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## RESEARCH ARTICLE

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### Key Points:

- Rice preferentially takes up lighter Hg isotopes from the soil and atmosphere
- Hg(II) photoreduction in paddy waters generates negative Hg-mass-independent fractionation in gaseous Hg(0), which is taken up by rice leaves
- Different degrees of Hg-mass-dependent fractionation are observed during the uptake of Hg by rice at active artisanal smelting sites and abandoned mining sites

### Supporting Information:

- Supporting Information S1

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## Understanding the Bioaccumulation of Mercury in Rice Plants at the Wanshan Mercury Mine, China: Using Stable Mercury Isotopes

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**Abstract** Rice can accumulate a substantial amount of mercury (Hg). At the Wanshan Mercury Mine (WMM), the bioaccumulation of Hg by rice was complicated by historical large-scale mining and active artisanal smelting activities. This study investigated the concentration and isotopic composition of Hg in rice roots, leaves and paddy soil collected from abandoned Hg mining sites and active artisanal smelting sites at the WMM. At all sites, correlations between  $\delta^{202}\text{Hg}$  and 1/THg were observed in soil, suggesting a mixing of Hg from waste calcine and unroasted Hg ore. Significantly positive correlations were also observed in THg concentrations between roots and soil ( $r^2 = 0.84$ ,  $p < 0.01$ ) and between leaves and total gaseous mercury ( $r^2 = 0.87$ ,  $p < 0.01$ ), reflecting that roots and leaves receive Hg mainly from soil and atmosphere, respectively. Large differences of  $-0.87 \pm 0.57\text{‰}$  and  $-1.85 \pm 0.57\text{‰}$  in  $\delta^{202}\text{Hg}$  between the root and soil were observed at abandoned Hg mining sites and active artisanal smelting sites, respectively, suggesting that roots preferentially accumulate lighter Hg isotopes from the soil. Offsets of 0.05‰ and 0.27‰ in  $\Delta^{199}\text{Hg}$  between rice roots and leaves, with higher  $\Delta^{199}\text{Hg}$  values in roots than leaves, were observed at abandoned Hg mining sites and active artisanal smelting sites, respectively. The Hg-mass-independent fractionation signal is believed to be caused by Hg(II) photoreduction in paddy water; however, the extent of photoreduction is variable among rice paddies. Overall, this study suggests that Hg isotopes can be a useful tool to understand the sources and bioaccumulation of Hg in rice paddies.

**Plain Language Summary** The geochemistry of mercury stable isotopes provides a new method to study the source, transport, and transformation of Hg in the environment. Rice accumulates Hg and can subsequently pose a health risk to the population, especially for those at Hg-polluted sites. This study utilized Hg isotopes as a tracer to understand the bioaccumulation of soil and atmospheric Hg by rice roots and leaves, respectively, at the Wanshan Mercury Mine. Our results show large differences in isotope ratios among soil and root compartments, suggesting that rice plants preferentially accumulated lower mass isotopes. The observed mass-independent sorting of the odd mass isotope ( $^{199}\text{Hg}$  and  $^{201}\text{Hg}$ ) indicates photochemical transformations of Hg(II) in the paddy prior to uptake by the rice. This study establishes Hg isotopes as a useful tool to understand Hg biogeochemical cycling in rice paddy ecosystems.

## 1. Introduction

Mercury (Hg) is a globally distributed pollutant. In aquatic ecosystems, a small fraction of Hg can be methylated to MeHg, a neurotoxin that can bioaccumulate through aquatic food chains and reach concentrations that are  $10^6$  to  $10^7$  times higher in fish than in the surrounding water (Chumchal et al., 2011; Lavoie et al., 2013; Poste et al., 2015). A similar MeHg biomagnification was reported in terrestrial food chains as well (Kwon et al., 2015; Rodenhouse et al., 2019; Tsui et al., 2012). Fish consumption is well known as a major MeHg exposure pathway for the global population (Mergler et al., 2007). In recent years, scientists have realized that rice paddies are also hot spots of Hg methylation (Liu et al., 2012; Rothenberg & Feng, 2012; Zhang, Feng, Larssen, Shang, & Li, 2010). At Hg-polluted sites, rice accumulates a substantial amount of MeHg in grains, and the consumption of rice can be another important human exposure pathway (X. Feng

et al., 2008; Zhang, Feng, Larssen, Qiu, & Vogt, 2010). However, unlike fish, which mainly contain MeHg (Al-Reasi et al., 2007; Kwon et al., 2012; Onsanit et al., 2012; Schartup et al., 2019), the majority of Hg in rice tissues (e.g., root and leaf) is in the inorganic Hg (IHg) form (Meng et al., 2010; Zhang, Feng, Larssen, Shang, & Li, 2010). According to Meng et al. (2010), the MeHg (methylated Hg)/THg (total Hg) ratios in roots and leaves are only  $0.0015 \pm 0.0012$  and  $0.00028 \pm 0.00026$ , respectively, at the Wanshan Mercury Mine (WMM).

