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Effects of soil properties on production and bioaccumulation of methylmercury in rice paddies at a mercury mining area, China

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ABSTRACT

Rice paddy soil is recognized as the hotspot of mercury (Hg) methylation, which is mainly a biotic process mediated by many abiotic factors. In this study, effects of key soil properties on the production and bioaccumulation of Hg and methylmercury (MeHg) in Hg-contaminated rice paddies were investigated. Rice and soil samples were collected from the active Hg smelting site and abandoned Hg mining sites (a total of 124 paddy fields) in the Wanshan Mercury Mine, China. Total Hg (THg) and MeHg in soils and rice grains, together with sulfur (S), selenium (Se), organic matter (OM), nitrogen (N), phosphorus (P), mineral compositions (*e.g.*, SiO_2, Al_2O_3 and Fe_2O_3) and pH in soils were quantified. The results showed that long-term Hg mining activities had resulted in THg and MeHg contaminations in soil-rice system. The newly-deposited atmospheric Hg was more readily methylated relative to the native Hg already in soils, which could be responsible for the elevated MeHg levels in soils and rice grains around the active artificial Hg smelting site. The MeHg concentrations in soils and rice grains showed a significantly negative relationship with soil N/Hg, S/Hg and OM/Hg ratio possibly due to the formation of low-bioavailability Hg–S(N)–OM complexes in rhizosphere. The Hg–Se antagonism undoubtedly occurred in soil-rice system, while its roles in bioaccumulation of MeHg in the MeHg-contaminated rice paddies were minor. However, other soil properties showed less influence on the production and bioaccumulation of MeHg in rice paddies located at the Wanshan Mercury Mine zone.

Introduction

Mercury (Hg), especially methylmercury (MeHg), is highly toxic and has a large capability to be bioaccumulated and biomagnified in food webs. Inorganic Hg (IHg), undergoing biotic and abiotic processes, can be transformed to MeHg, which poses a potential threat to human and wildlife health (Ullrich et al., 2001). It is commonly believed that the consumption of fish is the main MeHg exposure to humans (Mergler et al., 2007). Recently, higher MeHg levels were found in rice (*Oryza sativa L.*) than other crops

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(*e.g.*, corn and wheat), and studies indicated that rice paddies were hotspots for Hg methylation (Meng et al., 2014; Zhang et al., 2010a). As rice is a staple food for most populations in the world, MeHg bioaccumulation in rice is becoming a new concern, especially to inland inhabitants who seldom eat fish (Meng et al., 2010, 2014; Zhang et al., 2010a).

Previous reports showed that rice is a bioaccumulator of MeHg, which is mainly derived from paddy soils (Meng et al., 2010; Zhang et al., 2010a). The distribution of MeHg in rice tissues is different from IHg, and is usually greater in grains than other tissues (Meng et al., 2010; Zhang et al., 2010a). The formed MeHg in rhizosphere can be readily adsorbed into roots, where MeHg is combined with protein, polysaccharide and nucleic acid, and then is transferred to grains during the ripening period (Meng et al., 2011). However, phytochelatins present in the roots can more effectively chelate Hg(II) than MeHg, which prevents the divalent Hg(II) from entering into rice grains (Krupp et al., 2009), whereas atmospheric Hg is one of the important sources of IHg in aboveground tissues (*e.g.*, leaves) in Hg-contaminated area (Meng et al., 2010). Although many studies have been conducted, the mechanism of MeHg bioaccumulation in rice is still not well understood, and warrants further investigation (Meng et al., 2010, 2011, 2012, 2014; Qiu et al., 2008; Rothenberg et al., 2013; Zhang et al., 2010a).

Hg methylation in rice paddy soils is largely produced by sulfate-reducing bacteria (SRB), a principal methylator under anoxic conditions (Liu et al., 2014b; Wang et al., 2014b). This biotic process is usually mediated by a range of factors, such as bioavailability of Hg (Meng et al., 2014), source of Hg species (Zhao et al., 2016a), newly-deposited atmospheric Hg (Zhao et al., 2016b), water management (Wang et al., 2014b), selenite (Se) (Wang et al., 2016b; Zhang et al., 2012), sulfate (Liu et al., 2014b; Wang et al., 2016c), organic matter (OM) (Liu et al., 2014a), and pH (Zhao et al., 2016a). However, the potential effects of some key soil properties on Hg biogeochemistry in rice paddies, such as nutrients (*e.g.*, nitrogen (N), phosphorus (P)) and mineral compositions (*e.g.*, SiO_2, Al_2O_3, Fe_2O_3), are less understood. As described above, the MeHg present in paddy soils greatly affects the contaminated levels of rice. Therefore, factors mediating soil Hg methylation will ultimately affect the MeHg bioaccumulation in rice. However, the effects of soil properties are usually ambiguous. For example, OM, containing various O-, N- and S-bearing ligands, can complex Hg(II) (Skyllberg et al., 2006; Skyllberg and Drott, 2010), while OM is an important electron donor for SRB (Graham et al., 2012). In many studies, Hg/dissolved OM (DOM) concentration ratio is used to estimate the Hg-ligands interaction or Hg mobility in soil/sediment (Aiken et al., 2003; Åkerblom et al., 2008; Frohne et al., 2012; Haitzer et al., 2002; Hesterberg et al., 2001). As a matter of fact, both sulfides (Han et al., 2008; Skyllberg and Drott, 2010) and Se (Zhang et al., 2012) in soils have high affinity with Hg(II), while sulfate is the key electron acceptor for SRB (Shao et al., 2012). Therefore, the biogeochemical controls on Hg methylation in paddy soils are extremely complex and need further investigation, especially in the areas contaminated by long-term mining activities.

