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Redox changes in speciation and solubility of arsenic in paddy soils as affected by sulfur concentrations☆

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ABSTRACT

A substantial amount of sulfate is often supplied in paddy fields with concomitant applications of chemical fertilizers and manure for rice growth. It is unclear how solubility and speciation of arsenic (As) are affected by the levels of soil sulfate and their relationship to soil redox status and sulfur (S) and iron (Fe) speciation in a short cycle of soil reducing (flooding) and oxidizing (drying) periods. The objective of this study was to investigate the solubility of As in relation to chemical speciation of As and S in different levels of soil sulfate through a time series of measurements during a 40-day reduction period ($Eh < -130$ mV) followed by a 32-day reoxidation period ($Eh > 400$ mV) using X-ray absorption fine structure (XAFS) spectroscopy. An excess of sulfate decreased extractable and dissolved As in the soil reducing period due to retardation of soil reduction process that decreased soluble As(III) in the soil solid phase. The As species at the end of soil reducing period were 38–41% As(V), 46–51% As(III), and 11–13% As_2S_3-like species, regardless of initial S treatments. In the following soil reoxidation, As_2S_3-like species were sensitive to oxidation and disappeared completely in the first 2 days when the Eh value increased rapidly above 160 mV. The addition of extra sulfate to the soil did not result in the formation of neither reduced S species nor As_2S_3-like species. About 50% of As(III) to the total As persisted over 32 days of soil reoxidation period ($Eh > 400$ mV), suggesting some mechanisms against oxidation of As(III) such as physical sequestration in soil microsites. This study demonstrates that the extra SO_4 in paddy soils can help mitigate the dissolution of As in reduction and reoxidation periods.

1. Introduction

Arsenic (As) has been recognized as a critical food contaminant particularly in floodplains and paddy areas where rice is an important staple in the human diet (Honma et al., 2016; Ishikawa et al., 2016; Suda et al., 2016). Mobility and toxicity of As in soils and sediments are chiefly controlled by the oxidation state and retention to soil solid phases. Arsenic is more mobile and toxic in anoxic soils where trivalent As becomes more predominant than pentavalent As (O'Day et al., 2004). In soils and sediments, Fe(III) (oxyhydr)oxide minerals are strongly interact with As(V) and As(III), serving as an important sorbent in reduced and oxidized conditions (Makino et al., 2016; Suda et al., 2015; Yamaguchi et al., 2011). In paddy soils where the soil is periodically exposed to a wet and dry cycle, the solubility and chemical species of As are remarkably dynamic with concomitant alternations of soil redox conditions.

The fate of As in paddy soils is strongly controlled by redox chemistry of S and Fe. In anoxic soil conditions, microbial sulfidogenesis is a facile reductant of Fe(III) and As(V), which promotes As release into solution phases (Burton et al., 2011; Poulton et al., 2004). Alternatively, sulfide generated in anoxic conditions can stabilize As by inducing the coprecipitation with Fe sulfide minerals (e.g., pyrite) and As-sulfide-like species (e.g., orpiment and realgar) (Kirk et al., 2010; O'Day et al., 2004). In oxic soil conditions, Fe (oxy) hydroxides play a primary role in sequestration of As(V), and as a consequence, decrease the dissolved As in solution (Itai et al., 2010; O'Day et al., 2004). Therefore, the solubility and speciation of As in the paddy soil need to be understood with linking to Fe and S redox chemistry. A relatively short period of reducing and oxidizing cycle in the paddy field can alter solubility and speciation of As, Fe and S more dynamically than in wetlands where the soil is (semi) permanently inundated by water.

In rice paddy soils, a substantial amount of sulfate is often

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supplied with concomitant applications of chemical fertilizers and manure for rice growth. The supply of sulfate to soils decreases As uptake and translocation to rice grains, which is attributed to the enhancement of glutathione and phytochelatin formations in the plant cells (Bleeker et al., 2006; Nishida et al., 2016; Zhong et al., 2011). From the viewpoint of soil As chemistry, the increase of sulfate levels in soils may enhance the formations of As sulfide and Fe sulfide minerals to adsorb As in reducing conditions (Burton et al., 2014; Kirk et al., 2010), leading to the decrease of As solubility and potential availability to rice plants. However, it is unclear how solubility and speciation of As are affected by the levels of soil sulfate and their relationship to soil redox status and S and Fe speciation in a short cycle of soil reducing and oxidizing conditions (e.g., rice growing period). Previous studies reported that Fe sulfides (e.g., mackinawite) and As sulfides (e.g., orpiment) formed in reducing conditions can sequester and stabilize dissolved As (Burton et al., 2014; Couture et al., 2013; O'Day et al., 2004). To understand the significance of Fe/As sulfide minerals for As sequestration in the paddy soil, further studies are needed if the sulfide minerals are indeed formed and persistent in the variable redox conditions. The objective of this study was to determine the mechanism controlling As solubility and speciation in reducing and oxidizing paddy soils with different levels of SO_4. We focused on solubility and speciation of As in relation to their S and Fe during the time series of 40-day reducing period and a following 32-day reoxidizing period, using the chemical extraction and XAFS spectroscopy.

