CONTAM 04 Deploying ion selective sensors to investigate how diurnal subsurface redox cycling influences arsenic mobilization in a Bangladeshi aquifer

CONTAM 04.1 Overview
Arsenic (As) in well water has led to the largest environmental poisoning in history, affecting tens of millions of people in the Ganges Delta and elsewhere. Despite the tragic public health implications of this problem, we do not yet have a complete answers to the questions of why dissolved arsenic concentrations are so high in the groundwater of the Ganges Delta, and how sulfur cycling affects the biogeochemistry of As in natural environments. Some literature indicates that seasonal, cyclic variations in redox conditions can lead to arsenic mobilization through a cycle of (1) oxidation of arsenic-sulfide solids and sorption of As(V) to Fe(III) oxyhydroxides and (2) respiration of AsV bearing Fe(III) oxyhydroxides, leading to the release of As to the aqueous phase. Other recent studies have suggested an entirely new mechanism for arsenic mobilization. It may be that in phosphate limited conditions, microbial dissolution of minerals to gain phosphorus releases As incidentally from minerals such as apatite. Our activity over the past year has shifted to focus on laboratory microcosm experiments using soil and bacterial isolates from the site. We are investigation As release, sorption to biogenic minerals, and solubility in the presence of elemental sulfur.

CONTAM 04.2 Approach
Our current research has three components:

- We are comparing As release from mineral dissolution and Fe hydroxide respiration using the Bangladeshi soils in laboratory microcosms. Through these same experiments, we are testing the hypothesis that pond sediments are a major site of As release in Bangladesh through a comparison of As release from sediments collected from the paddy and the edge of the pond at our site.

- We are testing the hypothesis that As mobilization is largely controlled by sorption to biogenic minerals containing sulfide, as they appear to be far more sorptive to As relative to carbonate minerals. Using isolates from our site in Bangladesh, we are cultivating bacteria under conditions predicted by geochemical modeling software to result in the formation of differing types of minerals.

- We are investigating enhanced solubility of metals in the presence of polysulfides. The chemistry of As in sulfidic environments is extremely complicated due to the numerous soluble As-sulfide species predicted to form. The impact of elemental sulfur has been completed neglected in previous research and we hope to fill this gap.

CONTAM 04.3 Systems Description and Experiments
We are currently conducting experiments in the three areas described above.

- Comparison of As release mechanisms. To compare arsenic release from mineral dissolution and Fe hydroxide respiration, we incubated paddy and pond sediment under different conditions to measure the amount of As released. We designed the incubations to compare release by mineral dissolution (which should be higher under P limiting conditions and probably aerobic conditions) and reduction of arsenic-bearing Fe minerals. We did see some evidence for mineral dissolution (the live, P limited microcosm released more As than that with P added), but Fe mineral reduction led to greater release. Paddy and pond sediment behaved with similar trends (although we see more mobilization from pond sediment), but so far we have only tested the 0.5 m depth. When sulfide appeared, the arsenic decreased dramatically, but Fe stayed high. This is interesting, as it supports the preferential precipitation of As as As-S minerals over precipitation as Fe-As-S minerals (which has been a subject of some controversy in the literature). We are currently repeating this experiment at the 1m depth.

- Investigation of As sorption to biogenic minerals. From the Bangladeshi soil, we are maintaining three types of enrichment cultures: Fe-reducing, sulfate-reducing, and As(V) reducing. We are currently purifying isolates from all three enrichment cultures. We will investigate biogenic mineral formation by these isolates under varying chemistry (Fe/S(-II)/
S(0)/Carbonate) and how the biogenic minerals sorb arsenic. We will also test the availability of As(V) sorbed to standard minerals to the As(V) reducing isolates. Our first experiment uses FeRB in a solution only environment with As spiked and will compare it to one with S(II-) also spiked.

- Solubility of As, Pb, and Cd in the presence of elemental sulfur. We are looking at enhanced solubility of metals in the presence of polysulfides. See Figure 1 for a schematic.

**CONTAM 04.4 Accomplishments**

- See Figures 2 for Day 5 data for soluble As in sediment microcosms incubated under varying conditions.

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![Graph of Arsenic Levels on Day 5 in Paddy and Pond Soil](image)

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<tr>
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<th>Oxic</th>
<th>Anoxic</th>
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<tr>
<td>Killed</td>
<td>+P Killed</td>
<td>-P Anoxic</td>
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Figure 2. Soluble As at Day 5 for various microcosms. Text in the Table depicts the conditions for each treatment mobilization mechanism thought to be favored under a specific condition.

- We have enrichment cultures and isolates from our site, and have modeled the minerals predicted by geochemical modeling tools under varying conditions.

- Our preliminary data show that Pb(aq) and Cd(aq) concentrations are higher in the presence of S(0) than in the absence of S(0). Figure 3 shows the solubility of PbS(s) and CdS(s) in sulfidic solution in the presence and absence of elemental sulfur.
CONTAM 04.5 Future Directions
This year's work will include follow up on all three areas:

• 1) New soil from the site is currently being obtained with the help of our Bangladeshi collaborators. We will repeat the As mobilization mechanism experiment at a range of depths at both sites. Additionally, we will add a mineralogical component to hopefully more directly detect which minerals are being consumed through microbial activity.

• 2) Laboratory-based and geochemical modeling investigation of As sorption to biogenic compounds. Isolates from Bangladesh site will be incubated at a range of Fe/S(-II)/S(0)/carbonate levels to result in formation of various biogenic minerals. Precipitated solids will be analyzed by standard mineralogical techniques with the help of collaborators.

• 3) We are currently repeating the experiment to include a bigger suite of pH’s and S(-II) levels. Results will be modeled using FITEQL to determine best estimates for soluble complex formation constants.