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A new method of predicting the contribution of TGM to Hg in white rice: Using leaf THg and implications for Hg risk control in Wanshan Hg mine area☆

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ABSTRACT

Rice plants accumulate Hg from the soil and ambient air, however, evaluating the contribution of Hg from these two sources remains challenging. Here, we proposed a practical method to predict the contribution of total gaseous mercury (TGM) to Hg in white rice in Wanshan Hg mine area (WMM). In this study, rice was planted in the same low-Hg soil at different sites of WMM with varying TGM levels. Comparing to the control sites at IG (Institute of Geochemistry, Guiyang), TGM is the dominant source of Hg in rice leaves and white rice at TB (Tianba) and ZJW (Zhangjiawan) sites of WMM. Subsequently, a good correlation between the Hg concentrations in rice leaves and the concentration contributions of TGM to Hg in white rice was obtained. Such a correlation enabled feasible quantification of the contribution of TGM to Hg in white rice collected from the Wanshan Hg mine. The contribution of TGM to Hg in white rice across the WMM area was also estimated, demonstrating that white rice receives 14–83% of Hg from the air. Considering the high contribution of TGM to Hg in white rice, we compared the relative health risks of Hg via inhalation and rice consumption and found that inhalation, rather than rice consumption, was the major pathway for bioaccessible Hg exposure in adults at high-TGM sites. This study provides new knowledge of Hg biogeochemistry in Hg-mining areas.

1. Introduction

Mercury (Hg), a globally distributed pollutant is attracting increasing attention due to its toxicity to humans and ecosystems (Beckers and Rinklebe, 2017; Castoldi et al., 2001; Driscoll et al., 2013; Natasha et al., 2020; Wolfe et al., 1998; Zhang et al., 2017). Hg pollution has been aggravated since global industrialization, as anthropogenic activities emitted massive Hg to the environment (Jiang et al., 2006; Lindberg et al., 2007; Zhang and Wong, 2007). Traditionally, consumption of fish is regarded as the principal pathway of human Hg exposure for people (Li et al., 2014; Mergler et al., 2007). However, as a staple for more than 60% of humans, rice is known as another important Hg exposure source to humans, especially in Hg-contaminated areas (Feng et al., 2008; Zhang et al., 2010).

In Hg mining areas, soil, water, and atmosphere are usually seriously polluted by Hg (Ao et al., 2020; Brocza et al., 2019; Chang et al., 2020; Li et al., 2012; Niane et al., 2019; Sherman et al., 2012). The Wanshan Hg mine (WMM), located in Guizhou Province, China, is the third-largest Hg mine in the world. The mining history of WMM can be traced back to the Qin dynasty, 2000 years ago (Zhang et al., 2012). Hg in WMM has been extensively mined and released into the surrounding environment since the 1950s (Feng and Qiu, 2008). A recent study reported extremely high soil Hg levels (0.35–833.7 mg/kg) and total gaseous Hg (TGM) level (13–1287 ng/m^3) in the WMM area (Chang et al., 2020). Rice is a major crop grown in WMM and faces a risk of Hg pollution. IHg (inorganic Hg) including HgS, is the major form of Hg in paddy soil of WMM (Wang et al., 2020; Liu et al., 2019) and elemental Hg (Hg^0) is the dominant species of Hg in the air (Wang et al., 2007). Rice plants take up

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Hg from the soil and ambient air via root and leaf, respectively (Yin et al., 2013; Chang et al., 2021), and subsequently cause bioaccumulation of IHg and MeHg (methylmercury) in rice grains. It has been reported that IHg in rice grains mainly originates from soil and air while MeHg is from the soil (Liu et al., 2021; Qin et al., 2020). The TGM levels in WMM generally exceeded 50 ng/m^3, hence, the air may contribute substantial amounts of Hg to rice. The consumption of Hg contaminated rice has caused some damage to local residents, especially children (Feng et al., 2020). It is necessary to quantify the contribution of air Hg source to rice grains so that further remediation efforts can be appropriately carried out. Mercury stable isotopes have been used as a useful tool to trace the source of THg in rice grains. A previous study demonstrated that around 20% of THg in white rice originated from the ambient air in DSX (Dashuixi) and GX (Gouxi) sites (Figure S1) of WMM (Yin et al., 2013). However, the Hg isotope tracing method is often challenging to many Hg research groups, due to the lack of multiple collectors inductively coupled plasma mass spectrometry (MC-ICP-MS) that Hg isotope analysis required.