2. Materials and methods

2.1. Soil redox experiment

A soil (Aquents) was collected from the top 10 cm of paddy field at FM Hommachi, Tokyo University of Agriculture and Technology, Japan. Basic soil physicochemical properties were determined by standard procedures, and the results were summarized in Supplementary data (SD). Briefly, the soil had a loam texture (USDA classification) and a near neutral pH of 6.7, and contained 4.9% C. Total As concentration (12 mg kg^{-1}) was in the range of background levels. A soil redox experiment was conducted to assess As solubility and speciation in different S concentrations in a series of a consecutive reduction and oxidation process. To prepare the soils with three different S levels, the proper amount of deionized water (no S addition) or Na_2SO_4 solution was added to the air-dried soil and homogenized. The soils were then air-dried and passed through a 2 mm sieve. The final concentration of soil S was 253 (native S), 759, and 2530 mg kg^{-1}, and these were labeled as S0, S3, and S10 soils, respectively.

The methods and procedures of soil redox experiment were based on the previous study (Furuya et al., 2016). Briefly, 1700 g soil was filled in a 2.8 L container (18-cm diameter, 14-cm length, and 0.2-cm thickness). The soils were treated with $Na_2HAsO_4 \cdot 7H_2O$ solution to achieve the As concentration of 20 mg kg^{-1}, and homogenized soil slurry was prepared. This concentration of As was relevant to the environmental condition and was required for better XAFS spectra with a good signal-to-noise ratio. For the first 40 days of soil reducing period, the water levels were maintained at 5 cm above the soil surface by occasional additions of deionized water. Soil redox potential (Eh) and pH values at the depth of 7 cm were continuously measured using Pt and reference electrodes and a thin glass electrode, respectively. Aliquots of soil sample (~10 g) and soil solution were collected periodically from the center of soil column. At the end of the soil reducing period (day 40th), aliquots of soils (200 ± 10 g each) were transferred to 11 polypropylene columns (6-cm diameter, 8-cm length, 0.2-cm thickness) and excess water was drained from the bottom of the column until day 72nd (reoxidizing period). Platinum and reference electrodes were installed for the soil Eh measurement (Fujiwara Co., Japan). Up to 72nd day, the columns were periodically dismantled, and the soil samples were collected from the column center. The series of experiment was conducted at 25 ± 1 °C.

The soil samples collected during reducing and oxidizing periods were freeze-dried after centrifugation to remove excess water. Aliquots of freeze-dried soil were immediately vacuum sealed with deoxidants (AGELESS®, Mitsubishi Gas Chemical Company) to minimize redox changes for wet chemical analyses and XANES measurements. Soil As was extracted sequentially by 0.1 M CH_3COONH_4 solution, followed by 0.1 M HCl solution with a soil-solution ratio of 1 (0.5 g) to 80 (40 mL) for 1 h ($n = 3$) (Fulda et al., 2013; Furuya et al., 2016). The soil extract and soil solution were passed through a 0.45-μm membrane filter and analyzed for As by ICP-AES with a hydride generation method (Hitachi High-Technologies Co. Ltd., Japan). The concentration of As, S and other elements in the soil solution were also determined by ICP-AES.

2.2. XAFS spectroscopy

Speciation of As, Fe and S in selected samples from S0 and S10 treatments in the reducing period and oxidizing period were analyzed for XAFS spectroscopy. The XAFS measurements for As and Fe were conducted at the beamline BL5S1 of Aichi Synchrotron Radiation Center, Japan, and beamline BL01B1 of SPring-8, Japan. To avoid redox changes of elements, the samples were stored with deoxidants in vacuum until analysis. Vacuum-sealed soil samples were set on the beamline stage and XAFS data were collected at the As K-edge (11,867 eV) and Fe K-edge (7,112 eV) with a Si(111) monochromator in transmission mode or fluorescent mode with a 19 element Ge semiconductor detector at ambient temperature. The S K-edge X-ray absorption near-edge structure (XANES) measurement was conducted at beamline BL6N1 at Aichi Synchrotron Radiation Center, Japan. The beamline was calibrated at 2481.70 eV by the white-line peak of K_2SO_4 for S equipped with an InSb(111) monochromator. For S K-edge XANES measurements, fine soil particles sprinkled on a carbon tape were analyzed in a beamline chamber under a He gas environment in fluorescent mode. Details on the experimental setup and reference standards have been described previously (Furuya et al., 2016; Kameda et al., 2017; Yamamoto and Hashimoto, 2017) and in SD.

Background correction, normalization and LCF were performed on the XAFS data using the program, Athena ver. 0.9.22 (Ravel and Newville, 2005). The first-derivative As-XANES spectra possess a distinctive feature to characterize the oxidation state of As(V)-O, As(III)-O and As-S species, and the oxidation state of soil As was determined using XANES-LCF with reference compounds of $Na_2HAsO_4 \cdot 7H_2O$, $NaAsO_2$, and As_2S_3 (Burton et al., 2014). The first-derivative of Fe K-edge XANES spectra possess a distinctive feature to characterize the oxidation state of Fe(II) and Fe(III) (Chen et al., 2017), and the spectra of reference compounds including ferrihydrite, illite and biotite are compared with soil samples. The EXAFS-LCF using reference standards was performed on soil Fe spectra to identify the main Fe species. For LCF on soil S-XANES spectra, reference S compounds with oxidation states between -2 and $+6$ were used to determine the distribution of S species (Furuya et al., 2016; Hashimoto and Yamaguchi, 2013). Details of data process and LCF procedure were summarized in SD.

3. Results

3.1. As concentrations in solution and solid phases

Fig. 1 illustrates a series of changes in Eh, As, Fe and SO_4 in the