

Abstract

Soil samples (n = 45) and water samples (n = 111) were collected in the coastal zone of SW Bangladesh in wet (November) and dry (May) seasons in 2016 to identify the factors influencing soil arsenic concentrations. Soils are entisols formed from recently deposited, predominantly silt-sized sediments with low carbon concentrations typical of the local mangrove forests. Arsenic concentrations in bulk soil are higher in November than in May and vary little between sites. Arsenic concentrations in deionized H₂O extracts are ~2 orders of magnitude lower, indicating only ~1% of As is soluble. Water samples show that As concentrations are highest in groundwater from tubewells. Bulk soil As is positively correlated with As concentration in irrigation water, suggesting that As from irrigation water is added to the soil. Unlike other water types, As in rice paddy water is much higher in the wet season, consistent with some fields being irrigated with tubewell water. Arsenic in rice paddy water increases by soil sulfide dissolution, and decreases by dilution during the monsoon. Water soluble As in rice paddy soils is positively correlated with S and DOC concentrations in rice paddy soil extracts due to sulfide dissolution and complexation with DOC. Thus, waterlogging of rice paddy soils leads to reducing conditions, the absence of ferric oxyhydroxides that could sorb As, and the presence of sulfides that incorporate As. As soil pH increases from 7 to 8, $K_D(\text{soil/extract})$ increases, consistent with the observed positive correlation between irrigation water pH and bulk soil As concentration. Arsenic bioavailability could be decreased through soil aeration (draining and tilling) and by avoiding the use of groundwater for rice paddy irrigation.

Objective

- Identify the factors controlling arsenic concentrations in soil and surface waters

Background

The sample sites are located within the Ganges Delta System in the Bengal Basin. They are north of the Sundarbans National Park, the largest mangrove forest in the world. This region experiences a tropical, biseasonal climate. Samples were collected in May (dry season) and November (wet season). Sample types included Rice Paddy (RP), Tidal Channel (TC), Aquaculture (A), Rainwater, Tubewell (TW), Sundarbans mangrove forest (SS), and Pond Sand Filter (PSF).

Methods

- Soil and water samples were collected in May and November 2016 (Figs. 1 and 2).
- Bulk soil samples (fused in LiBO₂, then dissolved in dilute HNO₃) and soil extracts (1:5 soil: deionized water) were analyzed using ICP-OES, ICP-MS, IC, and a TOC analyzer.



Fig. 2: Examples of study area's biseasonal climate. Top: November 2016. Bottom: May 2016.

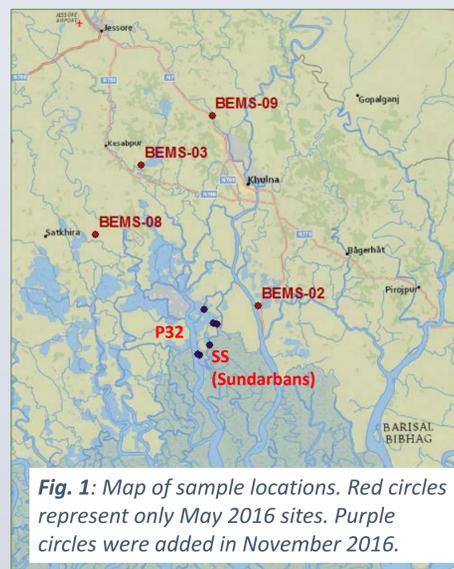


Fig. 1: Map of sample locations. Red circles represent only May 2016 sites. Purple circles were added in November 2016.

Results

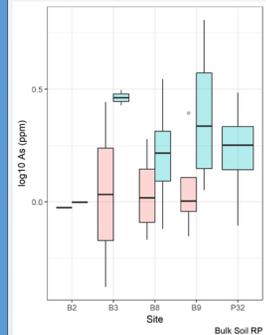


Fig. 3: Bulk soil As concentrations are highest at site B3, but overlap substantially between sites, so all sites are lumped together.