In a recent study, we reported the THg levels of rice grain (15–450 ng/g) in the WMM area (Chang et al., 2020). A positive correlation between Hg in rice grains and soil was not found in WMM (Chang et al., 2020; Meng et al., 2010). Interestingly, we further demonstrated a significant positive correlation between the THg levels in leaves and white rice (Chang et al., 2020), which implies that it may be possible to predict the Hg concentration levels in rice grains using the leaf THg. As rice leaf receives the majority of Hg from the ambient air (Qin et al., 2020; Yin et al., 2013), in this study, we conducted pot experiments to study whether the contribution of TGM to Hg in white rice can be predicted, by referring to the relationship between THg in leaves and white rice. Rice plants cultivated in the same low-Hg paddy soil under varying TGM conditions were analyzed. The study aims to develop a practical method to estimate the TGM or soil Hg contributions to total Hg (THg) in white rice across various WMM sites. We expect that the practical application of this study will be of use to guide Hg remediation and risk control in WMM.

2. Materials and methods

2.1. Experimental design

Pot experiments involving rice plant cultivation in the same paddy soil were performed at sites with low, moderate, and high TGM levels at the Institute of Geochemistry (IG, in Guiyang), Tianba (TB, in WMM), and Zhangjiawan (ZJW, in WMM) of Guizhou province, China, respectively, in summer of 2018 (Figure S1). Briefly, the IG and TB sites did not show evident atmospheric Hg pollution sources, but active Hg chemical plants were located near the ZJW site with a high TGM level. The TGM concentrations at the IG, TB, and ZJW sites were measured 3 times in July, August, and September, for longer than 30 min each time. The TGM concentrations were measured using an automated Hg vapour analyzer (LUMEX, RA-915 a.m., Russia). The geomean values of TGM were 11.2, 10.4, and 8.1 ng/m^3 in July, August, and September respectively for IG site; but for TB sites, it was 26.3, 33.3, and 23.9 ng/m^3 respectively; and for ZJW sites, that was 1695.2, 3854.4, and 576.9 ng/m^3 respectively. The geomean value of these three measured data were taken as the real TGM level at the experimental sites.

The paddy soil was collected from Enshi, the low Hg area in central China, and has THg concentration of 389 ± 16 ng/g. The soil was fully mixed and passed through a 4-mm sieve before use in the pot experiments. Storage boxes, 45 cm × 34 cm × 30 cm in size, each containing ~20 kg of paddy soil, were used for rice growth (Chang et al., 2020). The experimental soil was flooded about 10 days in advance before rice planting. Rice seedlings of the same batch, cultivated in the laboratory under hydroponic conditions, are about 4 weeks old before we planted them in each experimental box (n = 3). Rice and rhizosphere soil samples were harvested from each site and quickly transported to the lab at the maturity stage of rice. The soil samples were freeze-dried (−79 °C), crushed, homogenized, and passed through a 200-mesh screen. The rice plants were separated into different ground tissues (stem, leaf, and grain) and rigorously washed with tap water and 18.2-MΩ water (Milli-Q® Integral System). The ground rice tissues were also freeze-dried (−79 °C), and the grain samples were further separated into husks, bran, and white rice. The rice tissue samples were finely ground into powder with a grinding machine (IKA®A11 basic). Before each plant sample was processed into powder, the machine was carefully cleaned with 95% alcohol to avoid cross-contamination (Chang et al., 2020). All powder samples were sealed in polyester plastic bags and stored at room temperature for further chemical analysis.

