

Mineralogy and Arsenic Bonding in Bangladesh Rice Paddy Soils

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The objective of this paper is to review the mineralogical factors that impact the reactions of arsenic in the rice-paddy soils of Bangladesh, with emphases on mineralogical composition, mineralogical controls of soil-arsenic retention and release, and the implications of mineralogy to arsenic in rice culture.

METHODS OF MINERALOGICAL ANALYSIS

Soil samples for this study were collected from the 0-15 cm depth of *boro* (dry season) rice paddies in five *thanas* of Bangladesh, including Paba (High Ganges River Floodplain), Tala (Ganges Tidal Floodplain), Faridpur (Low Ganges River Floodplain), Brahmanbaria (Old Meghna Estuarine Floodplain), and Senbag (Old Meghna Estuarine Alluvium). Individual samples were air dried, separated into sand, silt, and clay particle-size separates. Individual samples were analyzed for total arsenic and total iron following total dissolution by closed vessel microwave digestion by HF/HNO₃. Additionally soil Fe was assessed by selective extraction with (i) citrate dithionite 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 arsenic associated with poorly crystalline Fe oxide, and (ii) pH 4.0, 0.1 M Na phosphate to determine readily exchangeable arsenic (1). 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

Soil mineralogy, though relatively similar with respect to the principal minerals present, was highly variable with respect to soil texture and mineral concentrations. The major factors influencing soil-surface mineralogy are alluvial source material, position in landscape, soil weathering, and soil management.

The principal reactive minerals were di- and tri-octahedral micas (especially biotite), high-Fe vermiculites, smectites, Fe-chlorite, and the Fe oxides, goethite, lepidocrocite, and ferrihydrite (Fig. 1A, B). All samples also contained quartz and feldspar. In the current study, gibbsite was not identified in any of the rice-paddy soils. Relatively low concentrations of calcite were observed in almost all Faridpur samples. Fe sulfides (pyrite, mackinawite) were detected in only a few 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 follows the following sequence: micas ® chlorite ® vermiculite ® 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 arsenic contents of the 472 surface soils in this study varied from 0.7 to 66.0 mg As kg⁻¹. Arsenic 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 with soil Fe-oxide minerals. Ammonium-oxalate extractable As averaged approximately 70 % of total arsenic. This result indicates that As was highly associated with the poorly crystalline Fe-oxide component. An average of 23 % of total As was extracted to pH 4.0, 0.1 M Na phosphate, indicating that most of the As was strongly bound and was not readily ligand exchanged by phosphate.

In an assessment of 15 high As soils, with soil 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 (mica, chlorite, vermiculite) edge sites was negligible. In the sand fraction, As was largely associated with Fe oxide weathering rinds within schist and weathered mica aggregates (Fig. 1C, D, E)

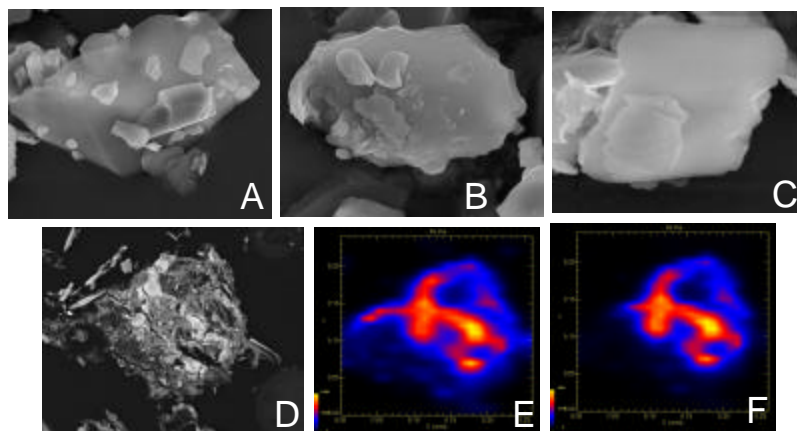


Fig. 1. (A) SEM of vermiculite from a Bangladesh rice-paddy soil; (B) SEM of biotite; (C) SEM of chlorite; (D) SEM of a weathered biotite aggregate (white ring in center is an Fe oxide weathering product); (E) map of Fe in aggregate D; (F) map of As in aggregate D (The close correspondence of the maps of Fe and As indicate that As in the weathered sand aggregate is largely associated with the Fe oxide weathering product.).

Both As³⁺ and As⁵⁺ species are largely retained by ligand exchange to soil Fe oxides, predominantly as inner sphere adsorption complexes at the oxide surface (Fig. 2).

