

## The application of surface complexation models to assess arsenic mobility in aquifers

**Postma, Dieke; Jessen, Søren; Quy Nhan, Pham; Larsen, Flemming; Thi Kim Trang, Pham; Quynh Hoa, Le; Vu Long, Tran; Hung Viet, Pham; Jakobsen, Rasmus**

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# Conference on Arsenic in Groundwater in Southern Asia

14-17<sup>th</sup> November 2011, Horison Hotel, Hanoi, Vietnam



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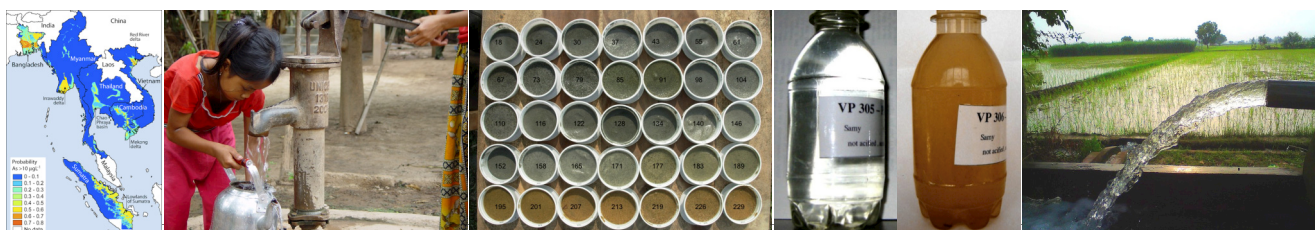
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Please show the name of the conference venue and hotel accommodation as below:

“HANOI HORIZON HOTEL – 40 CAT LINH, HANOI” (to the taxi driver)

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During our conference, fall season is in progress. The average temperature is between 18°C and 22°C. You might need to bring some warm clothing for our cool fall breeze and cooler evenings.

Also bring some walking shoes for the field trip

### **Banquet Invitation**

You are invited to a Welcome Reception on November 13 at 18.00 and a Conference Banquet on November 15 at 18:30. Prior to the Welcome Reception, you will register for the attendance and be delivered your name-card and the conference documents at the registration desk.

### **Oral presentation**

1. Presentations are 30 minutes including 10 minutes for discussion.
2. The Conference room is equipped with an overhead projector, and a computer (with Microsoft Office) connected to an LCD projector.
  - > Presenters should copy their files to the available computer set-up before the session.
3. It is strongly recommended to prepare your presentation using Power Point (MS-office) and to save your file in a USB disk. NB! When you save the file from your own computer to the USB stick please make sure to use the “embed fonts in the file” option.

### **Posters**

1. Posters must be formatted for A0-sized paper (portrait orientation) for color printing.
2. Poster presenters can send the poster file (in PPT or PDF) to the Secretariat (email: huong80412@yahoo.com) no later than November 10, 2011 so that we can arrange the print out and mount it for the poster session during the Conference.
3. The Posters will be presented around the Function Area in front of the Conference Hall. They will be on display during the whole conference.

Sunday, 13 November:

Registration: 17:30 – 20:00

Welcome reception: 18:00 - 20:00

Welcome speech by Assoc. Prof. Dr. Bui Duy Cam, Rector of Hanoi University of Science

## Programme

Monday, 14 November		
	Welcome chair <b>Pham Hung Viet</b>	Abstract page #
9:00 – 9:10	<b>Prof. Pham Hung Viet</b>	
9:10 - 9:20	<b>Assoc.Prof. Bui Cach Tuyen</b> , Deputy Minister of Ministry of Natural Resources and Environment and Director General of Vietnam Environment Administration	
9:20 – 9:30	<b>Prof. Mai Trong Nhuan</b> , President of Vietnam National University in Hanoi	
9:30 – 9:40	<b>Prof. Tran Dinh Kien</b> , Rector of Hanoi University of Mining and Geology	
9:40 - 9:50	<b>Mr. John Nielsen</b> , Ambassador of Denmark to Vietnam	
9:50 – 10:00	<b>Dr. Johnny Fredericia</b> , Director Management of the Geological Survey of Denmark and Greenland	
10:00 – 10:10	<b>Dr. Pascal Raess</b> , Deputy Country Director of the Swiss Agency for Development and Cooperation SDC, Embassy of Switzerland	
10:10 – 11:00	<b>Coffee</b>	
	<b>Arsenic and Health</b> chair <b>Pham Hung Viet</b>	
11:00 – 11:30	<b>Dang Thi Minh Ngoc</b> : <i>Arsenic contamination in groundwater in Viet Nam and it's adverse affects to public health</i>	41
11:30 – 12:00	<b>Allan H. Smith</b> : <i>Mortality risks from arsenic in drinking water ... what water concentration is "safe"?</i>	48
12:00 – 12:30	<b>Nasreen I. Khan</b> : <i>Modeling Dietary Intake of Arsenic in Drinking Water and Food: Impact on Human Health in Bangladesh</i>	26
12:30 – 13:30	<b>Lunch</b>	
	<b>Removal of Arsenic</b> chair <b>Stephan Hug</b>	
13:30 – 14:00	<b>Jiuhui Qu</b> : <i>The application of Fe-Mn binary oxide (FMBO) in the system of micro-flocculation and filtration for arsenic removal in groundwater</i>	57
14:00 - 14:30	<b>Sanjeev Chaudhari</b> : <i>Electrochemical Synthesis of Magnetite and its Applicability as an Adsorbent for Arsenic</i>	16
14:30 – 15:00	<b>Akshoy Kumar Chakraborty</b> : <i>Laboratory Studies of an Arsenic Remediation Process and Effective Utilization of ABSR</i>	14
15:00 – 15:30	<b>Dang Thanh Vu</b> : <i>Assessing Arsenic Adsorption Capacity of Natural Bentonite, Laterite and Zeolite</i>	28
15:30 -	<b>Coffee</b>	
15:30 – 17:00	<b>Poster Session</b> see list of contributions below	7