Wanshan mercury mine (WMM) is the largest Hg mine in China. Long-term Hg mining activities have resulted in serious Hg contamination to the local ecosystem such as soil, sediment, water, atmosphere, plants, and humans in the WMM (Li et al., 2009; Qiu et al., 2005, 2009; Wang et al., 2007). One of the greatest concerns in WMM is Hg contamination of rice paddies, which is attributed to the fact that flooding conditions can facilitate Hg methylation, and rice has a higher capability to uptake MeHg than IHg (Zhang et al., 2010a). The bioaccumulation factor (BAF) of MeHg in rice was about 2 to 3 magnitudes higher than IHg (Zhang et al., 2010a). Extremely high levels of MeHg (> 100 ng/g) are reported in the edible portion of rice from the WMM (Qiu et al., 2008), and consumption of rice has been demonstrated to be the major exposure pathway of MeHg to the local population (Li et al., 2015). Therefore, alleviating the exposure risk of MeHg caused by the Hg-contaminated rice is urgent.

In this study, we report the spatial distribution of total Hg (THg) and MeHg concentrations in soils and rice grains from 124 rice paddies of the WMM. These rice paddies were located either at abandoned Hg mining sites, or at an active artificial Hg smelting site. Meanwhile, multiple soil properties, such as S, Se, OM, N, P, mineral compositions (*e.g.*, SiO_2, Al_2O_3, Fe_2O_3) and pH, were measured to find the key factors determining the production and bioaccumulation of MeHg in rice paddies of the WMM. Better understanding of these key factors controlling the biogeochemical cycling of Hg in rice paddy ecosystem will help mitigate the problem of Hg-contaminated rice grains.

1. Materials and methods

1.1. Sample collection and preparation

Although large-scale mining activities in the WMM were ceased in 2001, small-scale artisanal smelting was still active when the samples for the current study were collected. Therefore, two typical areas were emphasized (*i.e.*, the abandoned Hg mining sites and the active artisanal Hg smelting site, Fig. 1). Historical Hg mining activities have produced roughly 125.8 million tons of mine waste materials, and several large tailings were formed at the head of major rivers of the WMM (Li et al., 2013). Along these rivers, there are rice paddies which use the river water for irrigation. The concentrations of total gaseous Hg (TGM) in ambient air and THg in precipitate at artisanal Hg smelting site were significantly higher than those around the abandoned Hg mining sites during the rice growing season (Zhao et al., 2016a). However, THg concentrations in irrigation water were found the higher levels in abandoned Hg mining areas (Zhao et al., 2016a).

In September 2012, rice had entered into full ripe stage, and paddy soils were in a moist state. Rice grain and corresponding soil samples adjacent to root surface (0–10 cm in depth) were collected using a wooden shovel from 124 rice paddies in the WMM (numbers of paddies in the abandoned Hg mining areas and the active Hg smelting site were 113 and 11, respectively, Fig. 1). These paddies with a 500 m interval from each other were mainly along major rivers of the WMM (*i.e.*, Gaolouping River (27°30′50.16″–27°30′39.85″N, 109°11′55.22″–109°10′26.17E), Aozhai River (27°32′53.381″–27°35′40.084″N, 109°12′17.002″–109°17′04.914″E), Huangdao River (27°30′46.20″–27°26′49.03″N, 109°14′00.11″–109°16′11.87″E), Dashuixi River (27°32′11.29″–27°32′05.38″N, 109°14′06.94″–109°18′26.53″E), Wawuping River (27°37′18.024″–27°37′13.388″N, 109°16′51.884″–109°21′28.511″E), Gouxi River (27°33′50.038″–27°33′45.849″N, 109°11′28.407″–

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