2.2. Mercury concentration analysis

For rice samples, approximately 0.2 g of rice tissue was digested in 5 mL of HNO_3 in a water bath for 3 h and then measured with Tekran 2500 cold vapour atomic fluorescence spectroscopy (detection limit: 0.1 pg Hg) and F732−VJ cold vapour atomic absorption spectrometry (Shanghai Huaguang Instrument Factory; detection limit: 0.05 ng/mL Hg) instruments following a previous method (USEPA, 1999). Approximately 0.2 g of a given soil sample was digested in a water bath (95 °C, 3 h) in 5 mL of aqua regia (HCl/HNO_3 = 3/1, v/v) and measured with the F732−VJ cold vapour atomic absorption spectrometry instrument (Li et al., 2005). Standard reference materials, GBW07405 (yellow-red soil) and GBW10020 (citrus leaf), and sample replicates were included in the THg analysis. The recoveries of THg for GBW07405 and GBW10020 were 103 ± 6% (n = 3) and 108 ± 7% (n = 3), respectively. The relative standard deviations of the Hg content in all duplicate samples were all within 10%. Additionally, the mercury and selenium concentrations in soil sites across the WMM area (Figure S1) are based on our previous work (Chang et al., 2020) and directly used for further analysis in this study.

2.3. The ratios of tissue Hg to soil Hg

The ratios of tissue Hg to soil Hg were calculated with the following expression: C_{tissue}/C_{soil}, where C_{tissue} is the Hg concentration of the rice tissue and C_{soil} is the Hg concentration of the corresponding rhizosphere soil.

2.4. Statistical analysis

Correlation coefficients (r^2) and significance probabilities ($p > 0.05$: insignificant; $p < 0.05$: significant; $p < 0.01$: very significant) were computed for the attained regression fits. Graphical analyses were performed with Origin 2020 and Microsoft Office 2013.

3. Results and discussion

3.1. Hg bioaccumulation in rice at the various TGM sites

The TGM level at the IG site averaged 9.6 ng/m^3, slightly higher than the background level in the Northern Hemisphere (1.5–1.7 ng/m^3) (Sprovieri et al., 2010). The THg concentration in the ground tissues at the IG site decreased in the following order: leaf (59.0 ± 3.0 ng/g) > stem (11.2 ± 2.2 ng/g) > bran (10.5 ± 0.1 ng/g) > white rice (3.1 ± 0.2 ng/g). The Hg concentration of the white rice at the IG site was much lower than the Chinese maximum limit for Hg in rice (20 ng/g, GB 2762–2017). Correspondingly, the ratios of tissue Hg to soil Hg followed the order of leaf (0.15 ± 0.009) > stem (0.028 ± 0.005) > bran (0.027 ± 0.001) > white rice (0.0077 ± 0.0003). Stable Hg isotope studies have demonstrated that Hg in rice tissue of stem and leaf are majorly originated from the air, even in the Hg-polluted soil sites of WMM (Qin et al., 2020; Yin et al., 2013). The much lower Hg concentrations and ratios of tissue Hg to soil Hg for the rice tissues at IG sites may still indicate that

