

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

CONTAM 04.1 People

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CONTAM 04.2 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 answer to the question of why dissolved arsenic concentrations are so high in the groundwater of the Ganges Delta. Recent 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) reduction of AsV bearing Fe(III) oxyhydroxides, leading to the release of As to the aqueous phase. Preliminary data obtained through previous CENS deployments suggests that diurnal trends in redox conditions may also be important in As mobilization.

CONTAM 04.3 Approach

This project is a continuation of previous field deployments of hydrologic and geochemical sensors investigating arsenic (As) contamination in Bangladesh, but includes expanded activity to encompass enclosure experiments conducted in the field, and laboratory microcosm and mesocosm experiments using soil and rice seeds from the site. The overall goal of the current study is to investigate the mechanisms leading to the previously observed daily oscillations in geochemical parameters, and how diurnal processes may influence As mobilization. Specifically, we will test the following hypotheses: (1) plant-induced processes including root oxygen and carbohydrate release and nitrate uptake drive daily oscillations in subsurface geochemistry at our site; and (2) daily oscillations in redox sensitive parameters may drive As mobilization to the aqueous phase at our site.

CONTAM 04.4 Systems/Experiments

1) Deployment in Bangladesh April 2008

In April, 2008, seven temperature sensors and nineteen ion selective electrode (ISE) sensors were deployed at the field site in Munshiganj, Bangladesh. The sensors were distributed between two locations at a depth of one foot. Both locations are near the center of the rice paddy, however, vegetation is present at one site and not at the other. At each location, there were thirteen sensors: 3 temperature, 2 ammonium, 2 nitrate, 2 chloride, 2 dissolved oxygen (DO), and 2 oxidation-reduction potential (ORP).

For the ISEs, a hole slightly greater than the diameter of the javelin/pilon was dug using an auger and the javelin/pilon was then inserted into the hole. Excess space surrounding the javelin was filled in with the soil removed during the digging process. The sensors/javelins were left in the paddy for a period of one week, at the end of which, they were removed.

2) Deployment at Madrona Marsh May 2008

In May, 2008, five temperature sensors and twelve ISE sensors were deployed at Madrona Marsh, located in Torrance, California. The sensors were distributed between three locations at a depth of one foot. The goal of having three locations was to further investigate the effects of vegetation on microbially dependent redox sensitive parameters, such as ammonium and nitrate. In one location, there is vegetation, while in the second, there is not.

The third location serves as a control, where vegetation is not present and sediment was autoclaved to remove any biotic effects. The sensors were placed directly into the marsh sediment and left in for a period of one week.

3) Temperature correction for ion selective electrode sensors

Having previously established that ISE sensors are very sensitive to temperature effects, it was necessary then to be able to correct the ISE measurements for the temperature effects. The ISEs were calibrated for both concentration (10E-1M to 10E-4M) and temperature (15°C to 35°C). The ISE sensors were placed in a beaker containing a known standard and kept in a temperature controlled water bath. Approximately an hour was allotted for each temperature setting for each concentration to allow for adequate equilibrating. The data over each stable range were averaged to obtain a "final" reading from each ISE sensor. The data are then analyzed using a multiple regression, least-squares method to obtain a relationship between the ISE voltage reading, concentration, and temperature. Method was learned from Yeon Jeong in Tom Harmon's group.

4) Hydroponic experiments

We will investigate whether a diurnal trend exists in root oxygen and carbohydrate leakage from Boro rice using seedlings grown in nutrient solution. Based on a method similar to those used in Marin et al (1992), rice seedlings from the Bangladesh rice paddy were grown in a hydroponic basal nutrient solution (Yoshida et al 1976), with pH adjusted to promote sufficient Fe uptake (Jugsujinda, 1976). Total organic carbon (TOC) and pH levels were measured during the day and night time, approximately twelve hours apart.



Figure 1 – Experimental set-up for hydroponic rice growth experiment.

CONTAM 04. 5 Accomplishments

1) Deployment in Bangladesh May 2008

A sample of the data obtained at the site is shown in Figure 2. Diurnal cycles are present in nitrate, ammonium, and chloride sensors.

Water samples taken from the field site throughout the day were analyzed for arsenic using GFAA. Arsenic levels from samples taken in the vegetated location showed a decreasing trend throughout the day. However, arsenic levels from samples taken in the non-vegetated location showed an increasing trend throughout the day.

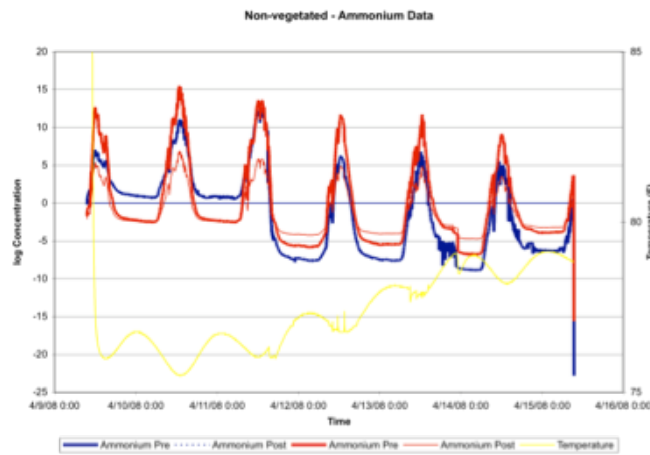


Figure 2 – Ammonium ISE sensor data from non-vegetated location during May, 2008, deployment.