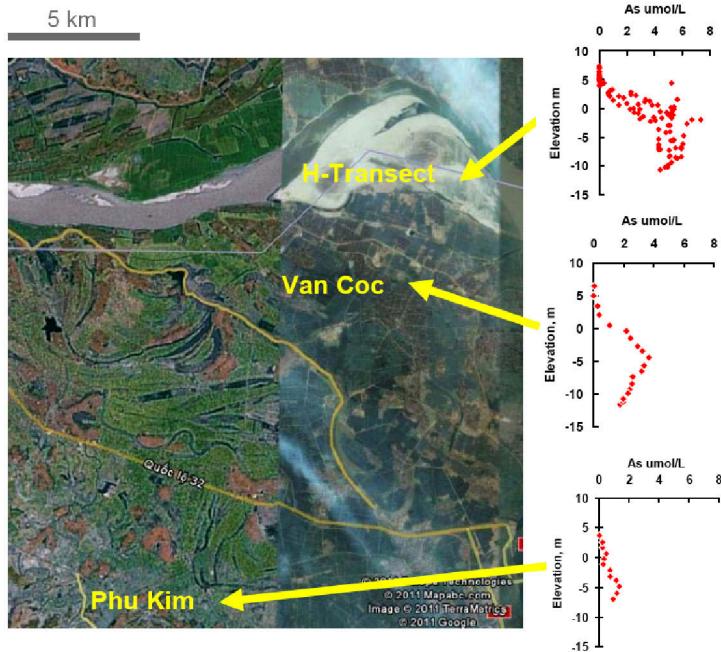
## Programme

Tuesday, 15 November		
	Hydrogeology chair <b>Michael Berg</b>	Abstract page #
9:00- 9:30	<b>Harue Masuda:</b> <i>Importance of aquifer structure to release arsenic into groundwater via convergent groundwater flow in a recharge zone in Sonargaon, Bangladesh</i>	34
9:30 – 10:00	<b>Holly A. Michael:</b> <i>Multi-scale modeling of physical and chemical effects on arsenic transport to deep wells in the Bengal Basin</i>	36
10:00 – 10:30	<b>Rebecca B. Neumann:</b> <i>Potential Impact of Rice Field Water Management Schemes on Arsenic Concentrations in Bangladeshi Wells</i>	40
10:30 – 11:00	<b>Coffee</b>	
Hydrogeology chair <b>Pham Quy Nhan</b>		
11:00 – 11:30	<b>Michael Berg:</b> <i>Distribution of As in groundwater of the Red River delta (Vietnam): Hydrochemical survey and 3D geospatial modeling</i>	12
11:30 – 12:00	<b>Shawn Benner:</b> <i>Defining and projecting groundwater arsenic levels to determine water use options in South Asia</i>	21
12:00 – 12:30	<b>Flemming Larsen:</b> <i>The use of bank infiltration from rivers as a means of reducing arsenic in abstracted groundwater, Nam Du well field, Vietnam</i>	27
12:30 – 13:30	<b>Lunch</b>	
Mapping & Surveys chair <b>Lex van Geen</b>		
13:30 – 14:00	<b>Huaming Guo:</b> <i>Spatial and temporal variation of arsenic concentration in shallow groundwater from the Hetao Basin, Inner Mongolia</i>	22
14:00 – 14:30	<b>Kongkea Phan:</b> <i>Arsenic and trace elements in paddy and agricultural soils and fish pond sediments in the Mekong River basin, Cambodia</i>	44
14:30 – 15:00	<b>Makhan Maharjan:</b> <i>Groundwater Arsenic Contamination and Mitigation Initiatives in Lowland, Nepal</i>	29
15:00 – 15:30	<b>Coffee</b>	
15:30 – 16:00	<b>Chansopheaktra Sovann:</b> <i>Spatial modelling of groundwater-arsenic-attributable morbidity and mortality in Cambodia</i>	49
16:00 – 16:30	<b>Stephan J. Hug:</b> <i>Avoiding exposure to high concentrations of arsenic, manganese and salinity and improving the acceptance of deep tubewells in Bangladesh</i>	23
16:30 – 17:00	<b>Introduction to field trip at Dan Phuong and Van Phuc</b>	5
18:30	<b>Conference Banquet</b>	

## Wednesday, 16 November

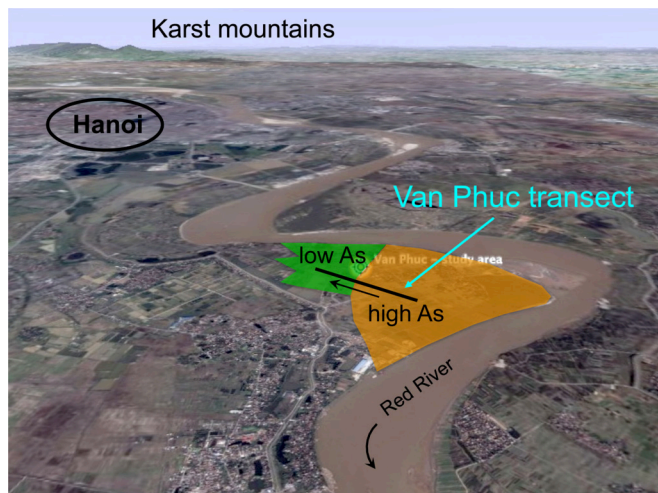
The field trip starts at 8:00 from the entrance of the Horison Hotel

Transfer by bus to the Dan Phuong area, about 30 km N of Hanoi



Near Dan Phuong we drive from the mountains towards the river and inspect some sampling sites, and their results, on the way. Near the river, there will be a demonstration of sampling and field chemical analysis methods by Vietnamese students.

Transfer to Van Phuc by boat on the Red River with lunch and entertainment on board. It is about a two hour boat trip. From the ferry port, transfer by bus to Van Phuc



Van Phuc is located 15 km downstream Hanoi in a meander of the Red River. This site features a sharp gradient of high and low arsenic concentrations along with contrasting redox conditions. An international research team\* established a network of observation wells to tackle biogeochemical and hydrological causes of arsenic mobilization, transport and retardation. Groundwater flow points towards Hanoi where large-scale pumping is drawing high-As groundwater from Holocene aquifers to Pleistocene aquifer. Various aspects of on-going studies will be presented on the spot. Van Phuc also offers the possibility to visit a communal water treatment facility and to see household-based sand filters.

\*Current team members: CETASD, Eawag, Columbia-LDEO, ETHZ, Karlsruhe, Manchester, MIT, WHO

Back at the Horison Hotel at about 6 pm



## Programme

Thursday, 17 November		
	Geochemistry chair <b>Dieke Postma</b>	Abstract page #
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9:30 – 10:00	<b>Andreas Kappler:</b> <i>Arsenic redox changes by reactive biogenic and abiogenic iron minerals</i>	25
10:00 – 10:30	<b>Benjamín C. Bostick:</b> <i>Arsenic Mineralogy and Phase Partitioning Across a Sharp Gradient in Arsenic Concentrations in Van Phuc, Vietnam</i>	13
10:30 - 10:35	<b>Alexander van Geen:</b> <i>Update on the ICDP project</i>	-
10:35 – 11:00	<b>Coffee</b>	
	Geochemistry chair <b>Shawn Benner</b>	
11:00 – 11:30	<b>Charlotte J. Sparrenbom:</b> <i>Arsenic mobilisation and anthropogenic ammonium sources in the groundwater in the Nam Du well field, Red River, Hanoi, Vietnam.</i>	50
11:30 – 12:00	<b>Dang Duc Nhan:</b> <i>Mobilization of Arsenic in groundwater in the southern Hanoi city (Viet Nam) as studied by isotopic and related techniques</i>	42
12:00 – 12:30	<b>Dieke Postma:</b> <i>The application of surface complexation models to assess arsenic mobility in aquifers</i>	46
12:30 – 13:30	<b>Lunch</b>	
	Arsenic in Soils chair <b>Flemming Larsen</b>	
13:30 – 14:00	<b>Linda C. Roberts:</b> <i>Arsenic porewater dynamics and As uptake by rice in intermittently and continuously flooded paddy fields in Bangladesh</i>	47
14:00 – 14:30	<b>S. Hilal Farooq:</b> <i>Fate of arsenic in agriculture soils in response to change in crop pattern and cultivation practices - A study from West Bengal (India)</i>	20
	Arsenic Microbiology chair <b>Andreas Kappler</b>	
14:30 – 15:00	<b>Brian J. Mailloux:</b> <i>Radiocarbon Analysis of Microbial DNA and PLFA from Arsenic Impacted Aquifers in Bangladesh.</i>	32
15:00 – 15:30	<b>Coffee</b>	
15:30 – 16:00	<b>Eva-Marie Muehe:</b> <i>Mobilization of sorbed and co-precipitated As from biogenic Fe(III) (hydr)oxides by the Fe(III)-reducer <i>Shewanella oneidensis</i> MR-1</i>	39
16:00 – 16:30	<b>Davide Merulla:</b> <i>A to Z development of a biosensor based microfluidic unit able to perform continous monitoring of arsenic in groundwater</i>	35
16:30 – 17:00	<b>Closure</b>	