Table 1

Site	Avg. Soluble As in RP Soil (ppm)	Avg. As in RP Bulk Soil (ppm)	% soluble
B2	0.01	0.97	1%
B3	0.03	2.25	1%
B8	0.04	1.36	3%
B9	0.02	2.17	1%
P32	0.02	1.57	1%

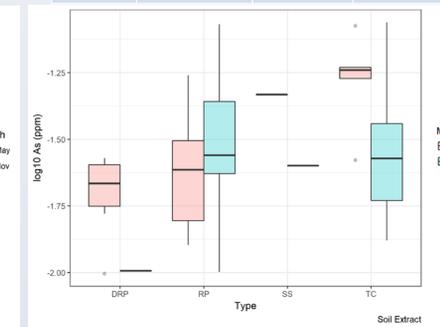
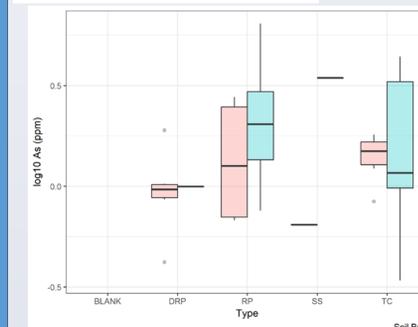


Fig. 4: Soil types: RP = Rice Paddy, DRP = Dry Rice Paddy, SS = Sundarbans, TC = Tidal Channel. Bulk soil As concentrations don't vary significantly by soil type or season. As in soil extracts also show little variation, except are higher in May TC samples. Rice paddy As concentrations are much higher in bulk soil than in soil extracts: ~1% of soil As is water soluble (Table 1).

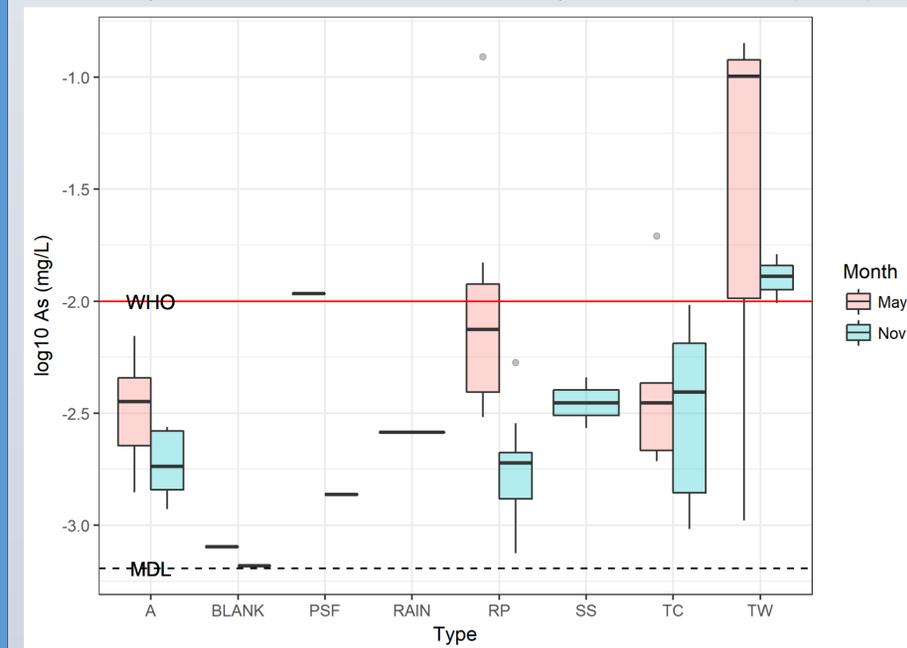


Fig. 5: Boxplot of As concentrations in water samples. Type abbreviations the same as for soils, plus A = Aquaculture (brine shrimp pond), PSF = Pond Sand Filter, TW = Tubewell. Reference lines: WHO = World Health Organization guideline, MDL = Method Detection Limit.