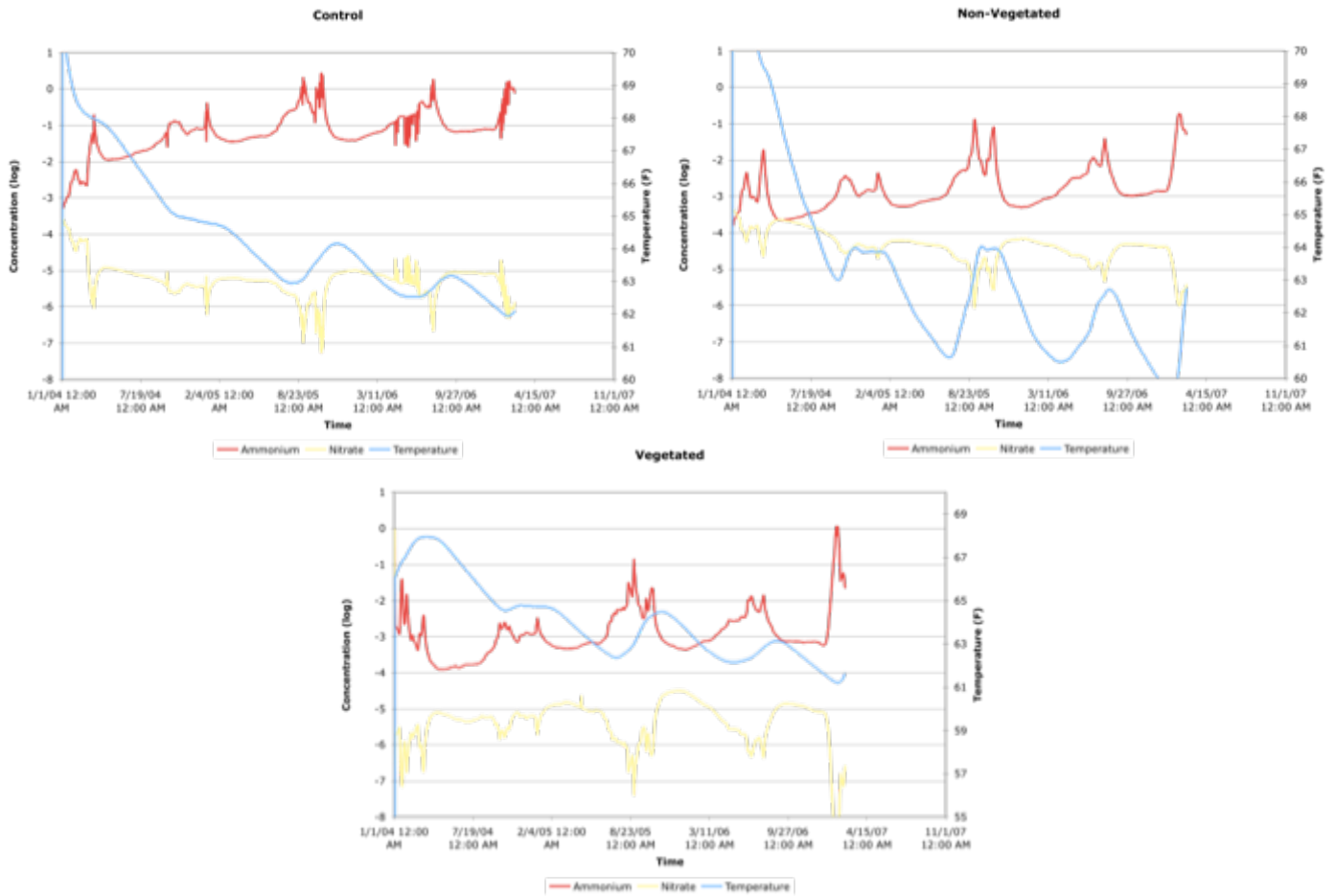


Figure 3 – Ammonium and nitrate ISE sensor data from all 3 locations during May, 2008, deployment.

3) Temperature.

Multiple regression analysis performed on the temperature calibration resulted in equations in the following format: $mV = b_0 + b_1 (\ln T) + b_2 (-\log C)$, where b are constants, T is temperature, and C is concentration. Figure 4 shows data from the temperature calibration for an ammonium sensor (calibration equation: $mV = -0.1(-\log C) + -0.43(\ln T) + 2.278$).

