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The translocation of antimony in soil-rice system with comparisons to arsenic: Alleviation of their accumulation in rice by simultaneous use of Fe(II) and NO_3^-

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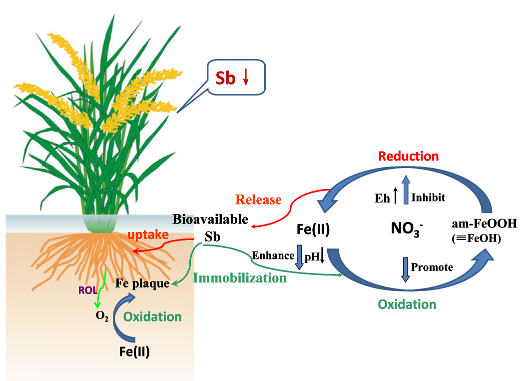
HIGHLIGHTS

- Synergistic effects of Fe(II) and NO_3^- on Sb accumulation in rice were investigated.
- Simultaneous application of Fe(II) and NO_3^- can immobilize more Sb in soils.
- Sb immobilization in soils was enhanced by Fe(III) formation and pH decrease.
- Compared with As, Sb was much more difficult to be uptaken by rice roots.
- Compared with As, Sb was much easier to be translocated from rice straw to grains.

GRAPHICAL ABSTRACT



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ABSTRACT

Antimony (Sb) accumulation in rice grains is a potential risk to human health. This study aims to develop agronomic practices that can reduce the accumulation of Sb in rice grain in contaminated soil. A pot culture experiment was conducted to investigate the effects of co-application of ferrous iron and nitrate (Fe(II) + NO_3^-) in paddy soils on Sb uptake by rice. The co-application of Fe(II) and NO_3^- promoted abiotic/biotic Fe(II) oxidation and mineralization in the rhizosphere soil and formation of Fe plaques, consequently, Sb bioavailability was significantly reduced by enhancing Sb immobilization on the newly formed Fe(III) (hydr)oxides. The results were compared with those for arsenic (As) in the same trial and it was shown that the two metalloids have different translocation behavior in the soil–rice plant system. The adsorption of Sb, especially the Sb(V), on Fe(III) (hydr) oxides was more significantly enhanced by the decreased soil pH after the application of Fe(II) + NO_3^- than that of As. The uptake of Sb by the roots of rice was much more difficult but it was much easier to be transported from the rice straw to the grains compared to As. The differences might be mainly caused by the different uptake mechanisms of Sb and As by rice plants from paddies. The bioavailable As(III) would be much more efficient in entering into the rice roots than Sb(III) through the aquaporin channel due to its much smaller ionic radius; the bioavailable As(V), entering into the rice roots via phosphate transporters, would also be more efficient in taking up by roots than Sb(V), which pathway from soil to rice roots remains unclear. These findings provide new insights into Sb biogeochemical behavior in soil–rice plant systems and demonstrate that co-application of Fe(II) and NO_3^- could be a promising strategy for safely-utilizing Sb contaminated sites in the future.

