

MOTIVATION

Bangladesh, a country of 157 million people, faces severe water resource challenges. It is estimated that 20% of the national population does not have access to safe drinking water due to pathogens, salination, and arsenic (As) contamination.¹ With ~90% of the population relying on groundwater for drinking water, Bangladesh aresenic poisoning is causing catastrophic effects on human health. There is considerable debate about the key controls on As concentration and mobility in this region. It is thought that groundwater drawdown may facilitate oxidation of As-laden pyrite.^{2,3} Or competitive adsorption from recharged phosphates from fertilizers or bicarbonate (HCO₃⁻) via microbial metabolism may release sorbed As.^{3,4,5} Alternatively, the liberation of As could simply be related to reductive dissolution of iron-oxyhydroxide (HFO), or goethite, that contains As in sorbed form, with organic matter (DOC) as the likely reductant.⁶ Previous analysis of the southwest (SW) Bangladesh shallow aquifer suggests limited drawdown, minimal groundwater velocities, similarities with tidal channel water composition, and the presence of HFO in sediments.⁷ The objectives of this study are to use reaction path modeling to identify the source and characterize extent of contamination of groundwater by salts and arsenic in a poldered area in SW Bangladesh.



STUDY AREA

The Ganges, Brahmaputra, and Meghna river networks carve the low-lying deltaic plains of southern Bangladesh. Much of the tidal mangrove forest ecosystem of the lower delta was converted to poldered (embanked) islands in the 1960s to sustain a population of 150 million through shrimp farming and rice production.⁸ Here we focus on Polder 32 (P32), which is 60 km², about 30 km south of the city of Khulna and about 60 km north of the Bay of Bengal (Fig. 1). SW Bangladesh experiences a humid, biseasonal climate with a dry season from November to May and wet season from June to October.¹ The region has a shallow aquifer system contained within the massive Holocene floodplains, consisting of poorly developed, immature silt and clay soils that are underlain by Himalayan-derived sands of the Pleistocene.⁹ Groundwater velocities are low and recharge is limited but likely.

Figure 1 | Polder 32 in southwest Bangladesh.

RESEARCH QUESTIONS

- 1. Is P32 groundwater a mixture of connate seawater and meteoric water, modified by progressive reduction?
- 2. If so, how do ancient seawater-meteoric water mixtures evolve to modern groundwater compositions with high arsenic concentrations?

METHODS

Ouestion 1:

• Calculated mixing curves from cation-Cl pairs from P32 shallow aquifer tubewell samples, rainwater samples, and a seawater composition.⁶

Question 2:

- Titrated methane (CH₄) in the presence of HFO, $As(OH)_4$, and initial compositions of (1) average dry season tidal channel water and (2) average wet season tidal channel water using Geochemists Workbench v. 9 React double-layer surface complexation model.
- Calculated Eh-pH diagrams and reaction traces in Act2 program using temperature = 25° C, pressure = 1.013 bars, activity of H₂O = 1.0, hematite suppressed, activity of $Fe^{2+} = 10^{-6}$, and activity of SO_4^{2-} based on *React*

Evolution of Saline and Arsenic Contaminated Groundwater in Southwest Bangladesh

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QUESTION 1



- samples and tidal channel samples (Fig. 2)

Figure 2 concentrations of conservative elements Na, Mg, and Sr with best-fit linear regression lines. All P32 groundwater samples are plotted in conjunction with the average of rainwater samples (RW), tidal channel samples (TC), and a seawater composition (SW) Taylor and Mclennan (1985).¹⁰ All concentrations are \log_{10} values in mg/L.

- Initial groundwater composition can be estimated by tidal channel water
- Addition of CH_4 (representative of DOC) leads to a reducing environment
- Oxygen is consumed, sulfate is reduced, Fe²⁺ dissolves (Fig. 4)
- Final pH is 7.4 to 8, compared to an average P32 groundwater pH of 6.9 (Fig. 5)
- Goethite dissolves and frees As, which is present in the reduced form (Fig. 6)
- Aqueous Fe and sulfide combine to form pyrite (Fig. 4, 5, 6)

Figure 4 | Reaction components of average (a) May and (c) **October tidal channel solutions versus CH₄ reacted. Box-and**whisker plot (b) shows measured ranges of fluid components $(Fe^{2+}, As(OH)_4^-, HCO_3^-, and SO_4^{2-})$ from groundwater samples. Diluted, wet season (October) model shows less change in components (note scale change in x-axis). Groundwater samples match the model final concentrations in $As(OH)_4^-$, $HCO_3^$ and Fe²⁺. But SO_4^{2-} is underestimated in the model.

Figure 5 | Minerals, sorbed fraction of As(OH)₄, and pH for

(a) May and (c) October tidal channel solutions versus CH_4

reacted. Slight increase in pH is associated with the reduction of







Rainwater and seawater compositions fall on regression lines of conservative elements from P32 groundwater

• Tidal channel samples have a greater range in conservative element concentration than groundwater samples • Rainwater Mg concentration is much lower than expected from mixing curve



Figure 3 | Maps of average measured As and dissolved organic carbon (DOC) concentrations (µg/L) of groundwater samples collected from tubewells in 2012-13 from (a) May and (b) October. GW DOC concentrations are unusually high. As and DOC concentrations are roughly correlated, which could support the hypothesis that reduction leads to As mobilization. Figure from Ayers et al. 2015.⁷

AsO₄

Figure 6 | Field Eh-pH diagrams for Fe and As including average (a) May (solid black line) and (b) October (dashed black line) tidal and P32 groundwater samples (blue) and tidal channel samples (red). In Fe, reaction traces move from goethite to pyrite predominance fields. Groundwater samples fall close to phase lines of goethite, pyrite, and Fe²⁺. Groundwater samples show presence of As⁵⁺ and As³⁺ species, and traces move toward reduced $As(OH)_3$

DISCUSSION

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- Seawater and rainwater fall close to the mixing lines for each cation-Cl pair, suggesting that ancient seawater and rainwater are the mixing endmembers for P32 groundwater
- Tidal channel water that deposits most sediments in the region is a mixture of seawater and meteoric water (as it falls on the mixing line), and is likely trapped as pore water during sediment deposition
- Progressive reduction driven by oxidation of DOC leads to reductive dissolution of goethite and mobilization of arsenic sorbed on HFO
- Dissolution of goethite will lead to the formation of pyrite from freed Fe²⁺ and reduced SO_4^{2-}
- Composition of groundwater samples fall near the goethite and pyrite phase boundary, indicating goethite is reduced and arsenic mobilized
- Model arsenic estimates fall within measured arsenic concentrations but additional release mechanisms may affect mobilization

CONCEPTUAL MODELS



Figure 7 | Conceptual model from Kocar et al. 2014. Particulate organic carbon (POC) transforms to dissolved DOC, driving biogeochemical reactions within zones of high or low hydraulic conductivity (K), with lower K associated with higher As. Triangles suggest HFO reactivity increases with sediment age and depth.¹¹



Figure 8 | Conceptual model from Kar et al. 2010. Reduction of HFO is associated with oxidative breakdown of organic matter, where bacteria assist in the As release. ¹²

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