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Enhanced immobilization of arsenic and cadmium in a paddy soil by combined applications of woody peat and $Fe(NO_3)_3$: Possible mechanisms and environmental implications

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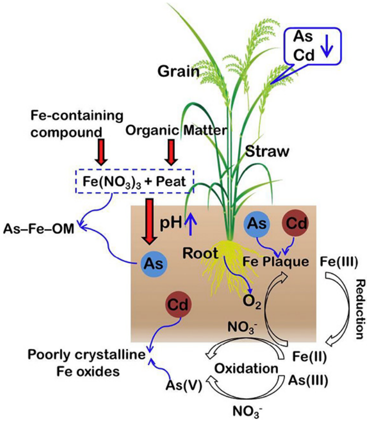
HIGHLIGHTS

- Combined applications of peat and $Fe(NO_3)_3$ decreased As(III) and Cd in porewater.
- The mobile portions of As and Cd in soil were decreased by peat + $Fe(NO_3)_3$.
- The immobile portions of As and Cd in soil were increased by peat + $Fe(NO_3)_3$.
- Formations of Fe plaques were enhanced by $Fe(NO_3)_3$ addition.
- Productions of poorly crystalline Fe oxides were enhanced by $Fe(NO_3)_3$ addition.

GRAPHICAL ABSTRACT



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ABSTRACT

Organic matter (OM) plays an important role in the mobility of heavy metal(loid)s. Peat containing abundant OM can be used as an organic fertilizer improving physical and chemical properties of soil. Previous studies indicated that the immobilization of heavy metal(loid)s by peat is affected by the presence of metal oxides and/or hydroxides and that Fe-enriched peat is very effective in immobilizing metal(loid)s. Accordingly, we hypothesize that simultaneous application of peat and Fe-containing compounds may pronouncedly immobilize heavy metal (loid)s. In this study, the effects of the combined applications of woody peat and $Fe(NO_3)_3$ on As and Cd mobilities and accumulations in rice during the whole growth period were investigated by a pot experiment. The combined applications of woody peat and $Fe(NO_3)_3$ significantly decreased As(III) and Cd in porewater due to pH increases induced by applications of $Fe(NO_3)_3$, and these decreases were enhanced with increasing $Fe(NO_3)_3$. In addition, simultaneous application of peat and $Fe(NO_3)_3$ significantly decreased mobile portions of As and Cd but significantly increased their immobile portions. Increasing $Fe(NO_3)_3$ increased the amount of As immobilized by poorly crystalline Fe oxides. The formation of Fe plaques and production of poorly crystalline Fe oxides were enhanced by $Fe(NO_3)_3$ addition, which also contributed to the immobilization of As and Cd in soil. Overall, the combined applications of woody peat and $Fe(NO_3)_3$ provided a strategy for simultaneously immobilizing As and Cd in

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soils and further alleviating their accumulations from soil to rice plants. In paddy soil, the frequent occurrence of iron redox activity due to the alternating wetting and drying cycles provided favorable conditions for interactions between Fe and OM, and this process and its associated metal(loid) immobilization may be more important than we thought and need further study.

1. Introduction

Rice has a high ability to take up and store As and Cd in its grains during its cultivation (Bralatei et al., 2015). Uptake of As or Cd by rice poses a threat to food safety by impacting both the quantity and quality of rice (Sebastian and Prasad, 2014; Honma et al., 2016). The consumption of rice with elevated Cd or As concentrations has been shown to pose potential health risks (de Livera et al., 2011; Seyfferth et al., 2014). Therefore, there are persistent demands for As and Cd minimization in rice.

Organic matter (OM) has an important role in metal(loid) mobility, and many previous studies have tried to decrease metal mobility by the addition of organic amendments such as pig manure (Tang et al., 2015), wheat straw (Gao et al., 2018), biochar (Huang et al., 2017; Yin et al., 2017), peat moss (Lee et al., 2013) and peat (Stanislawska-Glubiak et al., 2015). Generally, OM affects the mobility of heavy metal(loid)s through adsorption, complexation, and redox reactions (Wang and Mulligan, 2006). Woody peat is an intermediate from the transition of plant residues to coal and has abundant humic substances, which are a major constituent of soil OM (Yu et al., 2018b). Application of woody peat can effectively regulate the distribution of solid, liquid and gas phases of soil and maximum water content and improve soil water retention (Meng, 2005). It can also enhance soil microbial activity and the availability of soil nutrients and thus promote plant growth (Ma et al., 2017). Previous studies (Hu et al., 2010; Lee et al., 2013) indicated that peat can effectively immobilize heavy metal(loid)s and that different mechanisms are involved in the sorption of metals by peat; these mechanisms depend on the type of peat, its preparation and the type of metals and their concentration (Stanislawska-Glubiak et al., 2015). Furthermore, the immobilization of heavy metal(loid)s by peat is affected by the presence of metal oxides and/or hydroxides (de Oliveira et al., 2015). For example, Fe-enriched peat was most effective in immobilizing As(V). On the other hand, the mobility and bioavailability of As and Cd are significantly affected by the transformation of iron (Fe) oxides in soil (Liu et al., 2015; Yu et al., 2016b; Yu et al., 2017), and OM can affect the absorption of heavy metal(loid)s onto Fe oxides (Redman et al., 2002). Results from a previous study (Mikutta et al., 2014) showed that the adsorption of As(V) was fastest to Fe–OM coprecipitates formed at low Fe availability, indicating an important role in oxyanion immobilization for carbon-rich Fe precipitates. The interactions of OM with Fe oxides mainly occur through two pathways, i.e., adsorption and coprecipitation (Chen et al., 2014), and in acidic mineral soils, >80% of dissolved natural OM precipitates with Fe^{3+} (Mikutta et al., 2014). Interactions with OM during Fe precipitation can affect the environmental reactivity of the Fe oxides (Shimizu et al., 2013; Eusterhues et al., 2014) and alter the particle size and structural order of newly formed Fe oxides (Eusterhues et al., 2008; Mikutta, 2011). As a result, Fe oxides formed by coprecipitation with OM are more reactive sorbents for heavy metal(loid)s (Mikutta et al., 2014). Accordingly, we hypothesize that the simultaneous application of peat and Fe-containing compounds may pronouncedly immobilize heavy metal(loid)s.