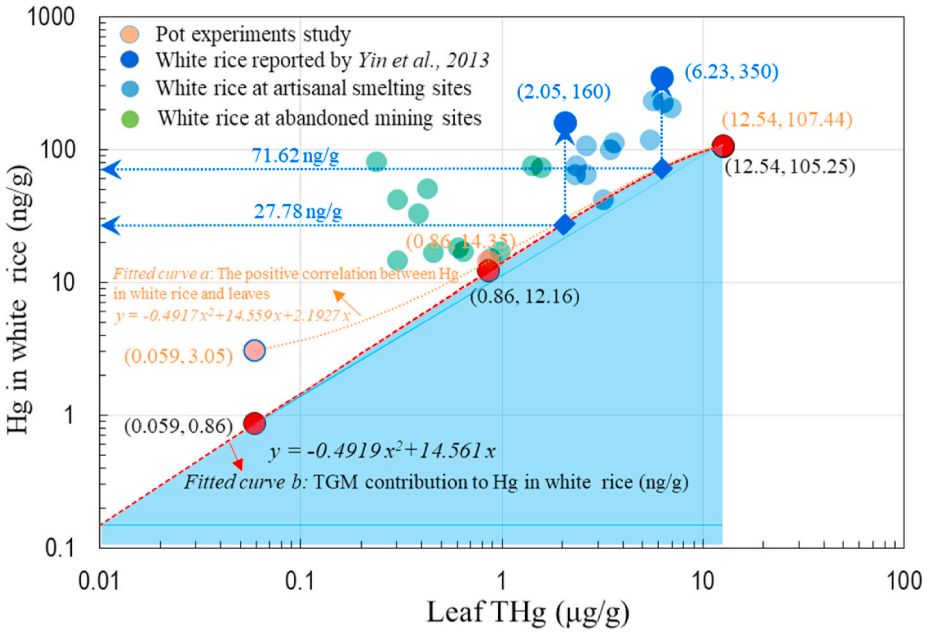

Fig. 1. Establishment and verification of the targeted equation that simulating concentration contributions of TGM to white rice.

Hg in the soil is less translocated to aerial parts. The stable Hg isotope labeling experiments (Cui et al., 2014; Strickman and Mitchell, 2017; Liu et al., 2021) have proved the weaker capacity of Hg translocation from rhizosphere to aerial parts. Many factors, such as Hg content, Hg speciation, microbial community, organic matter, presence of other elements (e.g., Se or S), may affect the Hg uptake and translocation processes by rice plants (Beckers et al., 2019; O'Connor et al., 2019; Li et al., 2019; Tang et al., 2019; Tang et al., 2020; Zhao et al., 2020; Natasha et al., 2020; Wu et al., 2020; Xing et al., 2020).

The TGM level at the TB site averaged 27.9 ng/m^3, which is 10 times higher than that in the Northern Hemisphere. The Hg concentrations of the rice tissues at the TB site decreased as follows: leaf (859.4 ng/g) > stem (142.1 ng/g) > bran (91.8 ng/g) > white rice (14.4 ng/g). The THg concentration in white rice at TB was slightly lower than the Chinese maximum limit for Hg in rice (20 ng/g). The ratios of tissue Hg to soil Hg of the rice tissues show a following decreasing order: leaf (2.13) > stem (0.35) > bran (0.23) > white rice (0.04). The Hg level in the rice leaves at the TB site was 14.6 times higher than that at the IG site, followed by the stem (12.7 times), bran (8.7 times) and white rice (4.7 times). Given that Hg in the rhizosphere is hardly transported upward, the elevated TGM should be responsible for the Hg increase in the ground rice tissues (leaf, stem, bran and white rice) at the TB site.

Although the TGM levels could be affected by many factors (During et al., 2009; Rinklebe et al., 2010; O'Connor et al., 2019), the TGM at the ZJW site was extremely high (range: 24–23,842 ng/m^3, average: 1556 ng/m^3) due to the extensive Hg emissions from the chemical plants nearby. The Hg concentrations of the rice tissues at the ZJW site decreased in the following order: leaf (12538.7 ± 995.6 ng/g) > bran (1643.5 ± 44.5 ng/g) > stem (1525.0 ± 10.4 ng/g) > white rice (107.4 ± 3.3 ng/g). Notably, Hg concentrations of the white rice at the ZJW site significantly exceeded the Chinese maximum limit for Hg in rice (20 ng/g). The ratios of tissue Hg to soil Hg of the rice tissues followed the order of leaf (23.68 ± 2.79) > bran (3.26 ± 0.73) > stem (2.89 ± 0.45) > white rice (0.20 ± 0.01). The Hg levels in the ZJW leaf samples was 212.5 times higher than that at the IG site, followed by the bran (156.5 times), stem (136.2 times) and white rice (35.2 times); At the TB site, it is summarized in the following order: bran (17.9 times), leaf (14.6 times), stem (10.7 times) and white rice (4.7 times). These results demonstrated that a high TGM level could cause notable Hg bioaccumulation in ground rice tissues. The significantly higher Hg levels in the leaves than those in the other tissues indicate that the leaves are the most sensitive rice tissue to the varied TGM level. Furthermore, it can be inferred that the potted soil Hg contributes very minor Hg to white rice, whereas atmospheric Hg, contributing IHg to white rice, is the dominant source contributor at both TB and ZJW sites.

