studies using relevant techniques (e.g., XANES). It also has been reported that the intervention of massive Hg can promote the uptake of soil Se by garlic plant in which a substantial amount of HgSe was detected by the XANES.⁵²

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.est.9b06486>.

Text S1, THg, TSe concentrations of the WMM soil in the field study; Text S2, understand correlations among soil Hg, TGM, and Hg levels in rice tissues; Table S1, Pearson's correlation matrix (*r*) among the Hg levels in paddy soils, air, and tissues of rice plants at nonartisanal mining sites and artisanal mining sites; Figure S1, study area and sampling sites; Figure S2, distribution of Hg in soil and rice tissues; and Figure S3, distribution of Se in soil and rice tissues (PDF)

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Notes

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