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Total mercury and methylmercury accumulation in wild plants grown at wastelands composed of mine tailings: Insights into potential candidates for phytoremediation☆

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ABSTRACT

Total mercury (THg) and methylmercury (MMHg) were investigated in 259 wild plants belonging to 49 species in 29 families that grew in heavily Hg-contaminated wastelands composed of cinnabar ore mine tailings (calcines) in the Wanshan region, southwestern China, the world's third largest Hg mining district. The bioconcentration factors (BCFs) of THg and MMHg from soil to roots ($[THg]_{root}/[THg]_{soil}$, $[MMHg]_{root}/[MMHg]_{soil}$) were evaluated. The results showed that THg and MMHg in both plants and soils varied widely, with ranges of 0.076–140 μg/g THg and 0.19–87 ng/g MMHg in roots, 0.19–106 μg/g THg and 0.06–31 ng/g MMHg in shoots, and 0.74–1440 μg/g THg and 0.41–820 ng/g MMHg in soil. Among all investigated species, *Arthraxon hispidus, Eremochloa ciliaris, Clerodendrum bunge, and Ixeris sonchifolia* had significantly elevated concentrations of THg in shoots and/or roots that reached 100 μg/g, whereas *Chenopodium glaucum, Corydalisedulis maxim, and Rumex acetosa* contained low values below 0.5 μg/g. In addition to the high THg concentrations, the fern *E. ciliaris* also showed high BCF values for both THg and MMHg exceeding 1.0, suggesting its capability to extract Hg from soils. Considering its dominance and the tolerance identified in the present study, *E. ciliaris* is suggested to be a practical candidate for phytoextraction, whereas *A. hispidus* is identified as a potential candidate for phytostabilization of Hg mining-contaminated soils.

1. Introduction

Mercury (Hg) is a highly toxic trace element that can be accumulated and biomagnified at high trophic levels via food chains (Lindqvist, 1991; Clarkson, 1993; Lindberg et al., 2007; Xia et al., 2010). The toxicity and mobility of Hg are dependent on its chemical forms in the environment. Methylmercury (MMHg), an organic form produced by anaerobic bacteria acting on inorganic Hg (IHg) under certain conditions, is the most toxic Hg species because of the accumulation and biomagnification in biota (WHO, 1990). Compared with other Hg forms, MMHg is effectively taken up and absorbed by organisms, with bioconcentration factors (BCFs) ranging from 10^4 to 10^7 (Stein et al., 1996), thereby posing an increased risk to human health and wildlife. The Minamata disease that occurred in Japan was caused by the consumption of fish and other seafood contaminated by MMHg.

Mercury mines are one of the persistent anthropogenic Hg sources to the environment. Historic mining and retorting of cinnabar ores release much elemental Hg (Hg^0) and water-soluble Hg compounds into nearby surroundings (e.g. Gray et al., 2004; Qiu et al., 2005, 2013), and may also generate numerous wastelands composed of Hg-enriched mine tailings (calcines) adjacent to abandoned retorts and adits. In China, significant quantities of Hg-enriched wastelands are found in the Wanshan Hg mining region, the largest national metallic Hg products center in Guizhou Province, of which cinnabar ore mining and retorting activities may date back to 221 BCE. Mercury concentrations in the calcines have been recorded as high as 4400 μg/g (Qiu et al., 2005), which are continuously releasing Hg downstream in the region. Hence, the

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wastelands that are composed of amounts of calcines have become major Hg sources to the surrounding ecosystems after the Hg mines have been abandoned for several decades (Gosar and Žibret, 2011; Tomiyasu et al., 2012), releasing Hg^0 and secondary Hg compounds via natural weathering and runoff into air, soil, and water that enter biota (Kocman et al., 2011).

Previous studies show that plant roots can uptake Hg from soil and transfer it to shoots, but the efficiency largely depends on the Hg form and its bioavailability in the soil solution (Baya and Van Heyst, 2010; Millán et al., 2006; Pérez-Sanz et al., 2012; Lu et al., 2016). Bioavailable Hg in soils varies with time and is usually operationally defined by various laboratory extraction procedures (Beckers and Rinklebe, 2017). Extractants such as water, ammonium thiosulfate, and neutral salts supposedly quantify the so-called bioavailable Hg fraction in soils (e.g. Menzies et al., 2007; Frohne and Rinklebe, 2013; Fernández-Martínez and Rucandio, 2013; Zhu et al., 2015). Generally, the highly toxic MMHg species are more easily taken up and transferred by roots from soils to shoots than IHg (Bishop et al., 1998; Gnamuš et al., 2000; Schwesig and Krebs, 2003; Rajan et al., 2008; Shiyab et al., 2009). Plants can also uptake Hg^0 from the atmosphere by direct adsorption through the leave stomata (Patra and Sharma, 2000), or via foliar uptake from atmospheric deposition (Millhollen et al., 2006). The process of Hg^0 reemitting from leaves to the atmosphere can also occur (Fay and Gustin, 2007). Total mercury (THg) concentrations in plants from uncontaminated control sites are usually less than 0.1 μg/g (Lindqvist et al., 1991), but are abnormally high in plants growing in abandoned Hg-mining regions (Higueras et al., 2006; Zhao et al., 2014; Fernández-Martínez et al., 2015). Therefore, under such conditions, plants may act as a significant pathway through which Hg enters terrestrial ecosystems. The evaluation of Hg, particularly MMHg accumulation, in plants from Hg-mining areas is of great concern.

