

Soil Mineralogical Controls on As Dynamics in Rice Paddy Soils

Richard H. Loeppert, Norman White, Bhajan Biswas, and Richard Drees

Soil & Crop Sciences Dept., Texas A&M University, College Station, TX 77843, USA
(r-loeppert@tamu.edu)

INTRODUCTION

Irrigation with arsenic-contaminated water will potentially impact food quality and agricultural sustainability in Bangladesh. Soil mineralogy strongly impacts the retention and release of arsenic (As). The objective of this study was to determine the mineralogical composition and predominant mineralogical controls on soil-As retention and release in the rice-paddy soils of Bangladesh.

METHODS AND MATERIALS

Soil samples for this study were collected from the 0-15 cm depth of *boro* (dry season) rice paddies in five *thanas* of Bangladesh. Individual samples were air dried, separated into sand, silt, and clay particle-size fractions. Individual samples were analyzed for total As and total Fe. Additionally soil Fe was assessed by selective extraction with (i) dithionite-citrate to determine total free Fe-oxide content, and (ii) pH 3.0, 0.2 M ammonium oxalate (in the dark) to determine poorly crystalline Fe-oxide content; soil arsenic was assessed by selective extraction with (i) pH 3.0, 0.2 M ammonium oxalate (in the dark) to determine As associated with poorly crystalline Fe oxide, and (ii) pH 4.0, 0.1 M Na phosphate to determine readily exchangeable As. Particle mineralogy was investigated by x-ray diffraction, synchrotron x-ray microprobe, XANES, SEM, and TEM procedures.

RESULTS AND DISCUSSION

Spatial Variability and Soil Mineralogy

The rice-paddy soils in the current study were relatively similar in principal mineralogy, but were highly variable in soil texture and mineral concentrations. The principal reactive minerals were di- and tri-octahedral micas, high-Fe vermiculites, smectites, Fe-chlorite, and the Fe oxides, goethite, lepidocrocite and ferrihydrite (Fig.1). In the current study, gibbsite was not identified in any of the rice-paddy soils. Relatively low concentrations of calcite were observed in many of the Faridpur and Tala samples. There was a positive correlation ($r^2 = 0.45$) between free Fe-oxide content and layer-silicate Fe content, indicating that the Fe oxides likely originated from the weathered high Fe layer silicates. Layer silicate weathering likely follows the sequence: micas \rightarrow chlorite \rightarrow vermiculite \rightarrow smectite. Fe-oxide content of the soil would be expected to increase with this weathering sequence for biotite mica, due to the release and reprecipitation of layer silicate structural Fe during weathering.

Arsenic Retention and Release by Soil Minerals

The As contents of the 472 surface soils in this study varied from 0.7 to 66.0 mg As kg⁻¹. As concentration decreased in the following approximate order by *thana* (Tala > Faridpur > Paba > Brahmanbaria > Senbag). Soil-As concentration was moderately correlated ($r^2 = 0.33$) with soil Fe-oxide content, indicating the probable association of As with soil Fe-oxide minerals. Ammonium-oxalate extractable As averaged approximately 70 % of the total As, indicating that As was predominantly associated with the poorly crystalline Fe-oxide phases. An average of 23 % of total As was extracted by 0.1 M Na phosphate, indicating that most of the As was strongly bound and was not readily exchanged by phosphate.

In an assessment of 15 high As soils, with As concentrations averaging 22.0 mg As kg⁻¹,

As was associated with sand (29.9 mg As kg⁻¹), silt (17.5 mg As kg⁻¹), and clay (34.1 mg As kg⁻¹) particle-size fractions. A synchrotron x-ray microprobe study indicated that As bonding to layer silicate edge sites was negligible. In the sand fraction, As was largely associated with Fe oxide weathering rinds within schist and weathered mica aggregates. Iron sulfide phases (pyrite and mackinawite) were identified in only a few of the rice-paddy soils of Bangladesh, but when present, these minerals would contribute to As bonding.

Implications to Dynamics of Arsenic in Rice Paddy Soils

The solubility of As in rice-paddy soils is strongly impacted by redox potential and the dissolution of soil Fe oxide, especially the highly reactive poorly crystalline Fe oxides, such as ferrihydrite (Fig. 2). Upon dissolution, surface-adsorbed As is also released, thus As toxicity is more problematic under flooded rice culture than under dryland conditions.

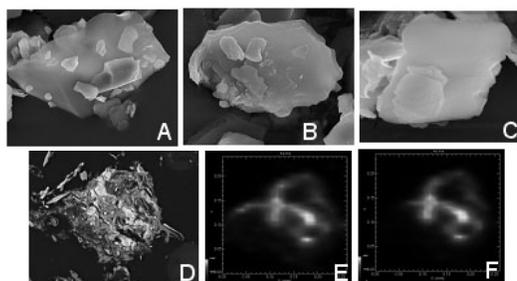


Fig. 1. (A) SEM of vermiculite from a Bangladesh rice-paddy soil; (B) biotite; (C) chlorite; (D) weathered biotite aggregate (white ring in center is an Fe oxide weathering product); (E) map of Fe in aggregate D; (F) map of As in aggregate D.

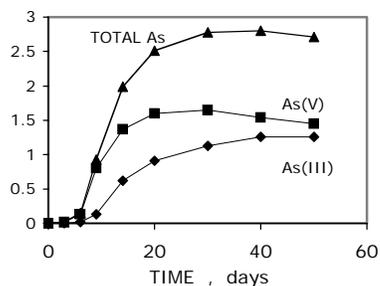


Fig. 2. The time dependent solubilization of soil As resulting from the dissolution of soil Fe oxide during flooding and reduction of a soil.

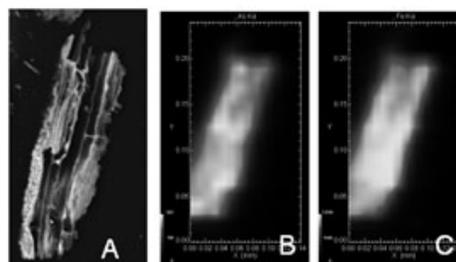


Fig. 3. (A) SEM of the Fe-oxide plaque of a rice root; (B) map of As associated with the plaque (the light colored region indicates a region of higher As concentration); (C) map of Fe associated with the plaque.

Under the conditions of flooded rice culture, the rice plant pumps oxygen to the roots. The oxygen results in an increase in redox potential at the root/soil-solution interface and the precipitation of Fe oxide at the root surface (Fig. 3). The mineralogy and morphology of this Fe-oxide plaque is influenced by soil environmental conditions, soil texture, mineralogy, soil-solution pH and dissolved ionic composition (especially Fe²⁺). The Fe plaque is a site for adsorption of dissolved As³⁺ and As⁵⁺, and will likely strongly impact As adsorption by plants.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge project partners John Duxbury (Cornell), A.T.M. Farid (BARI), M. Rafiqul Islam (BAU), Md. Jahiruddin (BAU), Craig Meisner (CIMMYT), M.A. Mazid Miah (BRRRI), G.M. Panaullah (CIMMYT), G.K.M. Rahman (BSMRAU). This project was supported by a grant from USAID-Bangladesh.