3.2. Predicting the TGM contribution to white rice

As air is the dominant source contributor of IHg in white rice at both TB and ZJW sites, it is possible to determine the IHg content that the air contributed to the white rice, given the observed positive correlation in THg between white rice and leaves in this experimental study (Fig. 1, fitted curve a: $y = -0.4917\ x^2 + 14.559\ x + 2.1927\ x$). Based on the fitted curve a, we can approximately infer that the concentration contribution of potted background soil Hg to white rice is 2.19 ng/g (x = 0 μg/g, y = 2.19 ng/g), accounts for 72% of THg in white rice at IG site. To optimize the simulated results, we deducted the concentration contribution value of the experimental low-Hg soil to white rice (2.19 ng/g), and thus the concentration contributions of IHg contributed by TGM to white rice at the IG, TB and ZJW sites are 0.86, 12.16, and 105.25 ng/g, respectively (Fig. 1, the red dots). In practice, the contribution of TGM to white rice is 0 when leaf Hg level is 0 under ideal conditions. Consequently, the targeted equation is then established based on the relationship between the Hg concentration in rice leaves and the TGM concentration contribution to white rice (Fig. 1, fitted curve b: $y = -0.4919\ x^2 + 14.561\ x$). In the targeted equation, $y = -0.4919\ x^2 + 14.561\ x$, x and y represent the Hg concentration in the rice leaves and the corresponding concentration contribution of TGM to white rice respectively (Fig. 1). The established targeted equation indicates that the source contribution of TGM to white rice can be predicted by directly measuring the THg in leaves and white rice in the WMM. To assess the accuracy of this equation, white rice varieties with known TGM contribution ratios (estimated by the Hg isotope tracer method) sampled at two WMM sites by Yin et al. (2013) were considered (Fig. 1, the two blue dots). By substituting the leaf Hg concentrations (2.05 and 6.23 μg/g) of these two rice varieties in the targeted equation, the TGM contribution to white rice was then calculated (27.78 and 71.62 ng/g, respectively, Fig. 1). The predicted contribution ratios (%) of TGM to the total Hg concentration in white rice were calculated to be 17.4% and 20.5%, respectively, which are close to the results estimated