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1. Introduction

Antimony (Sb), mainly associated with arsenic (As) in sulfide and oxide ores, is a toxic element. Excess intake of Sb results in many diseases in humans, such as cancers, cardiovascular disease, liver disease and respiratory disease (WHO, 2003). As food represents the main source of human exposure to environmental pollutants, the consumption of Sb polluted rice could therefore have a strong impact on human health (He and Yang, 1999). The Sb-containing compounds are globally considered as contaminants (Okkenhaug et al., 2012). The mining of these ores has resulted in elevated concentrations of Sb and As in the environment (Murciego et al., 2007). Both, Sb and As, exist mainly as oxyanions, primarily in III and V state in soil and aqueous environments (Filella et al., 2002; Wilson et al., 2010). Organic Sb species, resulting from microbial methylation, have also been found in soils and sediments (Duester et al., 2005). The toxicity of Sb-containing compounds is strongly dependent on their speciation (Filella et al., 2002; He et al., 2012), and increases in the order, methylated Sb species < Sb(V) < Sb (III), which is similar to that of As. Because of their chemical similarities, Sb and As are often considered to have similar biogeochemical behavior (Casiot et al., 2007). Rice paddies downstream of Sb mines can receive substantial inputs of the two metalloids (He, 2007), as a result of which their concentrations in soil far exceed the maximum allowable pollutant concentration for Sb (36 mg kg^{-1}) and As (25 mg kg^{-1}), recommended by the World Health Organization (WHO). Although the accumulation of Sb in rice is generally low (Pierart et al., 2015), concentrations of 225 and 0.93 mg kg^{-1} (Wu et al., 2011) were detected in the roots and grains of rice, respectively, near the Xikuangshan Sb mine in Hunan, China. Wu et al. (2011) showed that the daily Sb intake of the residents in the vicinity of Xikuangshan was 554 μg, considerably higher than the tolerable daily intake (TDI) of Sb (360 μg) recommended by the WHO. Rice was reported to account for about 33% of the direct Sb intake (Okkenhaug et al., 2012), which might pose health threats to humans. Recently, Okkenhaug et al. (2012) and Ren et al. (2014) found that Sb(V) is the main species in rice roots and shoots. Cai et al. (2015) found that rice was much more efficient in taking up Sb(III) than Sb(V), and Sb(V) was the predominant Sb species in rice roots, stems, and leaves. As of date, little data about Sb species in rice grain has been reported. Additionally, compared to the huge concerns over the translocation of As in the paddy soil–rice system, the biogeochemical behavior of Sb in the system has received very limited attention.

The adsorption of Sb, similar to that of As, onto ferric (hydr)oxides (Fe(III)), controls its migration in soil (Wilson et al., 2010). The migration rate of As(III) is much higher than that of As(V) because the latter has a higher affinity to Fe(III). On the contrary, neutral Sb(III) is more strongly bound to Fe(III) than the anionic Sb(V), which is responsible for higher migration rate of the latter in neutral and alkaline environments (Johnson et al., 2005). In flooded paddy soil, Fe(III) is reduced to Fe(II), a process combined with the reductive release of As(V) and Sb(V) (Wilson et al., 2010). It was reported that half of the Sb (V) combined with Fe(III) was reduced to highly toxic Sb(III) (Nakamaru and Altansuvd, 2014) after the Fe(III) was reduced to Fe (II) under flooded conditions, highlighting the elevated risks of Sb contamination in rice paddies. However, it is also reported that the formation of secondary amorphous Fe(III) (hydr)oxides, might play a detoxifying role for soil Sb under reducing conditions (Leuz et al., 2006).

