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Accumulation of total mercury and methylmercury in rice plants collected from different mining areas in China

Mei Meng [a], Bing Li [b], Jun-juan Shao [a], Thanh Wang [a], Bin He [a], Jian-bo Shi [a,*], Zhi-hong Ye [c], Gui-bin Jiang [a]

[a] State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China
[b] Ecological Civilization Construction Committee of Guiyang, Guiyang Research Academy of Environmental Sciences, Guiyang 550002, China
[c] State Key Laboratory for Bio-control and Guangdong Key Laboratory of Plant Resources, School of Life Sciences, Sun Yat-sen University, Guangzhou 510006, China

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ABSTRACT

A total of 155 rice plants were collected from ten mining areas in three provinces of China (Hunan, Guizhou and Guangdong), where most of mercury (Hg) mining takes place in China. During the harvest season, whole rice plants were sampled and divided into root, stalk & leaf, husk and seed (brown rice), together with soil from root zone. Although the degree of Hg contamination varied significantly among different mining areas, rice seed showed the highest ability for methylmercury (MeHg) accumulation. Both concentrations of total mercury (THg) and MeHg in rice plants were significantly correlated with Hg levels in soil, indicating soil is still an important source for both inorganic mercury (IHg) and MeHg in rice plants. The obvious discrepancy between the distribution patterns of THg and MeHg reflected different pathways of IHg and MeHg accumulation. Water soluble Hg may play more important role in MeHg accumulation in rice plants.

1. Introduction

As a global pollutant, mercury (Hg) exists in various environmental media and transforms among a variety of species in nature. The toxicity of Hg is closely related to its chemical forms (Clarkson, 1998). As the most toxic Hg compound, methylmercury (MeHg) can be considerably accumulated in the aquatic food web, leading to fish at higher trophic levels with 10^6 times higher Hg concentrations than ambient water (WHO, 1990; Stein et al., 1996; USEPA, 1997a). Seafood consumption is usually considered to be the primary route of human MeHg exposure (Clarkson, 1993). Studies have found that MeHg levels in human hair were positively correlated with fish consumption (Holsbeek et al., 1996; Al-Majed and Preston, 2000; Santos et al., 2002). However, recent studies in Guizhou province of China showed that consumption of rice grown at Hg mining areas was the main MeHg exposure pathway to local residents (Feng et al., 2008; Zhang et al., 2010a). Generally, total Hg (THg) levels in most foodstuffs are below the maximum permissible limit in China of 20 μg kg^{-1} d.w. for crops (GB 2762-2005; Meng et al., 2011). But the study in Wanshan found that THg levels in rice could reach up to 569 μg kg^{-1}, of which 145 μg kg^{-1} occurred in MeHg form (Horvat et al., 2003). Rice serves as the staple food for over half the world's population (FAO, 2006), and therefore intake of contaminated rice could result in a potential health threat to humans.

Significant MeHg accumulation in rice has currently drawn increased international attention. Initial reports mostly focused on the determination of Hg levels in rice and the assessment of human exposure risk through rice intake. Elevated MeHg concentrations were reported in rice collected from Wuchuan, with the results revealing that air inhalation was the main inorganic Hg (IHg) exposure route, while rice intake was the main MeHg exposure route (Qiu et al., 2006; Li et al., 2008a). Later studies found that MeHg in rice in Wanshan was about 2–3 orders of magnitude higher than that in the edible portion of other local crop plants, implying that the accumulation of MeHg in rice was high (Qiu et al., 2008). Some other Hg mining areas in Guizhou province have also been investigated, such as Qingzhen (Horvat et al., 2003; Søvik et al., 2011), Lanmuchang (Wang et al., 2005), Tongren (Li et al., 2011) and Danzhai (Feng and Qiu, 2008), but to a less extent compared to Wanshan and Wuchuan. Although large-scale Hg

* Corresponding author.
E-mail address: jbshi@rcees.ac.cn (J.-b. Shi).

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mining activities in these mines have been officially ceased, small-scale and artisanal Hg or gold smelting activities have revived since a few years ago due to the increase of Hg price in the Chinese market (Feng et al., 2008). To date, few studies have been conducted on rice plants in other Hg mining provinces in China other than Guizhou province. The possible pathways of MeHg accumulation have been recently discussed in several publications. On average, the bioaccumulation factors of MeHg in rice grain could be over 800 times higher than those of IHg (Zhang et al., 2010b). Most of MeHg are firstly accumulated in the leaf and stalk parts and then transferred to seed during the ripening period (Meng et al., 2010, 2011). MeHg was also found to be mainly enriched in the endosperm whereas IHg was mostly located in the rice bran layer (Rothenberg et al., 2011). However, investigations on MeHg accumulation mechanisms in rice plants are still quite limited, and the dynamic processes of MeHg absorption, transformation and translocation remains largely unknown.

As known, Hg in soil occurs in various forms that can be bound to different matrix phases and these matrix phases vary upon mobility, bioavailability and potential toxicity (Issaro et al., 2009). Therefore, THg has been regarded as a poor indicator for the toxicological and environmental hazards of Hg contamination in soil. Normally, water soluble Hg (Hg-w) is highly soluble, easily available to biota, and might serve as a main substrate for the methylation of IHg (Wallschlager et al., 1998; Boszke et al., 2006; Covelli et al., 2009). Studies in Wanshan have revealed a serious Hg contamination in local soil, with THg levels reaching up to 130,000 μg kg^{-1} (Lin et al., 2010). Since paddy fields are shallowly flooded during the rice growing season, Hg-w may play an important role in methylation and accumulation of Hg in paddy fields. Unfortunately, this has been ignored in most previous studies.

