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Understanding reduced inorganic mercury accumulation in rice following selenium application: Selenium application routes, speciation and doses

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HIGHLIGHTS

- Soil application with Se could reduce inorganic mercury (IHg) accumulation in rice.
- Foliar application with Se could increase Se but not IHg accumulation in rice.
- IHg-Se antagonism in soil-rice systems depends on Se doses and Se application routes.
- Se speciation (selenite and selenate) may play a minor role in IHg-Se antagonism.
- IHg-Se interactions in soil could be important in explaining IHg-Se antagonism.

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ABSTRACT

Selenium (Se) has recently been demonstrated to reduce inorganic mercury (IHg) accumulation in rice plants, while its mechanism is far from clear. Here, we aimed at exploring the potential effects of Se application routes (soil or foliar application with Se), speciation (selenite and selenate), and doses on IHg-Se antagonistic interactions in soil-rice systems. Results of our pot experiments indicated that soil application but not foliar application could evidently reduce tissue IHg concentrations (root: 0–48%, straw: 15–58%, and brown rice: 26–74%), although both application routes resulted in comparable Se accumulation in aboveground tissues. Meanwhile, IHg distribution in root generally increased with amended Se doses in soil, suggesting antagonistic interactions between IHg and Se in root. These results provided initial evidence that IHg-Se interactions in the rhizosphere (i.e., soil or rice root), instead of those in the aboveground tissues, could probably be more responsible for the reduced IHg bioaccumulation following Se application. Furthermore, Se dose rather than Se speciation was found to be more important in controlling IHg accumulation in rice. Our findings regarding the importance of IHg-Se interactions in the rhizosphere, together with the systematic investigation of key factors affecting IHg-Se antagonism and IHg bioaccumulation, advance our understanding of Hg dynamics in soil-rice systems.

1. Introduction

Mercury (Hg), a global pollutant, is a serious ongoing concern for both public and wildlife health. It has long been believed that selenium (Se) protects organisms from Hg bioaccumulation and toxicity (Bjerregaard et al., 2011; Koeman et al., 1973; Pařízek and Ošťádalová, 1967). Various mechanisms leading to biological Hg-Se antagonism have been proposed in mammals and aquatic organisms (Dang and Wang, 2011; Khan and Wang, 2009; Yang et al., 2008).

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Compared to Hg-Se antagonisms in aquatic environments, the inhibitory effects of Se on Hg bioaccumulation are less documented in terrestrial systems. Inorganic mercury (IHg) is the major Hg species in soils and sediments as well as the precursor of MeHg (Ullrich et al., 2001). Meanwhile, IHg is also the dominant species of Hg in plants (e.g., rice: 52–74%, Meng et al., 2014). Although foliar uptake of Hg from the atmosphere has recently been found to be an important route of IHg accumulation in plants (e.g., rice, Meng et al., 2010; Yin et al., 2013), IHg uptake from contaminated soils is still an important route of IHg phytoaccumulation (e.g., Horvat et al., 2003; Meng et al., 2010). Therefore, it is of great importance to investigate the IHg-Se interactions in soil-plant systems and explore the possibility of reducing IHg accumulation in plants via Se amendment. Shanker et al. (1996) first demonstrated that inorganic mercury (IHg) uptake by radish and tomato plants decreased by 17–92% under selenite and selenate additions (0.5–6 mg kg^{-1}) in sand and soil culture. It has been hypothesized that the inert IHg-Se complex and/or high molecular weight proteinaceous complex in the root could be responsible for the observed antagonism of Se against IHg in the hydroponic plants (Afton and Caruso, 2009; McNearJr. et al., 2012; Yathavakilla and Caruso, 2007). Additionally, Se was reported to counteract IHg phytotoxicity in garlic (Zhao et al., 2013): The total Hg uptake were reduced by ~20–90% under selenite or selenate additions (1–100 mg L^{-1}). Recently, an *in situ* field study showed that the presence of selenium in soil can reduce IHg accumulation in rice (Zhang et al., 2012). Similarly, reduction in total Hg or IHg accumulation has been reported in potted rice under Se amendment, e.g., in the research of Wang et al. (2014), total Hg in plants was decreased by 47% with 5 mg kg^{-1} Se application. Besides, Li et al. (2015) reported a 30% decrease of grain total Hg in Se amended treatments (0.75 mg kg^{-1}), and Zhao et al. (2014) found that Se addition (0.5–5 mg kg^{-1}) resulted in ~70–80% decreases of IHg levels in rice root and straw, but no significant change in grain. By comparing methylmercury phytoaccumulation following soil or foliar Se exposure, our recent studies also provided clear evidence that formation of IHg-Se complexes (identified by Hg L_{III}-edge synchrotron radiation X-ray absorption near edge structure, XANES) could be responsible for the decreased IHg availability to methylating bacteria and thus reduced methylmercury production in soils under Se amendment (Wang et al., 2016a,b). Despite those progresses in IHg-Se interactions, there remain knowledge gaps in our current understanding about how Se-specific factors (e.g., uptake routes, speciation, and doses of Se) could affect IHg accumulation in plants.

