Distribution and geochemical speciation of soil mercury in Wanshan Hg mine: Effects of cultivation

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ABSTRACT

The distribution and speciation of mercury (Hg) were investigated in contaminated soils collected from two adjacent land use systems (arid land and rice paddy) near the Wanshan Mercury mine, SW China. In both sites, fine soil aggregate size fractions (<231 μm) showed higher total Hg concentrations and higher soil organic matter contents than in larger aggregate size fractions (231 to 2000 μm). Compared to arid land, paddy soils are characterized by higher proportions of fine soil aggregates, higher soil organic matter and higher total Hg content. Soil Hg speciation, based on X-ray absorption spectroscopy (XANES) analysis, indicated that the majority (64–81%) of Hg in soils under both land use systems was associated with metacinnabar (β-HgS), indicating the precipitation of β-HgS in soils. We also observed the presence of bioavailable $HgCl_2$ and Hg(0) in soils at both sites, which may represent a considerable environmental concern. Our study clearly showed that different cultivation practices can largely change the distribution and speciation of Hg in agriculture soils.

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1. Introduction

Mercury (Hg) is an important pollutant due to its global distribution, bioaccumulation and toxicity (Yin et al., 2014). Mercury contamination is a widespread problem due to the increasing anthropogenic emissions and deposition of Hg to soils (Li et al., 2009; Yin et al., 2012). The mobility, bioavailability and toxicity of Hg in soils are strongly dependent on chemical speciation (Stein et al., 1996). Mining sites are "hotpots" of soil Hg contamination. The roasting process (500–800 °C) during Hg refining liberates elemental Hg(0) from Hg ores (Yin et al., 2013a) and produces gangue materials and waste calcines. Like Hg ores, gangue materials mainly contain cinnabar (α-HgS) and waste calcines contain secondary Hg phases such as metacinnabar (β-HgS), mercuric chloride ($HgCl_2$), Hg sulfates, and Hg oxides (Kim et al., 2000). In Hg mining areas, soil contamination is mainly derived by leaching Hg from tailings and deposition of Hg(0) emitted from the roasting facilities and tailings. Studies of speciation of Hg in soils from mining-impacted areas have identified mainly mercuric sulfides with minor Hg salts (e.g., $HgCl_2$) and Hg(0) present (Schuster, 1991; Fernández-Martínez et al., 2006; Rimondi et al., 2014). Soluble Hg salts are more easily transported and

typically serve as the substrate for Hg(II) reduction and methylation during various biological and abiotic processes. Methylmercury (MeHg) only represent a small fraction of the total Hg in soils, whereas it is a more toxic species and can be bioaccumulated in the food chains (Akagi and Nishimura, 1991).

The Wanshan Mercury Mine District (WMMD) is the largest historic Hg-producing district in China (Fig. 1). Long-term mining activities in WMMD have produced roughly 125.8 million tons of mine wastes, which are mainly consisted of the roasted calcines and gangue materials (Jiang et al., 2006). Mercury in mine waste has been eroded and transported to local soils (Zhang et al., 2004; Qiu et al., 2005). Contaminated soils in WMMD in turn are currently being utilized in paddy rice and arid land cropping practices (e.g. corn) (Qiu et al., 2008). This integrated cropping system has the potential to create changes in the physical, chemical and bacterial properties of the soil, which may affect the distribution and speciation of Hg, and potentially cause differences in MeHg production in the soils (Roulet et al., 1998, 1999; Farella et al., 2007). Relatively high levels of MeHg have been reported in rice paddies compared to arid land cropping soils (Kelly et al., 1997; Rothenberg et al., 2011). A recent study in WMMD demonstrated much higher MeHg concentrations in rice (up to 100 μg kg^{-1}), 10–100 fold higher than that of other arid land plants (e.g. corn, conola, tobacco and cabbage) (Qiu et al., 2008). Understanding the effect of contrasting

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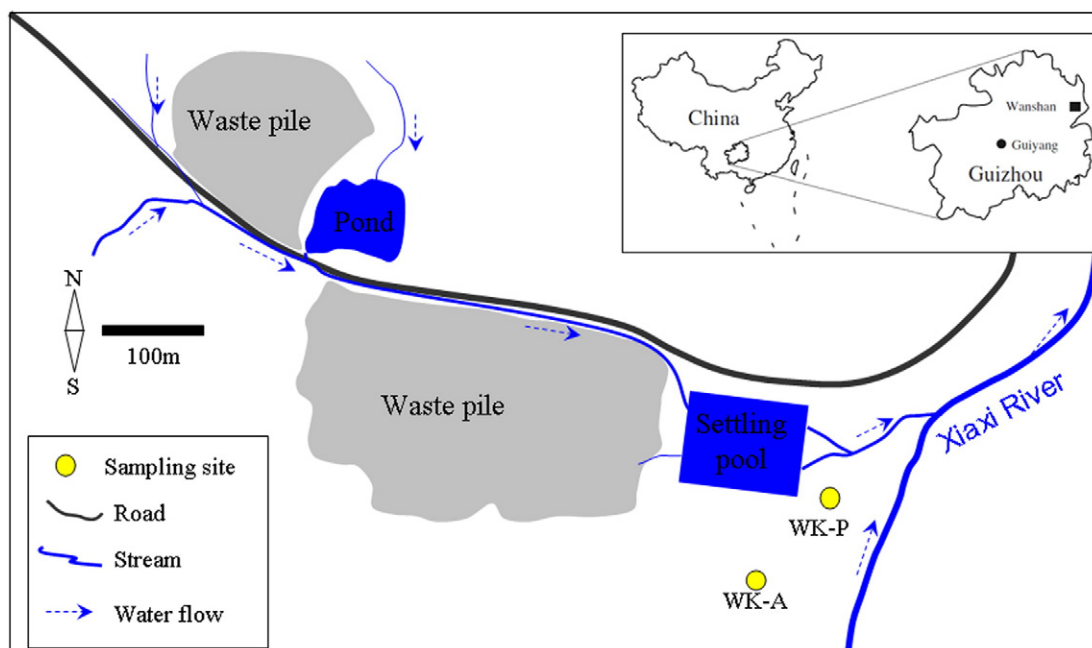 E-mail address: fengxinbin@vip.skleg.cn (X. Feng).