Our understanding of the bioaccumulation of Hg in rice plants has been improved by measuring the isotopic ratios of Hg. Mercury has seven natural stable isotopes ( $^{196}\text{Hg}$ ,  $^{198}\text{Hg}$ ,  $^{199}\text{Hg}$ ,  $^{200}\text{Hg}$ ,  $^{201}\text{Hg}$ ,  $^{202}\text{Hg}$ , and  $^{204}\text{Hg}$ ), which undergo both mass-dependent fractionation (MDF, reported as  $\delta^{202}\text{Hg}$ ) and mass-independent fractionation (MIF, reported as  $\Delta^{199}\text{Hg}$ ,  $\Delta^{200}\text{Hg}$ , and  $\Delta^{201}\text{Hg}$ ) during their cycling in the environment. Hg-MDF occurs during various biogeochemical processes, while Hg-MIF occurs mainly via photochemical processes (Blum et al., 2014). The MIF of odd isotopes ( $^{199}\text{Hg}$  and  $^{201}\text{Hg}$ ) in natural samples has been demonstrated to be mainly caused by aqueous Hg(II) photoreduction or MeHg photodegradation (Bergquist & Blum, 2007). In contrast, MIF of even isotopes (e.g.,  $^{200}\text{Hg}$ ) has been mainly observed in atmospheric samples and has been attributed to the photochemical oxidation of gaseous Hg(0) in the atmosphere (Chen et al., 2012; Gratz et al., 2010; Sun et al., 2016). In a previous study, distinct Hg isotopic signatures were observed in rice tissues (e.g., root, stem, leaf, and grain), soil, and atmospheric samples from the WMM, which is the most Hg-polluted site in China and the world (Yin, Feng, & Meng, 2013). In general, the  $\Delta^{199}\text{Hg}$  values of roots ( $-0.03\text{‰}$ – $-0.02\text{‰}$ ) and leaves ( $-0.37\text{‰}$ – $-0.14\text{‰}$ ) are similar to those of soil ( $-0.02\text{‰}$ – $-0.07\text{‰}$ ) and atmospheric Hg ( $-0.34\text{‰}$  to  $-0.24\text{‰}$ ), respectively, which suggests that vegetation takes up Hg from the soil and atmosphere by roots and leaves, respectively (Yin, Feng, & Meng, 2013). However, much lower  $\delta^{202}\text{Hg}$  values were observed in plant tissues than those in soil and atmospheric Hg, suggesting that Hg-MDF (with preferential uptake of lighter Hg isotopes) could occur during the uptake of soil and atmospheric Hg by roots and leaves, respectively (Yin, Feng, & Meng, 2013). Hg-MDF has been observed for vegetation uptake of Hg in many vegetated ecosystems, such as temperate forests and tundra (Demers et al., 2013; Douglas et al., 2019; Enrico et al., 2016; Jiskra et al., 2019; Obrist et al., 2018; Olson et al., 2019; Zheng et al., 2016).

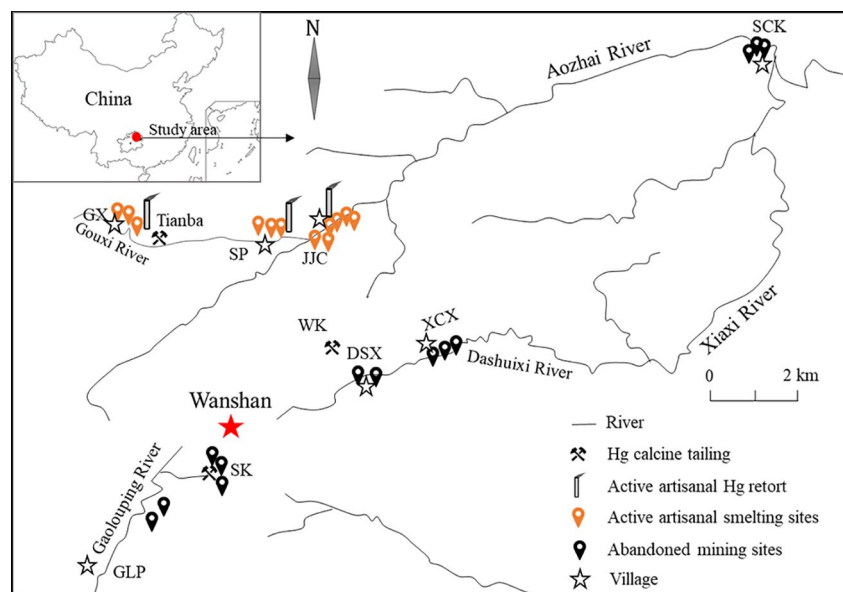
Mercury mining in the WMM has lasted for >2000 years since the Qin Dynasty. Large-scale Hg mining has been officially banned in the WMM since 2003; however, long-term mining activities have resulted in the intense release of Hg to nearby farmlands, where rice is commonly grown. At these abandoned Hg mining sites, high levels of Hg in soil ( $0.26$ – $496 \mu\text{g/g}$ ) (Zhang et al., 2012) and ambient air ( $17$ – $2,100 \text{ ng/m}^3$ ) (Dai et al., 2012) have been reported. With the temptation of profits, illegal active artisanal Hg smelting activities are still ongoing at a few sites in the WMM. At these new sites, soil Hg and total gaseous Hg (TGM) concentrations are higher than those at abandoned Hg mining sites. Regarding the WMM, it is believed that rice plants at the abandoned Hg mining sites are predominantly polluted by legacy Hg emitted from abandoned mine tailings, whereas rice plants at the illegal active artisanal Hg smelting sites receive Hg that was released from active artisanal smelting activities. Recent studies have demonstrated that newly deposited Hg is more bioavailable than legacy Hg and is more easily bioaccumulated in rice plants (Zhao et al., 2016). Vegetation takes up soil Hg by roots and takes up atmospheric Hg by leaves (Yin, Feng, & Meng, 2013). Given the differences in Hg pollution sources, bioavailable fractions and Hg levels, the isotopic signature of Hg in rice plants may be different at abandoned Hg mining sites and active artisanal Hg smelting sites.