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<b>Shawn G Benner:</b> <i>Emerging hydrologic influences on arsenic behaviour in south Asia</i>	10
<b>Asit Kumar Bera:</b> <i>Immunotoxic effect of inorganic arsenic in poultry birds</i>	11
<b>Antonis Chatzinotas:</b> <i>ARSOlux<sup>®</sup> – arsenic biosensor based on bioreporter bacteria</i>	15
<b>Runti Choudhury:</b> <i>Screening Of Groundwater Arsenic Contamination in Unexplored Parts of Brahmaputra Floodplains in Assam</i>	17
<b>Jessica Dittmar:</b> <i>Geomorphic and depth-dependence of organic matter chemistry within sediments of the Mekong Delta</i>	18
<b>Tamara R. Etmannski:</b> <i>Using Metrics to Determine the Sustainability of ‘Clean Water’ Technologies Currently used in West Bengal, India</i>	19
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<b>Nguyen Thi Hoa Mai:</b> <i>Adsorption and desorption of arsenic on Holocene aquifer sediments at Nam Du</i>	31
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<b>Ivan Mihajlov:</b> <i>Communication between low- and high-arsenic aquifers in Araihasar, Bangladesh and its role in the failure of deep aquifer community wells</i>	37
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<b>K.S. Patel:</b> <i>Arsenic contamination of water, dust and soil in central India</i>	43
<b>Matthew L. Polizzotto:</b> <i>Spatial and Temporal Variations in Groundwater Chemistry from an Arsenic-Contaminated Area of Cambodia</i>	45
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<b>Dang Thanh Vu:</b> <i>Phosphorus interference in colorimetric determination of arsenic in environmental samples</i>	56



# Development and Field evaluation of the IITB-Arsenic Filter

Tuhin Banerji<sup>\*</sup>, Sanjeev Chaudhari<sup>1</sup>

<sup>1</sup> Centre for Environmental Science and Engineering, Indian Institute of Technology, Bombay, India.

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Arsenic is present in groundwater in some parts of India. Despite the fact that a variety of treatment methods are available, the efficiency of these methods is not fully known [1]. With the revision of Indian standards for permissible levels of arsenic in drinking water to 10µg/L or lower, it is necessary to develop a treatment method, which would consistently meet drinking water standards of 10µg/L.

Many researchers have shown that the corrosion of Zero Valent Iron (ZVI) forms Hydrous Ferric Oxide (HFO) which can act as an adsorbent for arsenic. And the oxidation of Fe<sup>2+</sup> to Fe<sup>3+</sup> has also been reported to co-oxidize As(III) to As(V) [2]. Lab scale experiments were carried out by controlling oxidation of Fe<sup>2+</sup> followed by granular media filtration. Arsenic concentration of 10µg/L in treated water could be achieved with Fe/As ratios of less than 10. With the understanding developed from the lab scale experiments, a community scale ZVI based Arsenic Filter has been developed by Indian Institute of Technology, Bombay. Figure 1 shows the schematic of IITB-Arsenic filter. Water is pumped into the filter with direct inlet from handpump. The arsenic filter can be attached to existing handpumps and so it can be installed on any pre-existing borehole. The filter unit in this system consists of two tanks. Each tank is similar in design and can be considered as different stages for adsorption and filtration. Each tank has a section on top where the water is contacted with iron nails (ZVI). After ZVI contact, the water trickles down to the filter bed and in this process the oxidation takes place. The filter bed is made up of stone chips and gravel which is about 60-100cm deep. Coarse gravel is used as filter media so as to reduce the headloss.

Test units of the IITB-Arsenic Filter have been installed in the field in 5 villages in India and the results of these units have been presented in Table 1. From the results, it is clear that the filter is able to consistently achieve arsenic

levels around 10µg/L for initial arsenic concentrations ranging from 0.06 – 0.4mg/L. The flowrate of the filter is approximately 600L/hr at 0.9m<sup>3</sup>/m<sup>2</sup>/hr. Thereby the IITB-Arsenic Filter is able to consistently provide drinking water for about 200 families on a daily basis. The IITB-Arsenic Filter requires less cleaning (frequency is once in three months, and is done by the villagers) and therefore has low operation and maintenance costs. Also, it does not require monitoring of flow parameters and is easy-to-operate by unskilled personnel. Thus it is a suitable technology for rural India.

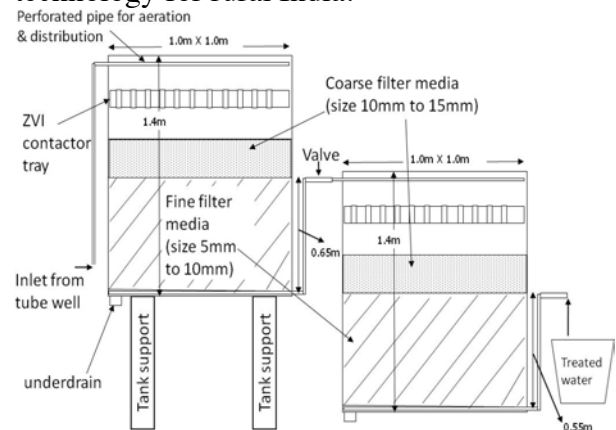


Figure 1. Schematic diagram of IITB - Arsenic Filter

Table 1. Average weekly collection results of field installations of IITB-Arsenic filter (sampling period October 2010- May 2011)

Village name	Sonakhali	Shikaripara	Kalyani Mod	Ghanguria	Polasi
<b>Raw</b> (mg/L)	<b>0.2654</b> (±0.0160)	<b>0.1842</b> (±0.0044)	<b>0.3822</b> (±0.0044)	<b>0.3854</b> (±0.0044)	<b>0.0622</b> (±0.0044)
<b>Treated</b> (mg/L)	<b>0.0089</b> (±0.0044)	<b>0.0097</b> (±0.0035)	<b>0.0108</b> (±0.0052)	<b>0.0096</b> (±0.0056)	<b>0.0100</b> (±0.0029)

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## Emerging hydrologic influences on arsenic behaviour in south Asia

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A recent rapid expansion in the number of arsenic researchers employing hydrogeologic tools in south Asia reveal both similar trends and key variables that dictate observed differences between field sites.