Paddy fields downstream of the Lianhuashan tungsten mine, which is located in the (sub)tropical areas in the Guangdong Province of China, have received substantial inputs of both As and Cd for several decades. Field surveys of the paddy soils showed that their total As and Cd contents are as high as 162 mg/kg (Liu et al., 2012) and 1.6 mg/kg (Yu et al., 2016b), respectively. Elevated As and Cd concentrations have also been reported in rice grain and straw in field transects toward irrigation inlets, respectively. In the present study, a rice pot experiment was conducted using the As and Cd cocontaminated paddy soil from the Lianhuashan mine under a combined amendment of woody peat and $Fe(NO_3)_3$. Our previous study (Wang et al., 2018) indicated that nitrate treatment significantly reduced As bioavailability in rice plants, and the Fe-containing compound $Fe(NO_3)_3$ was thus used in this pot experiment. As and Cd speciation in soils and their accumulations in the rice plants were monitored over the whole growth period, and the objectives of this study were (i) to investigate the effect of the simultaneous application of peat and $Fe(NO_3)_3$ on the mobility and bioavailability of As and Cd during the entire growth period of rice plants and (ii) to discuss the possible mechanisms responsible for peat + $Fe(NO_3)_3$-induced As and Cd immobilization in paddy soils.

2. Materials and methods

2.1. Soil description

Paddy soil used for rice pot experiment was collected 1 km downstream from the Lianhuashan mine area (UTM 27°42′53.46″N; 111°27′06.12″) in the Guangdong Province of China in March 2015. A comprehensive description of the mining area was provided in (Liu et al., 2010). Briefly, the Lianhuashan tungsten mine is one of the largest tungsten mines in southern China. Huge amounts of mine tailings are left behind after the mining operation was closed in 1991. During the rainy season, the acid mining drainages often flooded into nearby paddy fields, leading to lots of heavy metal(loid)s deposited in the surrounding areas. Therefore, the paddy soil of the Lianhuashan mine area was severely polluted by heavy metal(loid)s, especially As and Cd. The soil collected from the surface horizon (0–20 cm) of this region was sandy loam with a pH of 7.4, total Fe, N, P, K and OM contents of 41.5, 1.64, 1.73, 25.2 and 39.2 g/kg, and total Cd and As of 4 mg/kg and 132 mg/kg, respectively. The analysis methods for soil properties have been reported in a previous study (Yu et al., 2018a).

2.2. Pot experiments

The pot cultivation experiments were conducted in a climate-controlled greenhouse. Five treatments with three replicates for each treatment were set up as follows: (1) control (untreated soil), (2) soil + peat (5 g/kg dry weight of soil), (3) soil + peat (5 g/kg dry weight of soil) + $Fe(NO_3)_3$ (4 mmol/kg dry weight of soil), (4) soil + peat (5 g/kg dry weight of soil) + $Fe(NO_3)_3$ (8 mmol/kg dry weight of soil) and (5) soil + peat (5 g/kg dry weight of soil) + $Fe(NO_3)_3$ (16 mmol/kg dry weight of soil). The peat used in this study was collected from Indonesia in June 2014, and this region is characterized by a warm tropical climate; thus, the peat contains a high level of OM (89.02%) at a low pH (5.34). The concentrations of both As and Cd were below the limit of detection.

For each treatment except control, peat or peat + $Fe(NO_3)_3$ were applied to the soil surface and immediately mixed thoroughly with the soil before being transferred into 8 L pots (6 kg of soil per pot). In addition, chemical fertilizers that included P and K (P_2O_5: K_2O = 1: 1.5) were applied at a rate of 0.0625 g/kg dry weight of soil. Nitrogen fertilizer was applied by spraying urea at the rate of 0.3% (rice plants in each pot were sprayed with 1 L of 0.3% urea, i.e., 8.33 mmol/kg soil) on 25-April-2015. A nylon mesh bag (height of 20 cm and diameter of 80 mm, containing 600 g of soil) was placed in the center of each pot to create a rhizosphere environment as adopted by (Ultra et al., 2009),