In this study, rice plants and the corresponding rhizosphere soil were systematically collected from the WMM for Hg isotopic composition analysis. This study aims (1) to test whether the Hg isotope signals of rice roots and leaves are different at abandoned Hg mining and at active artisanal Hg smelting sites and (2) to understand the isotope fractionation of Hg during the uptake of Hg from the soil and the atmosphere by rice roots and leaves, respectively.

## 2. Materials and Methods

### 2.1. Study Area and Sampling

The WMM in Guizhou Province, SW China, is located in a typical karstic area with elevations from 205 to 1,149 m high. This region has a subtropical monsoon climate, with an annual precipitation rate of 1,200–1,400 mm and an annual temperature of  $17^\circ\text{C}$  (Zhang et al., 2012). Known as China's largest Hg deposit



**Figure 1.** Study area and sampling sites.

and the world's third-largest Hg deposit, the WMM is also called the “Mercury Capital” of China. Although large-scale mercury mining and smelting have not occurred for >10 years, mercury pollution remains serious in the WMM, especially at historical abandoned Hg mining sites and at ongoing illegal active artisanal smelting sites, as shown in Figure 1.

Paired rice plant and rhizosphere soil (0–25 cm depth) samples were collected at 25 sites in the harvest season in September of 2017. These sites include 13 abandoned Hg mining sites and 12 illegal active artisanal smelting sites (Figure 1). Three rice plants and in situ rhizosphere soil samples were randomly obtained at each site, and then samples at each site were uniformly mixed as one sample. Sample pretreatment details have been described in our previous study (Chang, Yin, Wang, et al., 2019). Briefly, stones and wood dust were picked out of the soil samples. The soil samples were then freeze-dried (−79°C), crushed, and passed through a 200 mesh sieve. The roots and leaves of rice plant tissues were thoroughly washed with tap water, washed with Milli-Q water (18.2 MΩ), freeze-dried (−79°C), and then powdered using a grinder (IKA®A11 basic). Before each sample was ground, the machine was wiped with alcohol pads to avoid cross-contamination. The TGM concentration at each site was measured three times during the growing season (July, August, and September) using an automated Hg vapor analyzer (LUMEX, RA-915AM, Russia), which has a detection limit of 0.5 ng/m<sup>3</sup> (Chang et al., 2020). The data were averaged to represent the long-term TGM concentration of each site.

## 2.2. Mercury Concentrations in Paddy Water, Soil, Roots, and Leaves

For THg analysis, approximately 0.1 g of soil samples were weighed into 25 mL colorimetric tubes and digested in a water bath (95°C, 3 h) using 5 mL of aqua regia (HCl/HNO<sub>3</sub> = 3/1, v/v). The solutions were then diluted to 25 ml by Milli-Q water and measured with F732–VJ cold vapor atomic absorption spectrometry (detection limit: 0.05 ng/mL Hg) following SnCl<sub>2</sub> reduction (Chang, Yin, Zhang, & Yao, 2019; Yin, Feng, & Meng, 2013). For plant samples, approximately 0.2 g of rice tissues were digested with 5 mL of HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> (4/1, v/v) in a water bath (95°C, 3 h) and measured with F732–VJ cold vapor atomic absorption spectrometry following BrCl oxidization, Milli-Q water dilution, and SnCl<sub>2</sub> reduction. Standard reference materials (SRMs), such as GBW07405 (yellow-red soil), GBW10020 (citrus leaves) and BCR-482 (lichen), were used to ensure quality control, and the recovery of the three reference materials are averaged at 109 ± 2% (2SD, n = 3), 91 ± 4% (2SD, n = 3), and 87 ± 5% (2SD, n = 3), respectively. The relative standard deviations of THg were all within 5% for sample duplicates.

Paddy water (0–8 cm depth) was sampled before the grain pustulation period in early August. The water samples were filtered (0.45 μm filter membrane, PES, JIN TENG®), transferred to 100 mL borosilicate glass

bottles; 0.5% (v/v) distilled ultra-pure HCl was added, and the solution was preserved in a refrigerator (4°C) under dark conditions. THg concentrations of paddy water samples were determined following BrCl (0.5%, v/v) oxidation, NH<sub>2</sub>OH·HCl neutralization, and SnCl<sub>2</sub> reduction using a dual-stage Au amalgamation method and cold vapor atomic fluorescence spectrophotometer (CVAFS) detection (Tekran 2500, Tekran Inc., Toronto, Ontario, Canada) (USEPA, 2002). The relative standard deviations of THg were within 10% for sample duplicates.