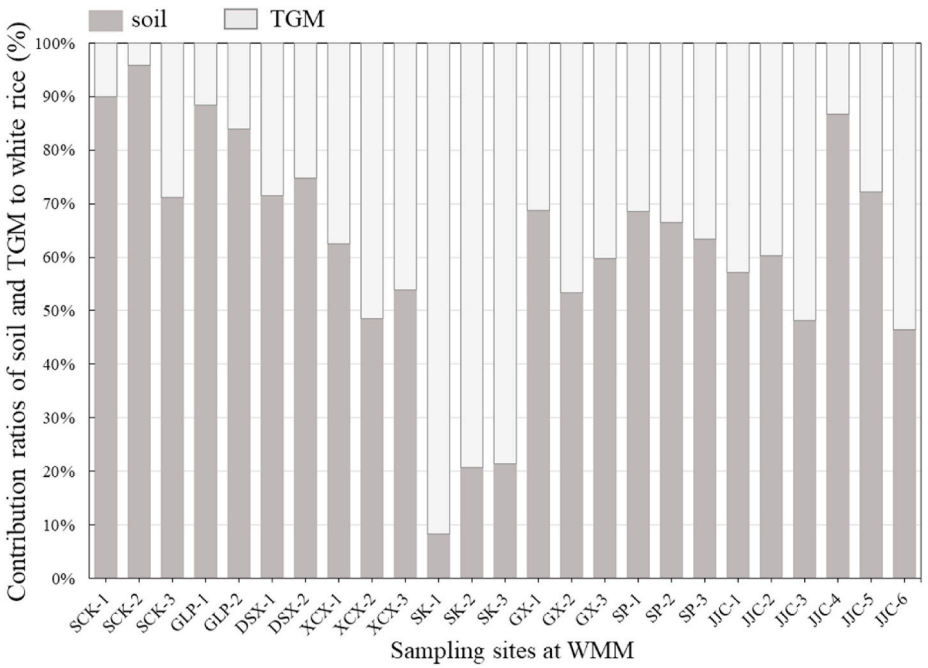

Fig. 2. Contribution ratios of TGM and soil Hg to Hg in white rice across WMM.

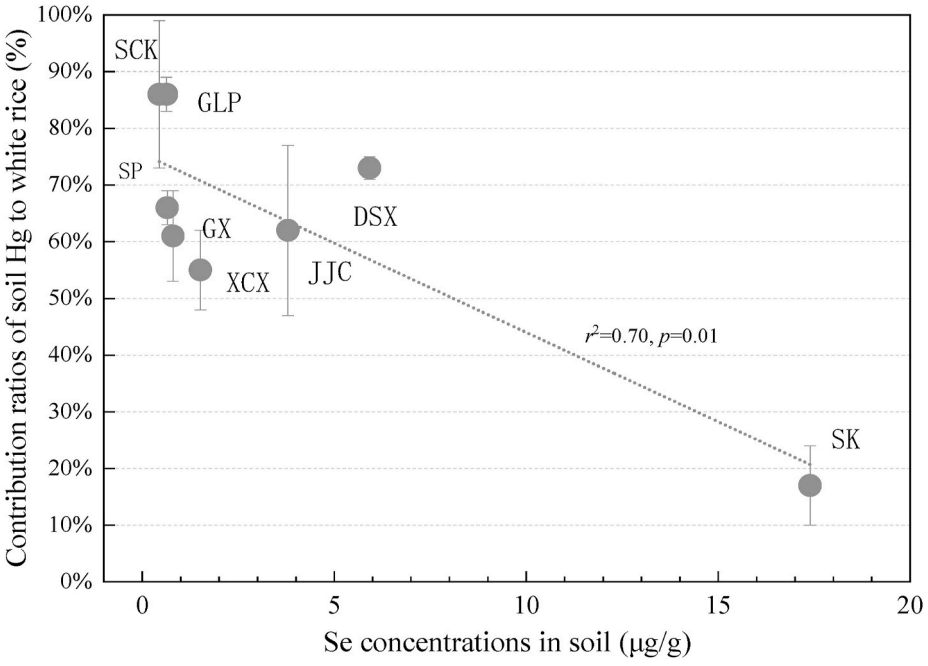

Fig. 3. Impact of soil Se on contribution ratios of soil Hg to Hg in white rice.

with the Hg isotope tracer method (22.6 ± 3.6% and 20.5 ± 0.7%, respectively), confirming the robustness of the equation proposed above in predicting the TGM contribution to white rice.