From a hydrologic perspective, the sedimentary units forming the aquifers in south Asia are remarkably similar due to the regional influence of changing sea levels on delta formation over the last 10,000 years [1, 2]. Aquifer hydraulic conductivities of the shallow aquifer are similar and most aquifers are capped by a silt aquitard of variable thickness. The regional deltaic topography is highly subdued and the underlying groundwater gradient is very low and generally towards the ocean and river systems [3, 4].

Where aquifer sediments are thicker, a distinct deep aquifer flow system can develop; where the water-bearing units are thinner, a deeper flow system may not be present. There is now evidence that the deeper aquifer can receive significant recharge from areas outside the known areas of arsenic releasing sediment [4]; this important observation suggests the potential for the deeper aquifer to be arsenic-free in perpetuity.

In the shallow aquifer system, where the vast majority of arsenic research is being conducted, determining flow direction is complicated by variations in the magnitude of seasonal changes in river levels, surficial recharge, groundwater pumping.

At sites where groundwater pumping is limited, seasonal changes in river level can dominate groundwater flow dynamics and produce seasonal reversal of groundwater flow direction [6].

Multiple lines of evidence indicate variations in the character of the overlying aquitard influences both the degree of local recharge to the aquifer and distribution of arsenic [7, 9]. Integrating biogeochemical processes associated with these physically-driven flow

perturbations remains an area of active research [10, 11].

Groundwater pumping induces complexity to the local flow system. Pumping is also likely increasing groundwater flow velocities (and reducing residence times), obscuring the local influence of changing river levels. Groundwater extraction also can redistribute arsenic to surface sediments [12]. Finally, deep aquifer wells, especially those used for irrigation, pose a threat to the deeper, largely arsenic-free, aquifer [5].

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## Immunotoxic effect of inorganic arsenic in poultry birds

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Arsenic is an environmental toxicant of high concern for human health as this pnictide present in the environment, in inorganic form, is toxic for plant, animal and birds [1]. Immunotoxicity due to long exposure of arsenic show great concern because of it gradual damage to immune system with suppressed immune function leading to chronic infection associated with multiple pathogens [2]. The present endeavor was undertaken to ascertain the toxic effect of arsenic in avian immune system. The residual arsenic could be detected in various tissues viz. muscle, liver, spleen, bursa and thymus of chicks fed with both concentration (4 mg/L & 8 mg/L drinking water) in a exponential manner depending on the duration of exposure. The phagocytic activity and cytotoxic effect, NO production were found to decrease in arsenic exposed chicks as compared to healthy control in *in vivo* studies. The *in vitro* experiment with mononuclear cells from both arsenic fed & healthy control groups resulted decrease in nitrite production. However, chickens fed with 8 mg/L arsenic showed maximum reduction in nitrite production compared to other groups. Similarly in *in vitro* experiment the nitrite production in both the groups were also found to decrease.

Relative expression of immunostimulatory gene i.e. iNOS gene and IL-2 gene were found to decrease significantly with time exposure in both doses (4 mg/L & 8 mg/L) of arsenic fed chicks, however, the expression of IL-2 gene with 4mg/L dose was found to increase initially followed by gradual decrease upto 45<sup>th</sup> day in *in vivo* studies. However in *in vitro* studies the decreased expression of IL-2 and iNOS gene maintained throughout the period of study. In apoptotic and caspase -3 activity studies, it revealed that arsenic induces apoptosis. DNA fragmented apoptotic bodies

as well as caspase -3 activity was found more in case of higher concentration (8mg/L) arsenic fed group. The IgA concentration in bile from both arsenic fed groups (4mg/L and 8mg/L) was found to reduce significantly upto 45 days. The IgY antibody in serum showed increase upto 45 day in 4mg/L group, however with 8mg/L, the quantity of IgY was found to increase upto 30 days followed by decrease. Therefore, the study concluded the immunosuppressive role of arsenic in avian system exploring the mechanism at both innate immune system and immunoregulatory genes.

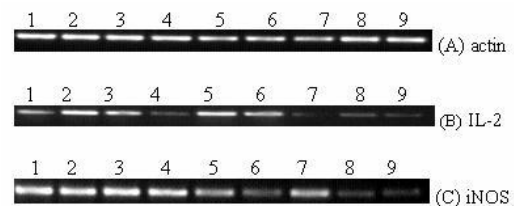


Figure 1. The mRNA expression level (*in vivo*) of beta-actin (A), IL-2 (B) and iNOS (C) gene in chicken splenocyte were detected by RT-PCR using specific primers. **Lane (1-3)**-Control 24hrs, 48 hrs, 72 hrs. **Lane (4-6)**- Arsenic fed chicken (4 mg/L) 24hrs, 48 hrs, 72 hrs. **Lane (7-9)** Arsenic fed chicken (8 mg/L) 24hrs, 48 hrs, 72 hrs. The amplified cDNA were resolved on 2 % (w/v) agarose gel and visualized by ethidium bromide.

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## Distribution of As in groundwater of the Red River delta (Vietnam): Hydrochemical survey and 3D geospatial modeling

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Arsenic (As) contamination of shallow groundwater used as drinking water is a widespread health threat in the developing world. The 14,000 km<sup>2</sup> plain of the Red River delta is among the most densely populated regions on the globe, with a density of some 1,200 people/km<sup>2</sup>. Of the 16.6 million inhabitants, 11 millions have no access to public water supply and are thus depending on other drinking water resources such as private tubewells. Given these facts, it is crucial to recognize the scale of the problem and to identify areas at risk.

Here we present the results of a groundwater survey of the entire Red River delta that is based on a sampling strategy where 1 sample was randomly collected in pre-defined grid cells of 25 km<sup>2</sup>. The generated hydrochemical atlas identifies reducing conditions and areas of predominantly safe and unsafe groundwater quality, and also gives information on salinity and >30 chemical parameters [2].

Arsenic concentrations varied between <0.1 and 810 µg/L, with 27% of the wells exceeding the WHO guideline value of 10 µg/L. This implies that ~3 million people are currently using groundwater with As levels >10 µg/L and 1 million use groundwater containing >50 µg/L, with both rural and urban populations being exposed to toxic levels of As.

The WHO guideline for Mn (400 µg/L) was exceeded in 44% of the wells which thus affects ~5 million people. In summary, 65% of the wells surpassed the WHO guidelines for safe drinking water which leads to the estimation that 7 millions delta inhabitants currently use unsafe groundwater.

Arsenic risk maps for South and Southeast Asia were recently developed using surface geology and soil properties in a geo-statistical model [1]. For the Red River delta we

developed a probability model based on three-dimensional stratigraphy of Quaternary geology (see Figure 1). This 3D risk model agrees with measured As concentrations in 74–84% of the wells, in spite of the frequently observed heterogeneity of As concentrations over short distances.