### 2.3. Mercury Isotope Analysis

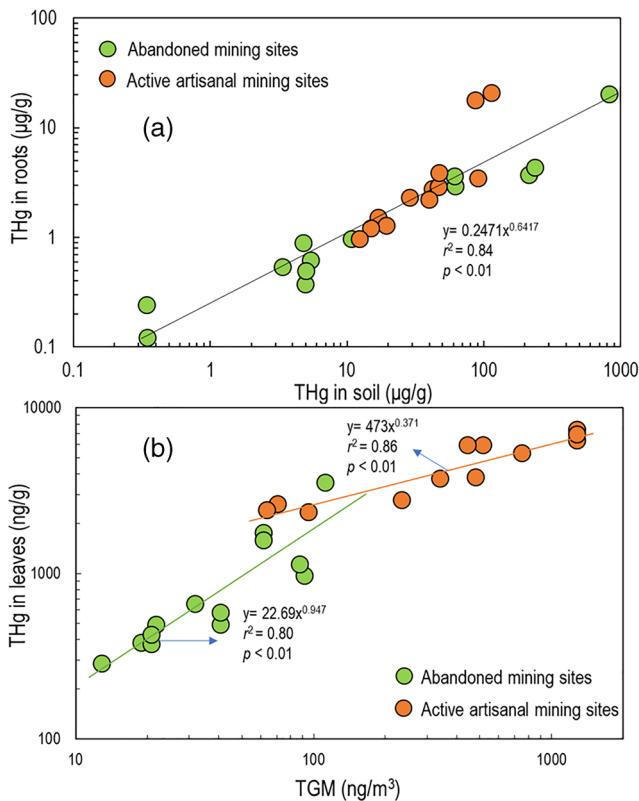
After the samples were digested, the digested solutions were diluted to 0.5 ng/mL Hg by adding a 10% HCl (v/v) solution before Hg isotope analysis using Nu-Plasma II multiple-collector inductively coupled plasma mass spectrometry (Yin et al., 2010). NIST SRM 3133 solution, with the Hg concentration and acid matrices matched to the sample solution, was measured before and after the samples. The  $\delta^{202}\text{Hg}$ ,  $\Delta^{199}\text{Hg}$ ,  $\Delta^{200}\text{Hg}$ , and  $\Delta^{201}\text{Hg}$  values were calculated relative to the NIST SRM 3133 solution, following the protocol by (Bergquist & Blum, 2007). The UM-Almadén secondary standard solution (0.5 ng/mL Hg in 10% HCl (v/v)) was measured in every 10 samples, which yielded average values of  $-0.56 \pm 0.10\text{‰}$ ,  $0.02 \pm 0.08\text{‰}$ ,  $0.02 \pm 0.06\text{‰}$  and  $-0.01 \pm 0.14\text{‰}$  for  $\delta^{202}\text{Hg}$ ,  $\Delta^{199}\text{Hg}$ ,  $\Delta^{200}\text{Hg}$ , and  $\Delta^{201}\text{Hg}$ , respectively (2SD,  $n = 7$ ), consistent with the recommended values (Blum and Bergquist, 2007). The results of BCR 482 ( $\delta^{202}\text{Hg} = -1.70 \pm 0.16\text{‰}$ ;  $\Delta^{199}\text{Hg} = -0.60 \pm 0.08\text{‰}$ ;  $\Delta^{200}\text{Hg} = 0.04 \pm 0.02\text{‰}$ ;  $\Delta^{201}\text{Hg} = -0.65 \pm 0.08\text{‰}$ ; 2SD,  $n = 3$ ) also agree well with those reported in previous studies (Estrade et al., 2010; Wang et al., 2017; Yu et al., 2016). The larger values of standard deviation (2SD) for either UM-Almadén or SRMs are used to reflect analytical uncertainties.

## 3. Results and Discussion

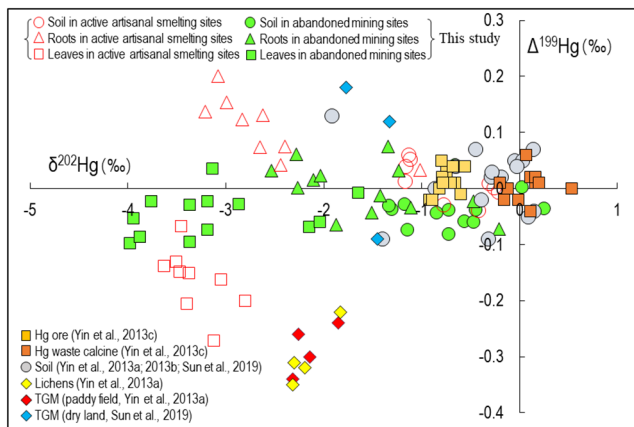
### 3.1. THg Concentrations

Active artisanal smelting sites showed a median TGM of 369 ng/m<sup>3</sup> (range: 64–1,290 ng/m<sup>3</sup>), which is approximately 10 times higher than that at abandoned Hg mining sites (median: 38.8 ng/m<sup>3</sup>; range: 13–113 ng/m<sup>3</sup>). Active artisanal smelting sites showed a median soil THg concentration of 36.8 µg/g (range: 15.0–114.6 µg/g), which is approximately 2.7 times higher than that at abandoned Hg mining sites (median: 13.5 µg/g; range: 0.35–833.7 µg/g) (Chang et al., 2020). Filtered THg in paddy water at active artisanal smelting sites ranges from 5.3 to 107.8 ng/L, with a median value of 43.7 ng/L, which is approximately 3.1 times higher than that at abandoned Hg mining sites (median: 13.9 ng/L; range: 2.4–82.9 ng/L). Soil THg showed positive correlations with filtered THg in paddy water both at abandoned Hg mining sites ( $r^2 = 0.96$ ,  $p < 0.01$ ) and active artisanal smelting sites ( $r^2 = 0.91$ ,  $p < 0.01$ ), indicating that Hg level in paddy water is determined by soil Hg. The higher Hg levels in soil, paddy water, and the atmosphere at active artisanal smelting sites have been attributed to the active artisanal smelting activities, which intensively released Hg to the surrounding environment.