3.3. *Understanding the TGM and soil Hg contributions to white rice in the WMM area*

The contributions of the TGM and soil Hg to white rice are conveniently ascertained with the established targeted equation regarding rice in the WMM area. Here, previously published rice Hg concentration data determined at 25 sampling sites by Chang et al. (2020) were adopted to better understand the source contributions of TGM and soil Hg to THg in white rice across the WMM area. As shown in Fig. 2, the soil Hg contribution ratios (%) to white rice greatly varied among the different sites with averages of 86 ± 13%, 86 ± 3%, 73 ± 2%, 55 ± 7%, 17 ± 7%, 61 ± 8%, 66 ± 3%, and 62 ± 15% at the SCK (Shencongkou), GLP (Gaolouping), DSX (Dashuixi), XCX (Xiachangxi), SK (Sikeng), GX (Gouxi), SP (Supeng), and JJC (Jinjiachang) sites of the WMM (Figure S1), respectively. The large variation in the soil contribution ratios ($p < 0.01$, *t-test*) may explain why no positive correlations were found between the soil Hg and rice Hg levels in the WMM area. It is worth noting that the soil Hg contribution ratios to white rice reached 86% at the SCK and GLP sites, whereas it only amounted to 17% at the SK site, which may indicate a high Hg mobility in the soil-rice system at

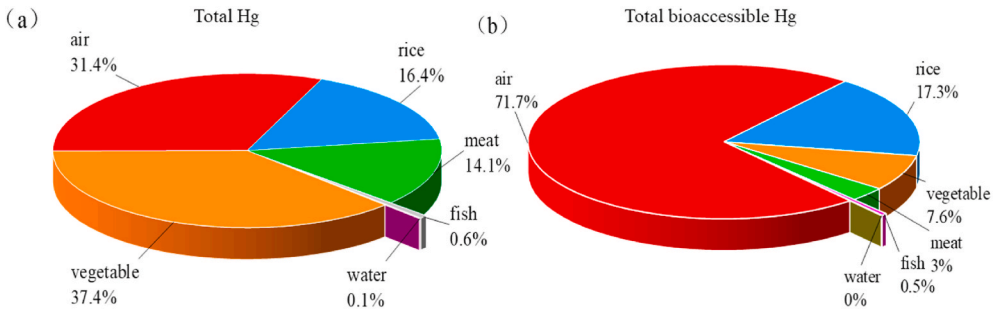

Fig. 4. Percentages of estimated THg (a) and total bioaccessible Hg (b) intake from different media for people at the high-TGM sites.

the SCK and GLP sites but a low Hg mobility at the SK site. We hypothesize that the high soil selenium (Se) level in the WMM area might lead to the difference mentioned above. Previous publications have confirmed that Se greatly decreases the soil Hg bioavailable level and inhibits Hg translocation from the soil to aerial parts due to the high binding affinity of Se with Hg in the rhizosphere (Li et al., 2015; Tang et al., 2016; Wang et al., 2016; Zhang et al., 2012; Zhao et al., 2014; Zhao et al., 2020). Notably, a significant negative correlation between the soil Se and Hg contribution ratios to white rice was observed ($r^2 = 0.79$, $p < 0.01$, Fig. 3), confirming that the soil Se may greatly affect the soil Hg contribution ratios to white rice, especially significant at the SK site, where the soil Se level reached 21.7 μg/g (mean: 17.4 ± 5.3 μg/g; > 3 μg/g is generally defined as an excessive level). We infer that strong Se–Hg interactions may occur at the SK site.