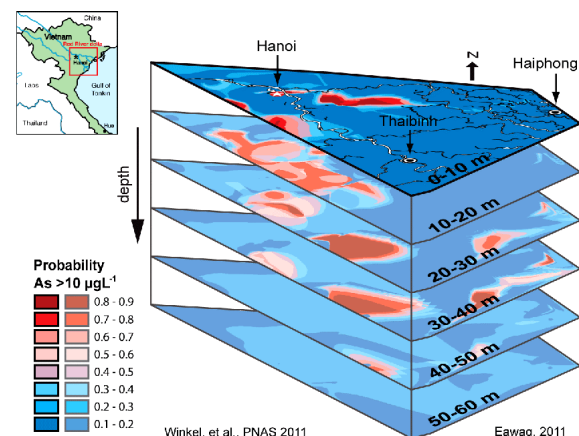


Figure 1. 3D distribution of As exceeding safe limits in the Red River delta, stacked in 10 m depth intervals.

The modeling further showed a 5-times higher risk of As contamination in Holocene aquifers than in Pleistocene aquifers [2]. The large hot-spots of dissolved arsenic present in the Pleistocene aquifers of Hanoi is therefore seen as an indication that >100 years of extensive deep water extraction has likely induced As to leach into these deep aquifers.

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## Arsenic Mineralogy and Phase Partitioning Across a Sharp Gradient in Arsenic Concentrations in Van Phuc, Vietnam

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Arsenic concentrations in aquifers reflect complex adsorption and mineral precipitation/dissolution processes that are affected by the chemical form of arsenic, iron, sulfur and other elements. To understand the distribution of arsenic in the environment, it is imperative to examine the concentration and speciation of arsenic and relevant elements in both the aqueous and solid-phases. To date, only a handful of such paired measurements have been made in part due to the difficulty in obtaining intact sediments and their entrained porewaters from relevant sites.

In April 2006, we used a needle sampler to collect sediment and porewaters at 10-30 m depth along a 1-km transect with contrasting arsenic concentrations in Van Phuc, Vietnam. The data were used to generate a high resolution cross section of both porewater and sediment geochemistry that reveals considerable changes in arsenic concentrations and retention. The cross section was used to target specific locations to install monitoring wells and collect cores for subsequent solid-phase speciation by X-ray absorption spectroscopy starting in December 2009.

The needle sampling transect indicates a sharp transition in dissolved arsenic concentrations, with the concentrations of arsenic lowest (1-2  $\mu\text{g/L}$ ) at the northern edge of the transect, increasing sharply (to  $\sim 400 \mu\text{g/L}$ ) in the center of the transect, and decreasing again more gradually at the southern edge of the transect. The sharp arsenic concentrations increase occurs over distance  $<100 \text{ m}$  and is concomitant with a change in sediment color and mineralogy. Gray-black sediments had Fe mineralogies dominated by Fe(II) and bear

high-As groundwater, while orange sands from low-As aquifers have more abundant Fe(III) minerals. In gray-black sediments, P-extractable As often exceeded 1 mg/kg, and represented a majority of total As (determined by XRF), while orange sediments contained similar concentrations of total As but had P-extractable As usually  $<0.3 \text{ mg/kg}$ . Considering either total As or P-extractable As, the apparent partition coefficients clearly vary considerably over the site, with much weaker As partitioning ( $<1 \text{ L/kg}$ , P-extractable As) observed in most reduced, gray-black sediments. The contrasts in partition coefficient and Fe mineralogy suggest that the form of arsenic in the solid phase changes across this gradient, a hypothesis reinforced by correlated changes in dissolved sulfate (high in low-As groundwaters, indicative of sulfate reduction) and iron concentrations (highest in high-As groundwaters). Despite this suggestion, arsenic is retained primarily as adsorbed arsenite and arsenite in aquifer sands from both gray-black and orange aquifers. Arsenic sulfides were occasionally extensive in gray, reduced sediments, but the prevalence of arsenic sulfide is not correlated directly to aqueous As levels. The subtle changes in speciation that influence As phase partitioning imply that minerals present in the solid-phase are not always a reliable indicator of the minerals that presently regulate dissolved As levels. Moreover, these data suggest that small changes in solution composition over time may affect dissolved As levels without changing the speciation of the bulk of As in the solid phase.



## Laboratory Studies of an Arsenic Remediation Process and Effective Utilization of ABSR

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A large number of academic research and technologies have been developed throughout the world over past 20-25 years with respect to removal of arsenic from drinking water. Some of the processes are successful in both theoretical and large scale plant operation. However, arsenic bearing solid residuals (ABSR) or brine accumulated poses a renewed environmental threat.

A laboratory column technique has been studied for arsenic removal using SUDHA absorbing media which is a mixture of synthetic amorphous alumino ferro silicate compounds.

Following observations are noted in repeated trial tests.

1. The new media reduces the arsenic content of raw drinking water from as high as 3 ppm to absolutely Nil arsenic content in filtrate water.
2. It is generally known in laboratory as well as in industry that arsenate adsorbs easily and preferentially than arsenite by different kinds of iron oxide and aluminum oxide based media e.g., GFH, G2, activated alumina etc. To achieve it, oxidation of As +3 to As +5 is necessary in the treatment process. In the present technique, oxidation of As(III) to As(V) is not a prerequisite step.
3. pH is not a critical factor in the adsorption process.
4. The present arsenic removal process is not affected by the presence of interfering contaminants generally occur in water e.g., hardness due to presence of CaCO<sub>3</sub>/HCO<sub>3</sub> content, silica, phosphate.
5. Backwashing step is not required as iron hydroxide is not precipitated in the packed bed column during operation.

## ARSOlux<sup>®</sup> – arsenic biosensor based on bioreporter bacteria

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Arsenic is a ubiquitous toxic metalloid causing serious health problems in large regions of the world where it contaminates drinking water resources with concentrations higher than the permissible levels of 10  $\mu\text{g As/L}$ . Due to seasonal variations and the heterogeneous distribution of the arsenic concentrations in the groundwater, cheap and rapid but nonetheless sensitive analytical devices allowing repeated large scale arsenic surveys are urgently required. We are currently developing a robust, precise and easy-to-handle test system, named ARSOlux<sup>®</sup> which is based on non-pathogenic *Escherichia coli* K12 bioreporter bacteria. The newly patented bioreporter strain contains a fusion of the natural resistance mechanism of *E. coli* against arsenite and arsenate and luciferase as the reporter protein. The bioreporter bacteria are freeze dried in ready to use glass vials (Figure 1) and stable for up to six months [1]. After rehydration with the water sample the bioreporter bacteria emit light if arsenic is present. The concentration dependent light emission is detected by a portable luminometer and permits analysis of arsenic concentrations down to 5  $\mu\text{g/L}$ . The biosensor is operated in a one-step procedure and shall be sold at a lower price than available chemical test kits. ARSOlux<sup>®</sup> will be further developed and marketed in cooperation with the Helmholtz Association. The performance of the arsenic biosensor was tested successfully in two field campaigns in Bangladesh in 2010.