Rice roots and leaves at active artisanal smelting sites also showed higher THg concentrations than those at abandoned Hg mining sites. The median THg concentrations of rice roots and leaves at active artisanal smelting sites are 2.81 µg/g (range: 0.96–20.6 µg/g) and 4.09 µg/g (range: 2.31–7.19 µg/g), respectively, which are approximately 2.5 and 6.3 times higher than those in rice roots (median: 1.13 µg/g; range: 0.12–20.0 µg/g) and leaves (median: 0.65 µg/g; range: 0.24–3.16 µg/g), respectively, at abandoned Hg mining sites (Chang et al., 2020). Some abandoned mining sites show higher THg concentration in soil and roots than those in active artisanal smelting sites (Table S1), due to the impact by Hg waste calcines. At all sites, the root THg positively correlates with the soil THg ( $r^2 = 0.84$ ,  $p < 0.01$ , Figure 2a), which suggests roots mainly take up Hg from the soil although newly deposited Hg is generally more bioavailable than legacy Hg (Branfireun et al., 2005; Zhao et al., 2016). The high correlations between THg concentrations in soil and paddy water mentioned above demonstrate that soil Hg, rather than newly deposited Hg, plays a key role in controlling Hg levels in paddy water. The leaf THg also positively correlates with TGM both at abandoned Hg mining sites ( $r^2 = 0.80$ ,  $p < 0.01$ ) and active artisanal smelting sites ( $r^2 = 0.86$ ,  $p < 0.01$ , Figure 2b), which is consistent with the fact that leaves receive the majority of Hg from the ambient air (Yin, Feng, & Meng, 2013). However, the relationship between Hg in air and leaves for the active Hg smelting sites appears to have a smaller log-log slope than for the abandoned mining sites (Figure 2b), which may indicate a decrease in gaseous Hg uptake by rice in paddies near the more contaminated active artisanal mining sites.



**Figure 2.** THg correlations between rice plant roots and soil (a) and between rice plant leaves and TGM (b) in the Wanshan Mercury Mine region, Guizhou Province, China. TGM, total gaseous mercury.



**Figure 3.**  $\delta^{202}\text{Hg}$  versus  $\Delta^{199}\text{Hg}$  in Hg ore, waste calcine, TGM, soil, roots, leaves and lichens at the Wanshan Mercury Mine. TGM, total gaseous mercury.

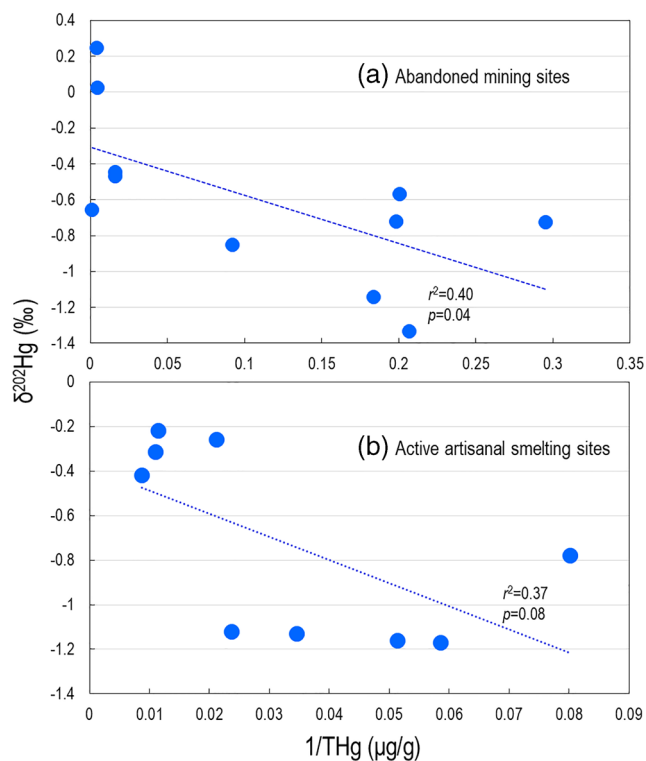
### 3.2. Isotopic Composition of Hg in Soil

As shown in Figure 3, soil collected from abandoned Hg mining sites showed  $\delta^{202}\text{Hg}$  values of  $-1.33$  to  $0.03\text{‰}$  and  $\Delta^{199}\text{Hg}$  values of  $-0.08$  to  $0.04\text{‰}$ , which are similar to those of soils collected from active artisanal smelting sites ( $\delta^{202}\text{Hg}$ :  $-1.17$  to  $-0.22\text{‰}$ ;  $\Delta^{199}\text{Hg}$ :  $-0.04$  to  $0.06\text{‰}$ ). These values are within the range of those previously reported for the WMM soils ( $\delta^{202}\text{Hg}$ :  $-2.38$  to  $0.72\text{‰}$ ;  $\Delta^{199}\text{Hg}$ :  $-0.06$  to  $0.14\text{‰}$ , Figure 3) (Sun et al., 2019; Yin, Feng, & Meng, 2013).