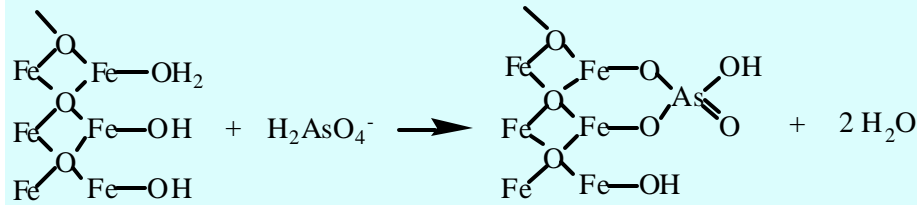


Fig. 2. Both As^{3+} and As^{5+} are largely adsorbed in the rice-paddy soils of Bangladesh by the formation of inner sphere surface adsorption complexes with soil Fe oxides.

Bonding to layer silicate edge sites was negligible compared to bonding to Fe oxides. Fe sulfide phases (pyrite and mackinawite) were identified in only a few of the rice-paddy soils of Bangladesh, but if present, these minerals would also expect to contribute to As bonding.

The dissolution and solubility of soil Fe-oxide minerals are highly redox dependent. Under reducing conditions, soil Fe-oxide minerals are solubilized, especially the highly reactive poorly crystalline Fe oxides, such as ferrihydrite. Upon dissolution, surface-adsorbed As is also released, resulting in the increased solubility of soil As.

Influence of Soil Minerals on Arsenic Dynamics in Rice Paddy Soils

The solubility of arsenic in rice-paddy soils is strongly impacted by redox potential and the dissolution and solubility of soil Fe oxide (Fig. 3). Arsenic toxicity is more problematic under flooded rice culture than under dryland conditions, because of the enhanced solubility of arsenic with the former.

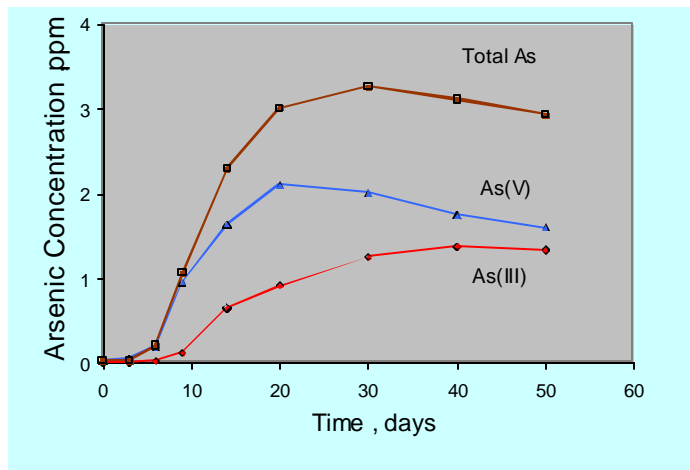


Fig. 3. The time-dependent solubilization of soil As resulting from the dissolution of soil Fe oxide during flooding and reduction of a soil.

Under the conditions of flooded rice culture, the rice plant pumps oxygen to the roots. The oxygen diffusing from the plant roots results in an increase in redox potential at the

root/soil-solution interface and the precipitation of Fe oxide (lepidocrocite, goethite, ferrihydrite) at the root surface (Fig. 4). The mineralogy and morphology of this Fe-oxide plaque is influenced by soil environmental conditions, including dissolved Fe^{2+} concentration, soil texture, and mineralogy, and soil solution pH and dissolved ionic composition. This plaque is also a site for adsorption of dissolved As^{3+} and As^{5+} , and is likely to strongly impact As adsorption by plants.

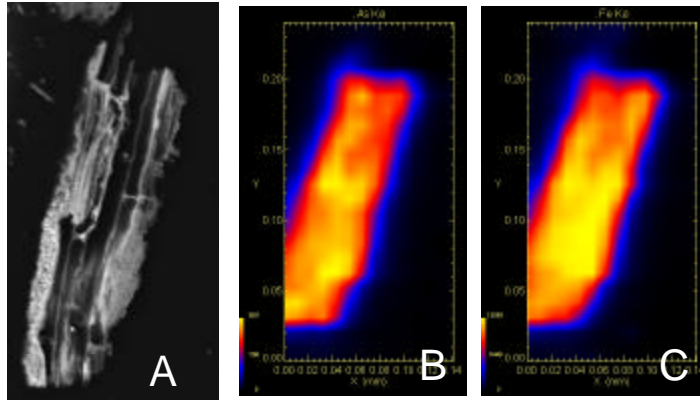


Fig. 4. (A) SEM of the Fe-oxide plaques of a rice root; (B) map of As associated with the plaque (the light colored region indicates a region of higher As concentration); (C) map of Fe associated with the plaque. In these images there is a high correlation between regions of high As and Fe concentrations, indicating that the As is associated with Fe oxide.

CONCLUSIONS

Fe-oxide minerals strongly impact arsenic dynamics in flooded rice culture, primarily because of their impact on arsenic solubility, retention, and release. Rice plants are able to modify their environment by the formation of an Fe-oxide plaque at the rice root surface, even in a highly reduced soil. This reaction likely strongly impacts arsenic retention by rice, though specifics of this reaction are still not fully understood.

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