4) Hydroponic experiments

Diurnal cycles were observed in both TOC data and raw pH measurements, along with alkalinity calculations. TOC data showed that organic carbon output from rice roots increased during the day and decreased at night. Additionally, pH and alkalinity decreased during the day and increased at night. Sources of pH changes could be directly or indirectly due to diurnal root exudates in the form of organic carbon, diurnal oxygen release

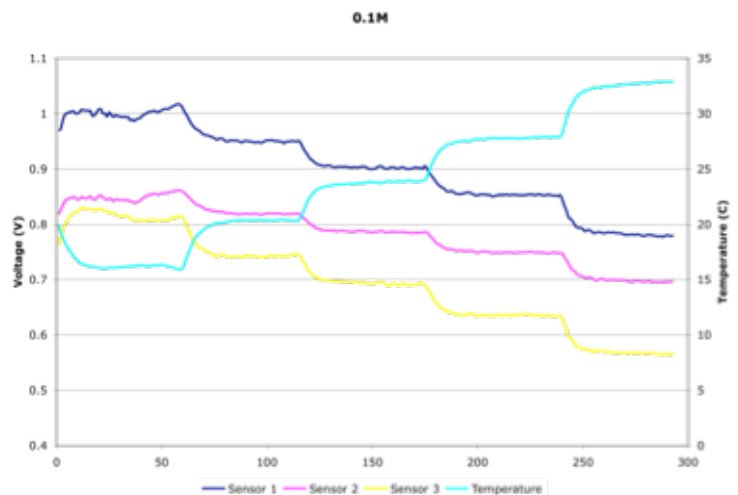


Figure 4 – Temperature calibration for ammonium ISE sensor.

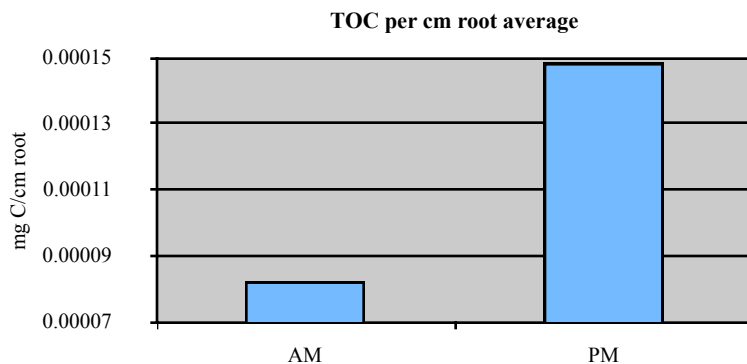


Figure 5 – Average organic output per cm of rice root

from roots (which is debated), diurnal redox state of solution, or complexation reactions. The effects of diurnal root exudates and the sources and effects of diurnal pH and alkalinity changes on chemical cycling and arsenic mobilization must be further explored. An understanding of these cycles and interdependencies may aid in the development of mitigation strategies for this large-scale problem.

CONTAM 04.6 Future Directions

This year's work will include 1) laboratory experiments investigating aqueous complexation of As and polysulfides, 2) laboratory-based and geochemical modeling of sorption studies, and 3) single and co-culture studies of iron-reducing and sulfur-reducing bacteria (FeRB and SRB). Detailed descriptions of these tasks are outlined below.

Task 1: Batch As₂S₃ solubility experiments

The solubility of As₂S₃ will be investigated in the presence and absence of elemental sulfur at a range of pH and sulfide concentrations to investigate complexation between arsenic- and polysulfides. We hypothesize that the presence of elemental sulfur, and consequent formation of polysulfides, will substantially increase the solubility of orpiment in sulfidic water. We will add metal-sulfides (lead, cadmium, zinc, and arsenic) to serum bottles with sulfide and elemental sulfur. Through investigating As₂S₃ in a variety of conditions and modeling the data with FITEQL, we will propose complexation constants for the As-S(0)-S(-II) aqueous system.

Task 2: Fe mineral sorption experiments

We will study sorption between As-sulfide and As-polysulfide species with Fe oxyhydroxides. We hypothesize that sorption of these complexes will significantly affect the mobility of these species of As in groundwater. We will conduct batch sorption experiments in both defined systems with reference Fe minerals including amorphous Fe oxyhydroxides, siderite, and pyrite, as well as slurries using sediment from an As-contaminated Bangladeshi Holocene aquifer.

Task 3: FeRB and SRB experiments

We will investigate the release/retention of As during Fe- and SO₄²⁻-reducing conditions. We hypothesize that S(0) will increase As mobilization under Fe and SO₄²⁻-reducing conditions. Additionally, we will test hypothesis that the relative formation of FeCO₃ versus Fe-sulfide minerals as microbial activity proceeds will control As mobilization through differential sorption of As. Working with Fe-reducing bacteria at varying levels of sulfide (which will vary the relative formation of FeCO₃ versus Fe-sulfide minerals), we will test the retention of As on the solid phase. Working with co-cultures of Fe- and SO₄²⁻-reducing bacteria, we will test how varying starting chemistry (sulfide, SO₄²⁻, and HCO₃⁻ concentrations) affects mineral precipitation and As sorption.

CONTAM 04.7 External Research Partnerships

Charles Harvey at MIT (Current)

Borhan Badruzzaman at BUET (Current)