Negative correlations can be observed between  $\delta^{202}\text{Hg}$  and  $1/\text{THg}$  for the soil at abandoned mining sites (Figure 4a,  $r^2 = 0.40$ ,  $p = 0.04$ ) and active artisanal smelting sites (Figure 4b,  $r^2 = 0.37$ ,  $p = 0.08$ ) in WMM, which suggests a mixing of Hg from two sources, the Hg waste calcines and the unroasted Hg ore. We noticed that soil associated with the highest THg concentrations was characterized by higher  $\delta^{202}\text{Hg}$  values of  $\sim 0\text{‰}$ . For instance, soil samples collected near the SK tailing ( $230 \pm 17 \mu\text{g/g}$ ; 1SD,  $n = 2$ ) and the JJC active artisanal smelting waste ( $75 \pm 24 \mu\text{g/g}$ ; 1SD,  $n = 3$ ) have mean  $\delta^{202}\text{Hg}$  values of  $0.14 \pm 0.32\text{‰}$  (2SD,  $n = 2$ ) and  $-0.26 \pm 0.10\text{‰}$  (2SD,  $n = 3$ ), respectively. These values are consistent with previous values of Hg waste calcines in the WMM ( $0.08 \pm 0.20\text{‰}$ , 2SD,  $n = 11$ ) (Yin, Feng, Wang, Li, et al., 2013) and other mining systems in the world (Donovan et al., 2013; Gehrke et al., 2011; Pribil et al., 2020). Hg waste calcines are therefore proposed as an important source end-member of Hg in WMM soil. The other endmember is characterized by a lower  $\delta^{202}\text{Hg}$  of  $\sim -1.3\text{‰}$ , which is close to previous results on the WMM Hg ore ( $\delta^{202}\text{Hg}$ :  $-1.08 \pm 0.2\text{‰}$ ) (X. B. Feng et al., 2010; Yin, Feng, Wang, Li, et al., 2013). Overall, we suggest that the majority of Hg in the WMM soil was originally derived from mining activities; either mine waste calcines or unroasted Hg ore contributed Hg to the soil. The  $\Delta^{199}\text{Hg}$  values of paddy soil ( $-0.04$  to  $0.06\text{‰}$ ) also suggest that Hg was sourced from Hg ores and mine waste because these materials are associated with near-zero  $\Delta^{199}\text{Hg}$  values (Yin, Feng, & Meng, 2013).

### 3.3. Isotopic Composition of Hg in Roots

Rice root samples collected from abandoned Hg mining sites and active artisanal smelting sites showed  $\delta^{202}\text{Hg}$  values of  $-1.57 \pm 1.42\text{‰}$  (2SD) and  $-2.58 \pm 1.30\text{‰}$  (2SD), respectively, which are all significantly lower than those of soil samples (Figure 3). A negative shift of  $-0.87 \pm 0.57\text{‰}$  in  $\delta^{202}\text{Hg}$  was observed from soil to roots collected from abandoned Hg mining sites (Figure 5a). Correlation analysis reveals that the  $\delta^{202}\text{Hg}$  of roots is significantly positively correlated with the  $\delta^{202}\text{Hg}$  of soil ( $r^2 = 0.36$ ,  $p < 0.05$ ) at abandoned Hg mining sites, which is again consistent with the fact that roots receive the majority of Hg from the soil, and roots preferentially take up lighter Hg isotopes from soil (Yin, Feng, & Meng, 2013). However, such a correlation was not found at active artisanal smelting sites ( $r^2 = 0.25$ ,  $p = 0.17$ ), and a larger shift of  $-1.85 \pm 0.57\text{‰}$  in  $\delta^{202}\text{Hg}$  was observed between roots and soil at active artisanal smelting sites (Figure 5a). The weak positive correlations between  $\delta^{202}\text{Hg}$  in soil and roots demonstrate that MDF associated with root uptake is highly variable from plant to plant at each site, it is difficult to collect representative soil samples in heterogeneously contaminated sites, or other factors control the isotopic composition of Hg in roots (e.g., translocation from leaves). The higher shift in  $\delta^{202}\text{Hg}$  between roots and soil at active



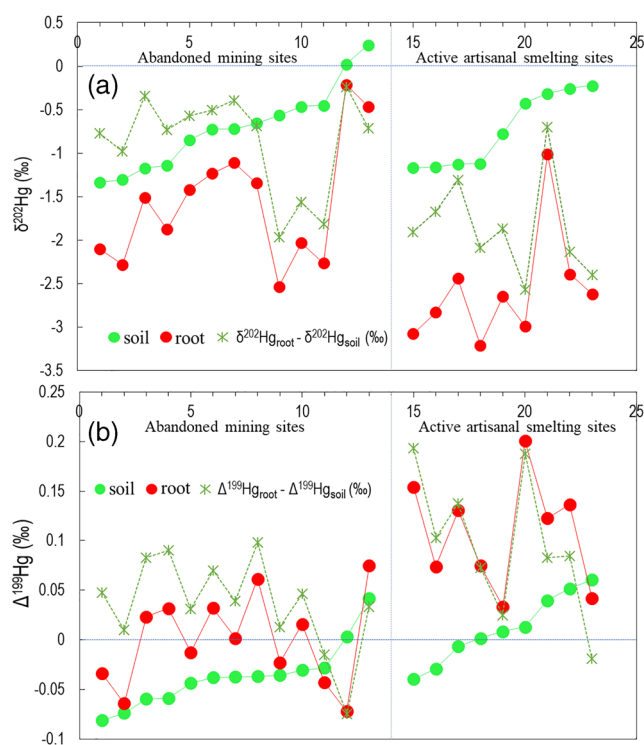
**Figure 4.**  $\delta^{202}\text{Hg}$  versus  $1/\text{THg}$  in paddy soil collected from the Wanshan Mercury Mine (a for abandoned mining sites; b for active artisanal smelting sites).