Within the last decade, THg and MMHg in soils, surface waters, and crops, in addition to Hg^0 in the atmosphere, have been widely characterized in the study area of the Wanshan Hg mine (e.g., Horvat et al., 2003; Qiu et al., 2005, 2009; Dai et al., 2013; Yin et al., 2016). Nevertheless, presently, few studies have been conducted regarding the effect of Hg on vegetation (Wang et al., 2011, 2012), particularly the wild species growing vigorously at Hg-enriched wastelands. The biomonitoring of THg and MMHg in the study area has concentrated mostly on agricultural crops consumed by humans, such as rice (Qiu et al., 2008, 2012a, b; Zhang et al., 2010), with a general lack of attention directed to THg and MMHg in naturally dwelling plants, which are likely playing an important role in Hg biomagnification in local terrestrial food chains (Abeysinghe et al., 2017). Therefore, the concentrations of both THg and MMHg in the wild plant species must be determined. Furthermore, if the species that effectively accumulate THg and/or MMHg can be identified, those species could be candidates for phytoremediation of Hg-contaminated soil.

To obtain primary information on the concentrations of THg and MMHg in the plant species growing at Hg-enriched wastelands in the Wanshan mining region was the aim of the present work. We also estimated the soil-to-root transfer efficiency of THg and MMHg in plant species to contribute to the understanding of THg and MMHg in the plant-soil ecosystem. Finally, species were evaluated for their feasibility for phytoremediation of Hg-contaminated soil.

2. Materials and experimental methods

2.1. Study area

The Wanshan District (109°07′–109°24′E; 27°24′–27°38′N) is in eastern Guizhou Province, southwestern China (Fig. 1). The annual average temperature and precipitation are 13.4 °C and 1300 mm, respectively. The agrotypes consist of yellow, red, and paddy soils. The primary minerals in the Wanshan Hg mine are cinnabar, metacinnabar, and elemental Hg. The cinnabar ore is associated with sphalerite, pyrite, and stibnite. Intensive cinnabar ore mining and retorting in Wanshan occurred for 630 years and ceased in 2004 (Qiu et al., 2005). Large quantities of mine-waste calcines were introduced into the surrounding area, producing substantial wastelands. Because of inefficient retorting processes, mine-waste calcines are enriched in secondary Hg compounds, such as metacinnabar, Hg sulfide, Hg chloride, Hg oxide, and elemental Hg, which are water-soluble and can be readily released into nearby sites via leaching processes (Biester et al., 1999; Kim et al., 2004). Because of the large reserves of cinnabar ores and elemental Hg outputs, Wanshan once was termed the “Mercury Capitol” of China.

Four wastelands, Wukeng (WK), Sikeng (SK), Shibakeng (SBK), and Gouxi (GX), were selected for the investigation of THg and MMHg in wild plants. The wastelands of SK, WK, and SBK experienced long-term, intensive cinnabar ore mining and retorting. In brief, SK is 0.8 km southwest of the town of Wanshan, and approximately 31.33 million cubic meters of mine-waste calcines were introduced nearby. WK is 2.5 km northeast of Wanshan, and approximately 44.5 million cubic meters of mine-waste calcines were introduced nearby. SBK is 2.5 km north of Wanshan, and approximately 2.83 million cubic meters of mine-waste calcines were introduced nearby. GX is an abandoned artisanal cinnabar ore mining and retorting site and used a mercuric chloride catalyst to recycle Hg. Calcines and catalyst wastes were observed at the sampling sites. All sampled areas were of barren wastelands, which were away from the water and characterized by alkaline pH, drought and high concentrations of Hg.

2.2. Sampling and analyses

2.2.1. Sampling of plants and soils

2.2.1.1. Plants and corresponding rhizosphere soil sampling. Plants were randomly collected from the wastelands of WK, SK, SBK, and GX during April 5–8, 2015, using a regular sampling grid of 5 m × 5 m. Within each sampling unit, a final sample consisted of three individuals of the same species and similar size. A total of 259 samples were collected during the sampling campaign. After collection, plant samples were in situ separated into roots and aerial shoots using stainless scissors after being washed with water from rivers adjacent to the sampling site. All roots and shoots were separately put into polyethylene bags and stored in coolers (+4 °C) and then shipped to the laboratory within 24 h. In the laboratory, all samples were thoroughly washed with tap water and then cleansed three times with deionized water (DI). An ultrasonic cleaning machine (JP040S; Shenzhen, China) was applied during the DI washing process to exclude adsorption of fine particles on plant tissues. Before grinding to a fine powder, the samples were lyophilized at −50 °C. All powdered samples were stored in polyethylene bags and sealed until analysis.

Corresponding rhizosphere soil of plants were simultaneously collected and stored in polyethylene bags to avoid cross contamination. In the laboratory, soil samples were air-dried at room temperature and then ground in a ceramic disc mill through a 200 mesh for analysis.

2.2.1.2. Plant diversity survey. A quadrat of 1.0 m × 1.0 m was selected for the plant species diversity survey. For each wasteland, a total of 10 quadrats were selected randomly to record individual numbers of all species. The total number of a plant species found in one quadrat was considered the “$Individual\ Plant\ Species_{number}$,” and the total number of quadrats that had a similar plant species was