Results (continued)

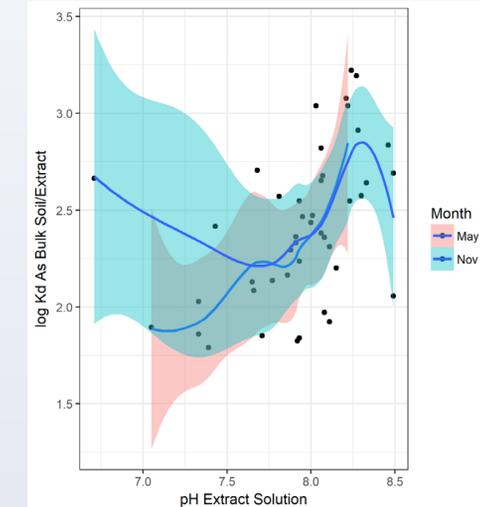


Fig. 6: As concentrations in bulk soil and DI water extract are not correlated, indicating partitioning equilibrium is not achieved. However, $K_D \text{As}(\text{bulk soil/extract})$ values seem to increase from pH 7 to 8.

Given that As concentrations do not seem to depend on one variable, we performed multiple linear regression to identify the factors controlling As in rice paddies:

1. Arsenic in RP water: $\log C_{As}^{\text{water}} = 0.83 * \log C_{S}^{\text{bulksoil}} - 0.39 * \text{pH}^{\text{water}} - 0.20 * \text{Monthnum} + 0.68$, $n = 9$, $\text{adj. } r^2 = 0.89$.
2. Arsenic in RP soil extracts: $\log C_{As}^{\text{soilextract}} = 0.74 * \log C_{\text{DOC}}^{\text{soilextract}} - 0.23 * \log C_{S}^{\text{bulksoil}} + 0.15 * \log C_{S}^{\text{soilextract}} - 3.15$, $n = 11$, $\text{adj. } r^2 = 0.69$.
3. Arsenic in RP bulk soil: $C_{As}^{\text{bulksoil}} = 13.3 * C_{As}^{\text{irrigwater}} + 1.89 * \text{pH}^{\text{irrigwater}} + 10.6$, $n = 5$, $\text{adj. } r^2 = 0.998$

Conclusions

- Water:** Nearly all tubewell samples have As > WHO guideline of 0.01 mg/L, while some rice paddy water samples in May exceed the guideline because some fields are irrigated with tubewell water.
- Rice paddy water:** Arsenic increases with increasing soil sulfur and decreasing pH, suggesting that As is liberated by sulfide dissolution. Arsenic in rice paddy water also decreases from month 5 to 11 due to dilution during the monsoon.
- Rice paddy soil extract:** Arsenic increases with extract DOC and S concentrations and decreases with increasing S in soil, suggesting that sulfide dissolution transfers As to soil porewaters, and that As is complexed with DOC in the extract solution. No correlation with P or Fe is observed, indicating that competitive adsorption with PO₄³⁻ on ferric oxyhydroxides does not control As solubility.
- Rice paddy bulk soil:** Arsenic is positively correlated with As concentration in irrigation water, suggesting that As from irrigation water is added to the soil. As pH increases from 7 to 8, $K_D(\text{soil/extract})$ increases. This is consistent with the observed positive correlation between irrigation water pH and bulk soil As concentration.
- Waterlogging of rice paddy soils leads to reducing conditions, the absence of ferric oxyhydroxides that could sorb As, and the presence of sulfides that incorporate As.
- Arsenic bioavailability could be decreased through soil aeration (draining and tilling) and by avoiding the use of groundwater for rice paddy irrigation.

Acknowledgements

- Office of Naval Research Grant # N00014-11-1-0683, National Science Foundation grant OCE-1600319
- Rossane Delapp (Vanderbilt University), Kushal Roy, Md. Rezaul Karim and Farjana Akhter (Khulna University), Saddam Hossain (Dhaka University), Basu Kumar (Dhaka University), Chelsea Peters (Vanderbilt University)