artisanal smelting sites has also been reported in a previous study (Yin, Feng, & Meng, 2013). Rice roots receive the majority of Hg from the soil; however, not all soil Hg is bioavailable to roots. Among soil Hg species, water-soluble Hg is most bioavailable to roots (Issaro et al., 2009). The difference in the  $\delta^{202}\text{Hg}$  shift between roots and soil at abandoned Hg mining sites and active artisanal smelting sites may be explained by the difference in water-soluble Hg isotope signatures. However, as soil collected from abandoned Hg mining sites and active artisanal smelting sites showed similar Hg isotopic signals, water-soluble Hg in the WMM soil is likely characterized by similar  $\delta^{202}\text{Hg}$  values. This can be supported by a previous study, which reported a consistent  $\delta^{202}\text{Hg}$  of  $0.69 \pm 0.24\text{‰}$  (2SD) in the water-soluble Hg in the WMM soil with a large range of soil THg levels (10–682 µg/g) (Yin, Feng, Wang, Bao, et al., 2013). We therefore hypothesized that the differences in the shift of  $\delta^{202}\text{Hg}$  between roots and soil were caused by different extents of Hg-MDF during the uptake of Hg at abandoned Hg mining sites and active artisanal smelting sites. As roots preferentially take up lighter Hg isotopes, the extent of Hg-MDF during the uptake of water-soluble Hg should theoretically increase when a lower percentage of water-soluble Hg is taken up by roots. This is exactly the case at active artisanal smelting sites. The significantly higher THg concentrations in soil collected from active artisanal smelting sites theoretically should release more water-soluble Hg to paddy water and result in higher THg concentrations in paddy water at active artisanal smelting sites. The THg in paddy water at active artisanal smelting sites is approximately 3.1 times higher than that at abandoned Hg mining sites, whereas the THg in rice roots at active artisanal smelting sites is approximately 2.5 times higher than that at abandoned Hg mining sites, suggesting that less water-soluble Hg was taken up by roots, thereby resulting in a larger shift in  $\delta^{202}\text{Hg}$  between roots and soil.

As shown in Figure 5b, no Hg-MIF was observed in root samples collected from abandoned Hg mining sites ( $\Delta^{199}\text{Hg}$ :  $0 \pm 0.10\text{‰}$ , 2SD); however, root samples collected from active artisanal smelting sites showed slightly positive or no Hg-MIF ( $\Delta^{199}\text{Hg}$ :  $0.11 \pm 0.12\text{‰}$ , 2SD). As the WMM soil lacks Hg-MIF ( $\Delta^{199}\text{Hg} \sim 0\text{‰}$ ), the positive  $\Delta^{199}\text{Hg}$  observed in this study suggests that aqueous Hg(II) photoreduction occurs in paddy water. As mentioned above, soil releases water-soluble Hg species to paddy water. Hg(II) photoreduction readily occurs in paddy water. In a laboratory study, photoreduction of aqueous Hg(II) with an initial  $\Delta^{199}\text{Hg}$  of  $\sim 0$ , in the presence of natural dissolved organic matter (DOM), released gaseous Hg(0) with a negative  $\Delta^{199}\text{Hg}$  signal and left the residue Hg(II) with a positive  $\Delta^{199}\text{Hg}$  (Bergquist & Blum, 2007). In a previous study, TGM samples (which mainly contain Hg(0)) collected above rice paddies in the WMM showed negative  $\Delta^{199}\text{Hg}$  values ( $-0.34\text{‰}$  to  $-0.24\text{‰}$ ), which were attributed to the photoreduction of Hg(II) in paddy water (Yin, Feng, & Meng, 2013). The positive  $\Delta^{199}\text{Hg}$  values of root samples at the active artisanal smelting sites again imply that paddy water was an important source of Hg to rice roots. No significant difference in  $\Delta^{199}\text{Hg}$  was observed between the roots and soil at both abandoned Hg mining sites and active artisanal smelting sites, considering the analytical error of  $\Delta^{199}\text{Hg}$  ( $\pm 0.05\text{‰}$ , 2SD). This is consistent with previous studies demonstrating that no significant Hg-MIF occurs during the uptake of Hg by vegetation (Sun et al., 2019; Yin, Feng, & Meng, 2013).

### 3.4. Hg Isotopic Composition in Rice Leaves

The  $\delta^{202}\text{Hg}$  values of rice leaf samples collected from abandoned Hg mining sites and active artisanal smelting sites are  $-3.11 \pm 1.52\text{‰}$  (2SD) and  $-3.31 \pm 0.51\text{‰}$  (2SD), respectively, similar to previous results for rice leaf samples from the WMM ( $-3.38$  to  $-2.88\text{‰}$ , according to Yin, Feng, & Meng, 2013). These values are much lower than previous results for TGM samples collected in the WMM in 2011 ( $\delta^{202}\text{Hg}$ :  $-2.14 \pm 0.42\text{‰}$ , 2SD, according to Yin, Feng, & Meng, 2013) and 2017 ( $\delta^{202}\text{Hg}$ :  $-1.52 \pm 0.46\text{‰}$ , 2SD, [Sun et al., 2019]). Considering that leaves receive the majority of Hg from the atmosphere, the negative shift in  $\delta^{202}\text{Hg}$  from



**Figure 5.** Mercury isotopic composition (a for  $\delta^{202}\text{Hg}$ ; b for  $\Delta^{199}\text{Hg}$ ) of soil and corresponding rice roots, and their differences between soil and root at individual sites at the Wanshan Mercury Mine.