In order to better understand the potential pathways of IHg and MeHg accumulation in rice plants, we emphasized our study on the following two aspects: (1) water soluble Hg (Hg-w) in soil from the root zone was measured to explain the bioavailability and accumulation process of Hg; (2) sampling areas were expanded to three provinces to verify the variation and consistency of THg and MeHg accumulation. The distribution patterns, possible sources and accumulation pathways of THg and MeHg in rice plants were discussed in detail. The results from this study could provide further information for better understanding the accumulation mechanism of Hg into rice plants.

2. Materials and methods

2.1. Sampling sites description

China is rich in Hg reserve, ranking the third in the world (Feng et al., 2008). Guizhou, Hunan and Guangdong provinces are three of the most important Hg producing areas in China. Moreover, rice is the major crop in these provinces and serves as staple food. In this work, ten typical mining sites were selected for sampling, among them five sites in Guizhou, including Danzhai (DZ), Lanmuchang (LMC), Tongren (TR), Wanshan Sikeng (WS) and Wanshan Wukeng (WS5), four sites in Hunan, including Dongping in Baojing (BJ) county, Chatian Chanshula (CSL), Chatian Jijian (JJ) and Niudouping (NDP) in Fenghuang county (with these three close to each other), and one Hg-contaminated mining site in Guangdong, that is, Fankou (FK) Pb/Zn mining site. Fig. 1 shows the map of the study regions.

Guizhou province is located at the center of the circum-Pacific mercuriferous belt (Gustin et al., 1999; Qiu et al., 2006). The total cinnabar deposit in this province represents approximately 70% of the total in China (Qu, 2004). Hg mining activities in Guizhou have introduced large amounts of uncontrolled gangues and mine tailings. As a result, crops grown at these Hg mining areas contained elevated Hg (Feng et al., 2008a; Qiu et al., 2008). Wanshan was once the largest conglomeration of Hg mines and refining plants in China (Lin et al., 2010). Several studies have reported rather high concentrations of Hg in different environmental media of this area (Horvat et al., 2003; Qiu et al., 2005; Lin et al., 2010). DZ, LMC and TR are all large Hg mines in Guizhou, but few studies have been reported on Hg accumulation in rice plants grown in these areas. Western Hunan province also situates an Hg belt, ranking the fifth largest in China. Chatian Hg mining deposit (CMD) is the most important mine in this Hg belt, with a long history of Hg mining. Previous studies have reported heavy Hg pollution in Pb/Zn mine area located in adjacent town in Fenghuang County (Li et al., 2007). Guangdong province is another important Hg producing area. Fankou Pb/Zn mine in Shaoguan city is the largest geological reserved mining area in Asia. As Hg is a major associated element in zinc ores, zinc smelting has led to serious Hg pollution (Li et al., 2008b). Studies showed that Hg levels in soils and vegetables of this mine exceeded the Chinese National Standard (GB 15618-1995; GB 2762-2005) by 32.3% and 9.4%, respectively (Wang et al., 2012).

2.2. Sample collection and pretreatment

During rice harvest season in 2010, a total of 155 rice plants were collected from the ten mining areas. Whole rice plant together with soil samples from the root zone (10–20 cm in depth) were collected from the first four sites, DZ ($n = 11$), WS ($n = 21$), LMC ($n = 15$) and FK ($n = 18$). Parts of rice plant (seed and husk, $n = 15$) as well as corresponding soil samples ($n = 15$) from the root zone were collected from each of the other six sites, BJ, CSL, JJ, NDP, TR and WS5. In all sampling sites, each sample was

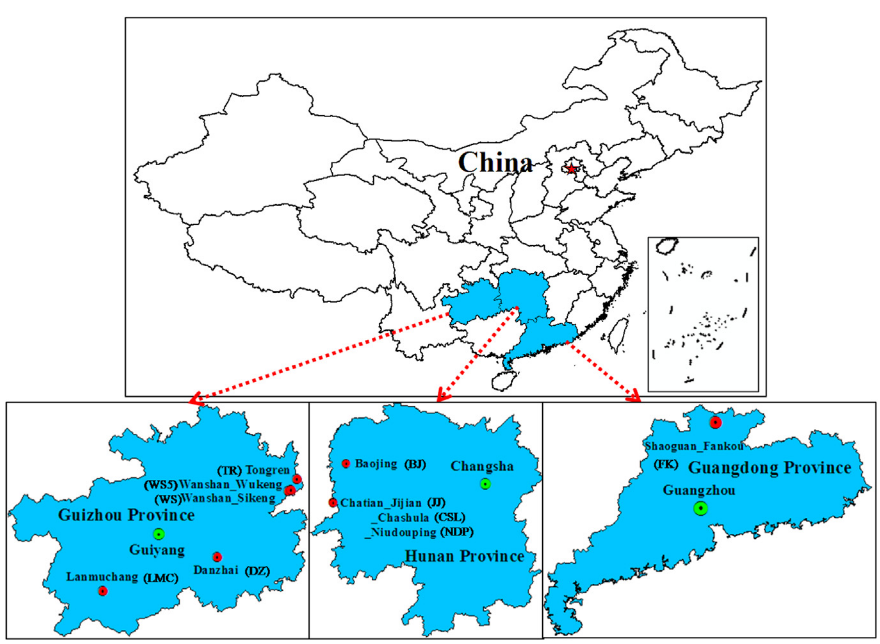

Fig. 1. Map of study regions. (●) indicates a sampling site.