Fig. 1. Sampling locations of sites in the Wanshan Mercury Mining District.

cultivation practices on soil Hg distribution and speciation is important in evaluating food Hg safety.

Chemical speciation of Hg in solids has been investigated using sequential extraction (Chadwick et al., 2013), solid-phase-Hg-thermo-desorption (Biester et al., 1999) and X-ray absorption spectroscopy (XANES) (Kim et al., 2000; Gray et al., 2004, 2006; Jew et al., 2010). Among those methods, XANES is well known by its direct and non-destructive advantages (Kim et al., 2000; Gray et al., 2004, 2006; Jew et al., 2010). Utilizing XANES, our previous study reported large differences in Hg speciation in two of the most important Hg contamination sources, roasted calcines and unroasted Hg ore, in WMMD (Yin et al., 2013a, 2013b, 2013c). However, contaminated soils in WMMD with different agricultural cultivation practices have not been investigated by XANES. This study then investigated the hypothesis that an alternating sequence of paddy rice and dry land cropping will affect changes in the distribution and speciation of Hg in soil. Soil samples collected from both rice and arid land cropping farmlands in WMMD were analyzed for total Hg (THg) and utilized EXAFS analysis to understand speciation and the relationship to cultivation practices in this historically-contaminated Hg mining region.

2. Materials and methods

2.1. Study sites and sampling

The WMMD is located in Guizhou Province, SW China (Fig. 1). Large-scale mining activities ceased at WMMD in 2001. Due to long-term Hg mining activities during the past hundreds of years, Hg waste tailings are widespread (Jiang et al., 2006), and leading to serious Hg contamination of the surrounding environment (Zhang et al., 2004; Qiu et al., 2005, 2008; Zhang et al., 2010; Yin et al., 2013a, 2013b, 2013c). This study chose sites near the Wukeng (WK) pile, which is seated at the head of the Xiaxi Stream, due to its proximity to two adjacent farmlands (sites WK-P and WK-A). The WK-P is a paddy field which is used for rice planting using water from upstream on the Xiaxi stream. The WK-A site, with a relative higher elevation (~4 m higher) than the WK-P, is a dry cropping farmland used mainly for corn.

At each site, approximately 2 kg of composite soil was collected into plastic bags prior to the laboratory processing. In the laboratory, soil samples were air dried, gently crushed to disaggregate larger clumps

(which did not significantly alter the aggregate size distribution), and sieved through a 2 mm nylon sieve to remove stones, coarse materials, and other debris. Samples were then stored in polyethylene bags. A portion of the sieved soils were ground to <150 µm by an agate grinder for THg analysis of the bulk soils.

2.2. Sieve analysis for soil aggregate size distribution

Approximately 500 g of the remaining air-dried 2-mm sieved soils was weighed and progressively passed through nine sieves (with 10, 20, 40, 60, 80, 120, 140, 180 and 200 mesh) (Gee and Bauder, 1986). The bulk soil samples were then separated into nine aggregate size fractions: 2000–850 µm (midpoint: 1425.0 µm), 850–389 µm (midpoint: 619.5 µm), 389–231 µm (midpoint: 310.0 µm), 231–180 µm (midpoint: 205.5 µm), 180–125 µm (midpoint: 152.5 µm), 125–105 µm (midpoint: 115.0 µm), 105–90 µm (97.5), 90–75 µm (midpoint: 82.5 µm) and <74 µm (midpoint: 37.5 µm). The weight of each aggregate size fraction was recorded and the loss of sample mass during the separation processes was no more than 2% of the total mass. The mass percentage of each aggregate size fraction within the bulk soil was calculated. Sieved soil fractions were then homogenized using a ZrO_2 homogenizer (01467-AB, SPI Supplies®), and stored in plastic bags for soil organic matter (SOM) content, THg concentration and Hg speciation analysis.

2.3. Soil organic matter content and total mercury concentration analysis

SOM contents in all sieved soil fractions were determined by reduction of Cr_2O_7(-II) by organic C and subsequent determination of unreduced Cr_2O_7(-II) by oxido-reduction titration with Fe(II) (Nelson and Sommers, 1982). THg in bulk soil and soil size fractions were analyzed by a Lumex RA 915$^+$ Hg analyzer (Lumex Ltd., Russia). The detection limit for THg was 0.5 ng g^{-1}. Quality control for THg analysis was addressed using certified reference material (NIST SRM 2710, Montana Soil I), with an average recovery of 98.0 ± 1.4% (2σ, n = 5). The enrichment factors (EFs) of Hg in each aggregate size fraction with respect to bulk soil was calculated as EF = THg$_{fraction}$/THg$_{bulk}$, where THg$_{fraction}$ and THg$_{bulk}$ were the concentrations of THg in a given aggregate size fraction and the bulk soil sample, respectively.