TGM to leaves suggests that leaves also preferentially take up lighter Hg isotopes from the atmosphere. The preferential uptake of lighter Hg isotopes by vegetation has been suggested by many recent studies (Demers et al., 2013; Enrico et al., 2016; Obrist et al., 2018; Sun et al., 2019; Yin, Feng, & Meng, 2013; Zheng et al., 2016).

The  $\Delta^{199}\text{Hg}$  values of leaf samples are  $-0.05 \pm 0.08\text{‰}$  (2SD) and  $-0.16 \pm 0.12\text{‰}$  (2SD) at abandoned Hg mining sites and active artisanal smelting sites, respectively, indicating slightly negative or no Hg-MIF. As no significant MIF was observed in the WMM Hg ore, Hg waste calcine, and soil (Figure 3), they should not be a direct Hg source for rice leaves. In a previous study, more negative  $\Delta^{199}\text{Hg}$  values were observed in rice leaves ( $-0.37$  to  $-0.14\text{‰}$ ) and TGM ( $-0.34$  to  $-0.24\text{‰}$ ) in the WMM in 2011, which were explained by the photoreduction of Hg(II) in paddy water (Yin, Feng, & Meng, 2013). This would be supported by reverse Hg-MIF signals between rice root and leaf samples. Especially at active artisanal smelting sites, roots showed a positive  $\Delta^{199}\text{Hg}$  ( $0.11 \pm 0.12\text{‰}$ , 2SD), and leaves showed a negative  $\Delta^{199}\text{Hg}$  ( $-0.16 \pm 0.12\text{‰}$ , 2SD). It is believed that soil released a substantial amount of water-soluble Hg to paddy water, and Hg(II) photoreduction in paddy water produced Hg(0) with negative Hg-MIF signals and Hg(II) with positive Hg-MIF signals in the residual in paddy water. Rice roots receive a substantial amount of Hg(II) from paddy water, whereas rice leaves take up a substantial amount of Hg(0) emitted from paddy water; therefore, they are characterized by positive and negative Hg-MIF signals, respectively.

According to this study, a larger offset of  $\sim 0.27\text{‰}$  in  $\Delta^{199}\text{Hg}$  was observed between rice roots and leaves at active artisanal smelting sites, whereas the offset was much smaller at abandoned Hg mining sites ( $\sim 0.05\text{‰}$ ), indicating different extents of Hg(II) photoreduction in paddy water between abandoned Hg mining sites and active artisanal smelting sites.

Different extents of Hg(II) photoreduction result in variable degrees of Hg-MIF. Among different rice paddies, the photoreduction of Hg(II) in paddy water is thought to be variable because Hg photoreduction in paddy water is controlled by many factors, such as water clarity, water depth, and the geochemical fate of paddy water (e.g., TOC and pH). In this study, abandoned Hg mining sites were irrigated by the Dashuixi River, whereas active artisanal smelting sites were irrigated by the Gouxi River (Figure 1). Given Hg(II) photoreduction was governed by Hg and DOM concentrations (Bergquist & Blum, 2007), differences in Hg and DOM concentrations between the two rivers may be an important reason for the differences in Hg(II) photoreduction in paddy waters. In this study, the exact reason for the differences in Hg(II) photoreduction between abandoned Hg mining sites and active artisanal smelting sites will not be discussed because detailed information about paddy water was not collected during the growing season.

#### 4. Conclusions and Environmental Implications

Mercury isotopes can be a robust tool to reveal details about the biogeochemical cycling of Hg in rice paddy ecosystems. A previous study investigated the isotopic composition of Hg rice tissues and demonstrated that  $\Delta^{199}\text{Hg}$  values of root and leaf are similar to that of soil and atmospheric Hg, respectively, which suggest that vegetation takes up Hg from soil and atmosphere by root and leaf, respectively (Yin, Feng, & Meng, 2013; Yin, Feng, Wang, Bao, et al., 2013; Yin, Feng, Wang, Li, et al., 2013). Meanwhile, the much lower  $\delta^{202}\text{Hg}$  values in plant tissues compared to soil and atmospheric Hg, suggesting Hg-MDF could occur during the uptake of soil and atmospheric Hg by root and leaf, respectively (Yin, Feng, & Meng, 2013; Yin, Feng, Wang, Bao, et al., 2013; Yin, Feng, Wang, Li, et al., 2013). In this study, we demonstrated that different degrees of Hg-MDF can occur during the uptake of soil Hg by rice roots at different sites, which can be seen by the negative shifts in  $\delta^{202}\text{Hg}$  between root and soil at abandoned Hg mining sites ( $-0.88 \pm 0.57\text{‰}$ ) and active artisanal smelting sites ( $-1.85 \pm 0.57\text{‰}$ ). We also demonstrated that soil releases water-soluble Hg

into paddy water, which can be photoreduced. Hg(II) photoreduction not only generates negative Hg-MIF signals in gaseous Hg(0), which can be recorded in rice leaves, but also leaves positive Hg-MIF signals in paddy water, which is taken up by rice roots. However, we caution that the photoreduction of Hg(II) may be highly variable among rice paddies, resulting in different extents of Hg-MIF in rice roots and leaves. Although the reason was not well explored in this study, we suggested that the Hg-MIF in rice paddies may be affected by water chemistry. As this study was based on field research, many factors were overlooked due to time considerations, and we expect to perform further laboratory studies to better investigate how the water chemistry (e.g., TOC and pH) will affect the extent of Hg-MIF in rice plants.

### Data Availability Statement

Data sets of this research can be found in a public domain repository (<http://www.dx.doi.org/10.11922/sciencedb.00474>).

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