Figure 1. ARSOlux<sup>®</sup> glass vials containing freeze dried bioreporter bacteria and portable luminometer for arsenic measurement.

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## Electrochemical Synthesis of Magnetite and its Applicability as an Adsorbent for Arsenic

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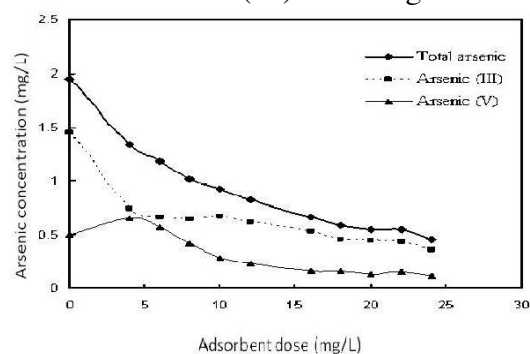
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Arsenic is a known carcinogen and various adsorbents have been developed for arsenic removal from drinking water. Most of these adsorbents have their advantages and disadvantages [1]. Magnetite has been reported to be a promising new adsorbent for arsenic removal from water [2]. But the synthesis of magnetite is costly and labour intensive. So efforts were made to develop an electrochemical method to synthesize magnetite. In this laboratory scale method the synthesised magnetite had all the properties of chemically synthesised magnetite. This Electrochemical-magnetite (EC-magnetite) was then tested for its arsenic adsorption capabilities. Various parameters affecting adsorption of arsenic by magnetite were studied. Based on these results it can be said that EC-Magnetite has a good adsorption capacity of Arsenic (arsenite and arsenate on EC-magnetite were 109 and 122 mg of arsenic/gm of magnetite at pH 7). There also is evidence for partial oxidation of As(III) to As(V) as shown in Figure 1. From the figure, it can be seen that at the low sorbent doses there is an increase in As(V) and a reduction in the total arsenic concentration. At higher dose of magnetite the reduction in total arsenic and As(V) concentration followed similar trends. The decrease of total arsenic might be due to the adsorption of As(V) on magnetite since the adsorption of As(V) on magnetite is more favorable than As(III). In electrochemical generation of magnetite, at higher pH maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>) could be formed, which may also be transformed from magnetite [3] and maghemite having oxidation property has been reported before [4].

The adsorption rate was relatively fast and equilibrium was achieved within few minutes. Under comparable conditions better removal was observed for As(V) than As(III). There is no significant effect of pH in the range of 6.0 –

8.0 on As(III) removal whereas As(V) removal decreased as the pH value increased. The presence of phosphate (1 mg/L) and silicate (10 mg/L) decreased the efficiency of As(III) removal by magnetite. Sulfate (960 mg/L) and bicarbonate (120 mg/L) had negligible effect on the removal of As(III) with magnetite.



**Figure 1. Plot of residual arsenic concentration vs varying magnetite dose showing the oxidation of As(III).**

Groundwater sample contaminated with arsenic was also treated with magnetite and showed a favorable adsorption of arsenic. Due to the granular characteristics of the prepared EC-magnetite, the solid liquid separation is easier and rapid compared to Hydrus Ferric Oxide. This insoluble iron based compound can be used for column operation. Further studies need to be carried out to make it viable for small scale or community scale filters.

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## Screening of Groundwater Arsenic Contamination in Unexplored Parts of Brahmaputra Floodplains in Assam

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Based on the results of a Rapid Assessment program carried out in 2004-05, an initiative of arsenic screening program for the Brahmaputra Floodplain in Assam was undertaken by this group of authors, in collaboration with the Public Health Engineering Department (PHED) and UNICEF. A rigorous three phase testing procedure, involving three different instruments, Arsenator, UV-1 Spectrophotometer and the Atomic Absorption Spectrophotometer (AAS) was adopted for the program. The results yielded were reasonably consistent, showing good analytical performances. A considerable 29.8 percentage of about 56,180 samples had elevated arsenic concentrations above the WHO permissible limits of 10 ppb and 7.95% of the 56,180 samples analysed had concentrations above the BIS permissible limit of 50 ppb. Data available from the three tire analysis were used for preparation of district level arsenic concentration maps using ArcGIS 9.2, from which the total vulnerable areas could be delineated for appropriate remedial measures, supported by the output of the focused research on release process and mechanism. An estimated population of 7, 22,603 were found to be exposed to the risk due the arsenic contamination above permissible limit. The study revealed that the concentrations were localised at certain pockets of the floodplain and is narrowly spread than the GBM floodplain in Bangladesh and West Bengal, thus emphasizing the need emphasizing the need for extensive spatial and vertical multiple-depth aquifer-based study of arsenic concentration in the region, which could further assist in exploring the key cause of arsenic occurrence in the region. As part of a multi-pronged solution to the problem, development of removal technologies through improvement of indigenous media based conventional filtration, and more importantly,

provision of drinking water from extensive surface water sources crisscrossing the vast Brahmaputra valley, indicated promising mitigation options.

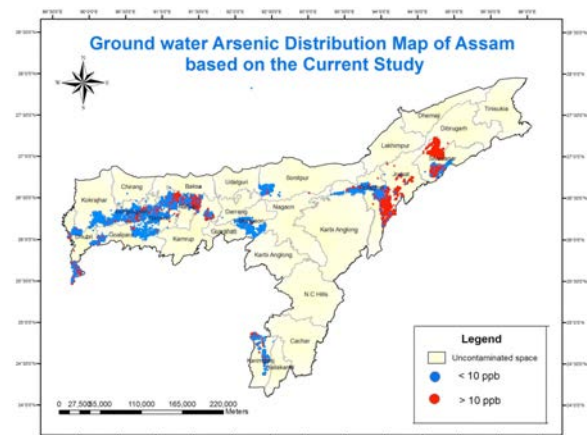


Figure 1. Groundwater arsenic contamination of Assam based on WHO permissible limits of 10 ppb.

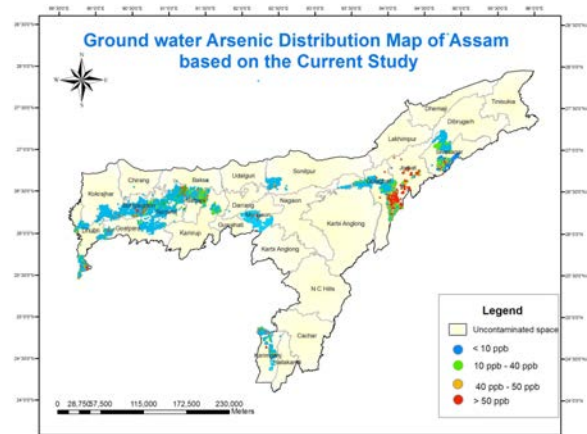


Figure 2. Groundwater arsenic contamination of Assam based on BIS permissible limits of 50 ppb.