3.4. Concern about the potential Hg exposure risk at high-TGM sites

The Hg exposure risk has always been a matter of concern and the main Hg sources for humans strongly depend on the locations and the dietary habits (Driscoll et al., 2013). The occurrence of the Minamata disease incident in Japan was related to the consumption of fishery products with high MeHg caused by the discharge of Hg-containing industrial wastewater (Bjorklund et al., 2019). Additionally, human activities such as artisanal gold mining, can also pollute the surrounding environment (water, air) and result in fish contaminated by Hg, increasing the intake risk of Hg by the local duo to their habit of eating fish (Mason et al., 2019). However, a previous study shows that the consumption of rice is the major pathway of human Hg exposure, and the Hg in the air (~93 ng/m^3) only accounts for 2% of the total Hg intake for residents in the WMM area (Zhang et al., 2010). Given the highly elevated TGM level of ~1556 ng/m^3 at the ZJW site affected by Hg-related chemical plants, we hypothesize that the Hg intake through inhalation may be surprisingly high. Additionally, due to the much higher bioaccessibility of elemental Hg (Hg^0, ~80%) than that of IHg (~7%) in the human body (WHO, 1990), the associated Hg risk should be re-examined to deeply reflect its potential threat to human health. In this study, we approximately assessed the potential total Hg and total bioaccessible Hg intake levels from different media. As detailed in Table S1, the THg intake is ~99.15 μg/day (equal to ~1.65 μg/kg bw/day, 60 kg weight) at the high-TGM sites, which is significantly higher than the provisional tolerable weekly intake (PTWI) of 4 μg/kg bw/week (equal to 0.57 μg/kg bw/day) (JECFA, 2010), potentially suggesting an uncommon risk for the people living nearby Hg-related chemical plants. Further analysis indicates that the Hg intake via inhalation accounts for 31.4% of the THg intake, much higher than that generally occurring at average TGM levels (only 2%, at 93 ng/m^3) (Zhang et al., 2010), indicating that inhalation and vegetable consumption might be the major pathways of THg exposure for residents (Fig. 4a). It is worth mentioning that the total bioaccessible Hg intake from different sources is reported for the first time here, according to the varied bioaccessibility levels of the different Hg forms to humans. The bioaccessible Hg intake reaches ~34.71 μg/day at the high-TGM site (ZJW), which is equivalent to 0.58 μg/kg bw/day, coincidentally similar to the PTWI. A new finding, as shown in Fig. 4b, is that the daily bioaccessible Hg intake via inhalation contributes approximately 24.9 μg/day, accounting for 71.7% of the total bioaccessible Hg intake, revealing that inhalation, not rice consumption, is the major pathway of the daily bioaccessible Hg intake for people at the high-TGM sites. The high TGM can not only contribute much IHg to rice grains and increase the Hg intake risk of people via rice consumption but also elevate elemental Hg inhalation of people at high-TGM sites directly. Therefore, much more caution and actions should be implemented to avoid the potential damage of the high TGM to the human body.

4. Environmental implications and conclusions

This study proposed a practical method to predict the TGM contribution to white rice in the WMM area. It yields some advantages over the previous Hg isotope tracing method, because it operates conveniently and gets rid of the dependence on the high-end instruments of MC-ICP-MS. By establishing the correlation between the THg concentrations in rice leaves and the concentration contributions of TGM to Hg in white rice, we can roughly estimate the TGM and soil Hg contributions to white rice, thus enabling further environmental control and remediation. Based on the new method introduced by the study, we can conclude that leaf THg concentration determination is a feasible and convenient way to predict the TGM contribution to white rice in the WMM area. We encourage researchers to conduct more field research to put this idea into practice. Furthermore, the TGM and soil that contribute Hg to white rice greatly vary across the WMM area. Thus different remediation strategies need to be implemented at different sites. The Hg risk assessment indicates that air and vegetables are the most important exposure media in terms of the THg intake, and inhalation is the major exposure pathway of the total bioaccessible Hg intake for people at the studied high-TGM sites.

Author statement

Chuanyu Chang: Conceptualization, Methodology, Software, Data curation, Funding, Writing – original draft preparation, Writing-Reviewing and Editing. Runsheng Yin: Writing- Reviewing and Editing. Fang Huang: Funding, Writing- Reviewing and Editing. Ruirui Wang: Writing- Reviewing and Editing. Chongying Chen: Writing- Reviewing and Editing. Kang Mao: Writing- Reviewing and Editing. Xinbin Feng: Writing- Reviewing and Editing. Hua Zhang: Funding, Writing-Reviewing and Editing.

Notes

The authors declare no competing financial interest.

Declaration of competing interest

The authors declare that they have no known competing financial

interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2021.117727.

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