Soil and foliar application with Se are the main way to increase Se uptake in soil-rice systems (Li et al., 2010; Premarathna et al., 2012). Meanwhile, selenite and selenate are the main Se species for plant uptake from soil (Ellis and Salt, 2003; Mikkelsen et al., 1989). In this study, pot experiments were conducted to evaluate the effects of Se application routes (i.e., soil or foliar application), speciation (i.e., selenite and selenate) and doses on IHg accumulation in rice (*Oryza sativa* L.) and to further elucidate the underlying mechanisms of Se and IHg interactions in soil-plant systems.

2. Materials and methods

2.1. Soil

Soil was collected from the surface (0–20 cm depth) of a rice paddy field in Yixing, Jiangsu Province of China in March 2014. The soil was air-dried, sieved to 2 mm and mixed homogenously. The soil was characterized by low pH of 5.5 (by HQ30d, HACH, USA) and organic carbon of 2.1% (by vario TOC cube, Elementar, Germany). The ambient concentrations of Hg and Se in the soil were 0.2 mg kg^{-1} and 0.9 mg kg^{-1}, respectively.

The soil was spiked with mercury nitrate monohydrate (80 mg Hg mL^{-1}, Sigma Aldrich) to reach a total Hg concentration of 2.4 mg kg^{-1} in the soil, mixed thoroughly using a stand mixer (KENWOOD KMM770, England), and equilibrated for 20 days under flooding conditions. Our previous studies indicated that changes in Hg bioavailability generally leveled off after 20 days (Ma et al., 2015; Zhong and Wang, 2006), and thus 20 days' equilibrium time was chosen in this study. The spiked Hg concentration was within the range of total Hg levels in contaminated paddy soils in China e.g., 1.3–790 mg kg^{-1} (Qiu et al., 2005; Zhang et al., 2009). Changes in soil IHg concentrations during the whole experimental period (i.e., equilibration and rice cultivation) were less than 2% (e.g., due to IHg methylation or plant uptake) and were ignored in the following discussion.

2.2. Experimental design

Two application routes of Se, i.e., soil and foliar application, were examined in this study. Different doses of selenite (Se(IV)) or selenate (Se(VI)) were used. There were totally five treatments for soil application and four treatments for foliar application, plus a control, with triplicates per treatment (details in Table 1 and below). In addition, a blank was used, in which rice plants were cultivated in a low-mercury soil (soil without IHg spiking, total Hg: 0.2 mg kg^{-1}), to minimize IHg uptake from the soil and thus estimate IHg uptake from the atmosphere.

In the case of soil application with Se, Se (in the form of Na_2SeO_3 or Na_2SeO_4, Sigma Aldrich) was spiked into the soil before flooding: The amended Se doses were 0.5, 3.0 and 6.0 mg kg^{-1} for selenite (i.e., 0.5Se(IV), 3.0Se(IV) and 6.0Se(IV) treatments), and 3.0 and 6.0 mg kg^{-1} for selenate (i.e., 3.0Se(VI) and 6.0Se(VI) treatments), respectively. The Se doses were carefully chosen based on the reported Se toxic threshold to rice plants (Rani et al., 2005), as well as the background Se levels in the test soil (i.e., 0.5–6 mg/kg spiked Se versus 0.9 mg/kg background Se).

For foliar Se application (Na_2SeO_3 or Na_2SeO_4), Se was applied twice on day 60 (during stem extension stage) and day 80 (during heading stage) of plant growth, respectively, and sprayed carefully onto leaves and stems using aerosol sprayers. Consequently, the amended Se doses were 30 g ha^{-1} (i.e., Se(IV)-low and Se(VI)-low treatments) and 80 g ha^{-1} (i.e., Se(IV)-high and Se(VI)-high treatments), comparable with those used in previous studies (Chen et al., 2002; Premarathna et al., 2012). During spraying, the pots were covered with plastic wrap to avoid Se input into the soil, and those pots were separated from the other pots to avoid cross-contamination by Se.

For all treatments, pots were filled with soil (2.5 kg pot^{-1}) and flooded to 2 cm above soil surface throughout the experiments. Basal application of 0.27 g kg^{-1} $Ca(HPO_4)_2 \cdot H_2O$, 0.24 g kg^{-1} KCl and 0.30 g kg^{-1} $CO(NH_2)_2$ was supplied before transplanting of rice seedlings, which was repeated on days 30 and 60 days after transplanting. Overall, 79 mg P kg^{-1}, 150 mg K kg^{-1} and 167 mg N kg^{-1} were supplied per pot during the entire experimental period. After 20-day equilibration under flooding conditions, two thirty-day-old rice seedlings of Wufengyou2168 (*indica*) were transplanted into each pot. Rice plants were cultivated for 120 days (June 15 to October 12, 2014) in a glasshouse at ambient temperature (15–38 °C).

2.3. Sampling

At grain maturity, soil samples were collected from each pot. The soil samples were vacuum-packed, placed into a portable ice box, and transferred to the laboratory immediately. Then the soil samples were freeze-dried (Labconco, USA) and analyzed for Se and