## Geomorphic and depth-dependence of organic matter chemistry within sediments of the Mekong Delta

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Naturally occurring arsenic (As) in groundwater aquifers is widely recognized as a threat to water resources. An estimated 100 million people worldwide are exposed to hazardous levels of As in their drinking water, predominately in South and Southeast Asia [1]. Biologically-driven reductive dissolution of As-bearing Fe(III)-(hydr)oxides and As(V) are generally accepted to be the dominant mode of As release [2], resulted from microbial degradation of organic matter (OM) under limited oxygenation within soils/sediments [3]. As the release process is governed by OM and its decomposition mechanisms and rates, it is crucial to understand the nature and reactivity of OM.

Within the Mekong Delta of Cambodia, As release to groundwater was recently identified to occur mainly in the shallow clay layers of permanently saturated wetlands [4]. In contrast, lesser amounts of As are released in the surficial clay layers below seasonally saturated wetlands. The two locations therefore provide an ideal opportunity to study the nature of OM and compare its reactivity during decomposition in similar environments under different redox conditions. Accordingly, we seek to determine how different geomorphic features result in different quantities and type of OM, and to link the characteristics of OM to the quantity of As release.

During a field trip in July 2010 two 1 m deep soil profiles from two different locations (permanently and seasonally saturated wetlands), were sampled for OM characterization. Visual inspection of the seasonally saturated wetlands profile showed two different OM morphologies with leaf-type OM in the upper and amorphous OM in the lower part of the profile, while no leaf-type OM was found in the permanently saturated wetlands. ATR-FTIR spectroscopy revealed significant

differences between the two materials, especially in the areas of C=O vibrations of carboxylates and of CH and NH (amide II) bending motions.

Two high-resolution sediment sequences up to 12 m depth in both seasonally and permanently saturated wetlands are presently being examined by ATR-FTIR spectroscopy. Further, synchrotron-based FTIR spectra of transition zones and of the organic matter-mineral assemblages are being investigated. The specific chemical states are then be related to reactivity through incubation studies. Collectively, the results of this study will provide valuable insights into the role and heterogeneity of OM driving As liberation.

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# Using Metrics to Determine the Sustainability of ‘Clean Water’ Technologies Currently used in West Bengal, India

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Using the most conservative estimates, it has been reported that approximately 35 million people in the Bengal Basin (Bangladesh and West Bengal, India) are drinking water that contains >50 ppb of arsenic [1]. This situation caught international attention after the WHO referred to it as the “largest mass poisoning of a population in human history.” This led to the creation and introduction of several different arsenic removal technologies into the local market. Unfortunately, recent studies suggest that many filter technologies are not effective and are unreliable when used outside the laboratory [2]. It has been proposed that this is due to the combination of various technological, economic and social causes. For example, not all designs are economically viable for the average local income of rural users, or perhaps the technology requires specialized knowledge to operate or maintain and thorough education programs for the users have not been initiated.

This study is using Process Analysis Method [3] to determine which technologies are most sustainable in the West Bengal region of the Bengal Basin. This method requires a review of various technology-specific indicators including water quality, quantity, flow rate, longevity, user-ability, initial cost, recurring costs, origin of materials and environmental waste, to name a few. The clean-water technologies included in this study range from household to community, arsenic-removal filters/plants and water harvesting methods. A preliminary trip to West Bengal is planned for April 2011 in which foundations for future field work will be established. Extensive field work will commence in December 2011 whereby different technologies will be observed and tested, samples taken and users surveyed. The initial sustainability metrics will be completed prior to the commencement of the field research. This model will be made

using available data compiled from previous studies and data accessible from manufacturers and operators of systems that are currently in use.

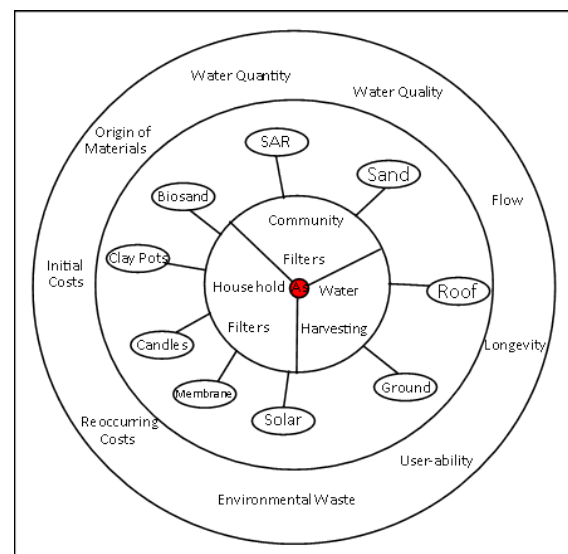


Figure 1. Visual of several indicators and technologies that will be used to create sustainability metrics.

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## Fate of arsenic in agriculture soils in response to change in crop pattern and cultivation practices - A study from West Bengal (India)

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In many agricultural fields of West Bengal, arsenic (As) contaminated groundwater is used for irrigation. This leads to the accumulation of As in upper few centimeters (typically 0-25 cm) of soil profile [1,2]. The accumulation of As in arable sediments dependent mainly on cultivating crop, as different crops require different quantities of water to be pumped into agriculture fields; and the cultivation practices. A study has thus been undertaken to investigate the fate of As in upper soil horizons (0-25 cm) of different agricultural fields.

Two agricultural fields (Field-1 & Field-2) cultivating different crops and following different cultivation methods were selected in Malda district of West Bengal (India). Field-1 is a paddy cultivating agricultural field which is irrigated by water containing 137  $\mu\text{g/L}$  of As and follows the tradition paddy cultivation technique. In this method, harvested crop is cut from the middle of stem and the remaining half of the stem and roots are ploughed for the next cultivation. As soon as, fields are filled with water, decay of remaining plant matter starts that induces reducing conditions and also leads to the formation of organic acids. On the other hand, Field-2 is a wheat cultivating agricultural field and is irrigated with water having 67.3  $\mu\text{g/L}$  of Arsenic. In wheat cultivation, the ripped crop is cut from bottom of stem and the left over is burnt in the field. Such practice leaves very little organic carbon in the wheat fields. The presence of lower organic carbon (OC) in wheat soils (average OC 0.6%) than the paddy soils (average OC 1.1%) clearly reflects the effect of cultivation methods on soil-organic carbon relationship.

Though, the water irrigating the paddy field had twice the concentration of As, than the water irrigating wheat field but still the As concentration in paddy soils ranges between

Sampling depth (cm)	Arsenic concentrations in soils (mg/kg)	
	Paddy soils	Wheat soils
0-5	15	18
5-10	16	23.5
10-15	17	26
15-20	16	18.5
20-25	14.5	18

Table 1. Variation of As concentration with depth in Paddy and Wheat soils.