Fe(II) is subjected to both spontaneous chemical oxidation (Liu et al., 2006) and biological oxidation (H. Li et al., 2016; X. Li et al., 2016) in flooded paddy soils. O_2 released from developed aerenchyma of rice plants can oxidize Fe(II) in the rhizosphere to Fe(III), which coats the root surfaces to form Fe plaques (Liu et al., 2006). Fe plaque was proved to have high affinity for As and Sb (Cai et al., 2015; Huang et al., 2011), and could reduce their bioavailability to rice plants. Besides the chemical process, the NO_3^--reducing-Fe(II)-oxidizing bacteria also have the ability to oxidize Fe(II) to Fe(III) by using NO_3^- as an electron acceptor under anaerobic conditions (Xiu et al., 2016; Liu et al., 2018). A field study in Bangladesh showed that the injection of NO_3^- into sediments could reduce the mobility of As (Harvey et al., 2002), which was attributed to anoxic biological oxidation of Fe(II) to Fe(III). Another study by Xiu et al. (2016) in groundwater also showed that an anaerobic NO_3^--reducing-Fe(II)-oxidizing bacterium (*Pseudogulbenkiania* sp. Strain 2002) could effectively oxidize Fe(II) to lepidocrocite (a form of Fe (III)), which could immobilize As(III) and As(V) without changing their states. It was evidenced that in natural paddy soils, NO_3^--reducing-Fe(II)-oxidizing bacteria could be readily developed in the presence of Fe(II) and NO_3^- when the soil condition changed from oxic to anoxic (H. Li et al., 2016; X. Li et al., 2016). In fact, in a recent study (Wang et al., 2018), we investigated the effect of co-application of Fe(II) and NO_3^- on As accumulation in rice plants and speciation in soil in a pot trial using paddy soil contaminated with As and Sb from Xikuangshan mine area. The results showed that Fe(II) oxidation coupled with NO_3^- reduction could immobilize the As via its incorporation into secondary Fe (hydr) oxides (Fe(III)) in flooded paddy soil. Consequently, As uptake in rice plants was alleviated. Therefore, it can be hypothesized that biological oxidation of Fe(II) might also have important contribution to the immobilization of Sb, being the congener of As, in paddy soils. Regulating the content of NO_3^- coupling with Fe(II) oxidation in paddy soil may reduce the accumulation of Sb in rice plants. Elucidating of the possibility could not only provide a new insight into the fundamental aspects of Fe/N/Sb biogeochemical cycles, but also be helpful for improving the current agronomic strategy in Sb-contaminated paddy soils.

In the present study, we investigated the behavior of Sb in soil–rice plant system during the entire growth period using the experimental approach employed in our previous study on As (Wang et al., 2018), as described above. The specific objectives of the present study were as follows: 1) to compare Sb and As translocation from soil to rice plant systems by analyzing the concentrations of Sb in rice plants; 2) to deduce the possible mechanisms of the alleviation of Sb accumulation in rice upon co-application of Fe(II) and NO_3^- by determining the Sb content in Fe plaques and its speciation in the rhizosphere soil.

2. Materials and methods

2.1. Pot experiments

Surface paddy soil (0–20 cm) was collected from paddy fields 1 km downstream from the Xikuangshan mine area (27°42′53.46″N; 111°27′06.12″) in the Hunan Province of China in October 2012. The soil was transported to the green house, air-dried, and passed through a 2 mm sieve. Soil pH, CEC, TOC, and the other related characteristics, along with the details of treatment and management of the pot trails were described in a previous study (Wang et al., 2018). In present study, the soil properties were also presented in the Supporting information (SI, Table S1) and the management of the pot trails was described generally in the following section. The total Sb (T-Sb) and As (T-Sb) content in the soil were 145 ± 10.9 and 86.3 ± 6.13 mg kg^{-1}, respectively. A 25 μm nylon mesh bag (20 cm height, 6 cm diameter, containing 600 g soil) was placed in the center of 8 L plastic pot to create the rhizosphere (rhizosphere soil), and the remaining soil (5.4 kg) outside the bag was considered as the non-rhizosphere. The base fertilizer $CO(NH_2)_2$, P_2O_5 and K_2O were applied at the rate of 0.499, 0.0625 and 0.0937 g kg^{-1} dry weight soil, respectively. The amendments $FeCl_2$ and $NaNO_3$ were applied simultaneously at the rate of 0.54 and 7.5 mmol kg^{-1} dry weight soil. Five treatments namely: (1) no additives (control), (2) Am-FeOH (0.1% w/w amorphous ferrihydrite), (3) $FeCl_2$ (0.54 mmol kg^{-1} dry weight soil, Fe(II)), and (4) $NaNO_3$ (7.5 mmol kg^{-1} dry weight soil, (NO_3^-)), were set for comparison with the Fe(II) + NO_3^- treatment. Then the plastic pots were maintained at flooded conditions with tap water. Two weeks later, three UU128 rice seedlings, with uniform sizes were transplanted into each rhizosphere bag. For all the five treatments, soil pots were prepared in