14.5-17 mg/kg (av. conc. 15.7 mg/kg), which is much lesser than the As concentration of wheat soils (18-26 mg/kg, av. conc. 20.8 mg/kg). A relatively higher influx of As through irrigation water but lower As accumulation in paddy soils indicate the existence of a mechanism responsible for removal of As from these soils. However, the wheat field shows that relatively moderate As influx through irrigation water can cause build up of As in absence of an effective removal mechanism. These findings are in line with the earlier studies made by Farooq et al. 2010 [3], which highlights the role of organic carbon in mobilization of As from paddy soils. The findings of this work can be applied for whole South East Asian region, as they follow the same agriculture practices.

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## Defining and projecting groundwater arsenic levels to determine water use options in South Asia

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More than 100 million people are at risk of exposure to dangerous levels of geogenic arsenic in drinking water across South Asia (1). Arsenic within rocks of the Himalayas is liberated to the sediment load of the major river systems and ultimately deposited within the massive deltas of South Asia. Upon burial, arsenic is released to the aqueous phase through microbially driven reduction of arsenic and iron, leading to contamination of groundwater now commonly used for human consumption. Fueling this process is organic carbon that stimulates microbial activity and, with limited oxygen supply, anaerobic metabolisms. Resulting concentrations of arsenic, however, are distributed unevenly in the subsurface as a result of heterogeneity in groundwater flow and biogeochemical processes (2). While such heterogeneity makes predicting groundwater arsenic concentrations difficult both spatially and temporally, it provides an opportunity to potentially extract water safe (or safer) for human consumption.

Here we describe the fate controlling processes of arsenic with a coupled biogeochemical-hydrologic model (see *ref* 3) for the Mekong Delta (Figure 1) and illustrate changes in groundwater quality with land use alterations—a key driver in determining long-term temporal variation in arsenic distribution. With the parameterized model, the impact of land use changes, ranging from increased groundwater abstraction to pond development, on the distribution of arsenic are forecast. For areas where low-arsenic groundwater is not available, we further examine possible solutions, including alternate water resources, for providing safe drinking water to the local populous.

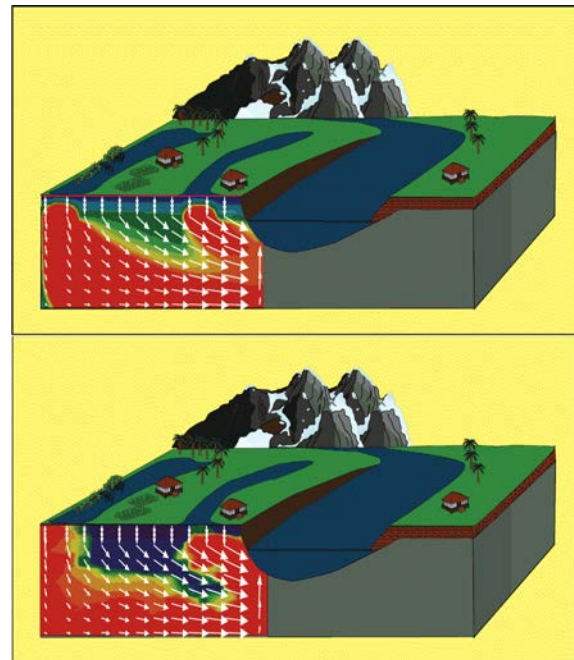


Figure 1. Simulated (top) and measured (bottom) groundwater arsenic concentrations within a transect of the Mekong Delta in Kean Svay, Cambodia.

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# Spatial and temporal variation of arsenic concentration in shallow groundwater from the Hetao Basin, Inner Mongolia

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## 1. Introduction

High As groundwater is a serious environmental issue in China, threatening the health of millions of people. Reducing aquifers are believed to be associated with groundwater As enrichment in some areas of Northwest China, especially in Xinjiang, Inner Mongolia [1], and Shanxi [2]. High As concentration was firstly reported in drinking groundwater in 1994 in the Hetao basin. Spatial variability of As concentration is not only attributed to variation in local geology [1], but also surface hydrologic conditions [3]. High As groundwaters generally occurs in shallow alluvial-lacustrine aquifers [1]. Surface water irrigation and groundwater extraction control groundwater tables, which would not only alter the redox boundary of groundwater system [4] but also change groundwater flow [5]. It may lead to temporal variation in groundwater As. The understanding of spatial and temporal variation in groundwater As is urgently needed in order to ensure the safety of drinking water.

## 2. Spatial variation of groundwater As

Arsenic concentration is very patchy in the basin. High As groundwater mainly occurs in shallow alluvial-lacustrine aquifers, above which there are thick clay/peaty clay layers. These layers with low permeability and high organic matter content prevent atmospheric oxygen from diffusing into aquifers. In the areas with no clay layer in the uppermost strata, As concentration ranges between 2.0 and 20 µg/L, while in the areas with thick clay layers it is greater than 100 µg/L.

In addition, water ways (including irrigation channels and drainage channels) and hydrogeologic control As distribution in shallow groundwater. Near the water ways, low As groundwaters were found (<50 µg/L), due to intensive interaction between groundwater and surface water enriching

oxygen. Groundwater As is also dependent on hydrogeologic conditions. In recharge areas (mainly alluvial fans), low As groundwater is presented because of moderate-high flow rate.

## 3. Temporal variation of groundwater As

Most studied groundwaters show an increase trend in As concentration in four years, especially for the groundwaters with As concentration >100 µg/L. In contrast, concentration of the redox-sensitive trace element U generally decreases.

Seasonal variation in As concentration was also observed. In November, when the water table increases due to flood irrigation of the farmland, groundwater As mostly increases relative to those in July. The µ-synchrotron X-ray fluorescence analysis (µ-XRFA) and sequential chemical extractions of the aquifer sediments show that leaching of exchangeable As and the dissimilatory iron reduction are the mechanisms for As release.

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## Avoiding exposure to high concentrations of arsenic, manganese and salinity and improving the acceptance of deep tubewells in Bangladesh

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In several districts of Bangladesh, over 80% of shallow tubewells (STWs) are affected by arsenic concentrations above 50 µg/L. Deep tubewells (DTWs) are among the preferred mitigation options for reducing exposure to arsenic.

During field studies around the town of Sreenagar (30 km South of Dhaka) we collected water samples from existing STWs, DTWs, monitoring wells (5-230 m depth) and newly installed DTWs. Analysis of water samples from 2005-2011 identified three types of groundwater currently used for drinking: (1) Shallow water from 20-100 m deep dark-grey aquifers with high As-concentrations (100-1000 µg/L), intermediate-high Fe (2-11 mg/L), intermediate Mn (0.2-1 mg/L), relatively low EC (400-900 µS/cm) dominated by Ca-Mg-HCO<sub>3</sub><sup>-</sup>. (2) Water from 140-180 m deep light-grey sediments with low As (<10 µg/L), intermediate Mn (0.4-1.0 mg/L), intermediate Fe (1-5 mg/L), low total organic carbon, nitrogen and ammonia, and intermediate EC (1200-1800 µS/cm) dominated by Ca-Mg-HCO<sub>3</sub><sup>-</sup>-Na-Cl. (3) Water from 190-240 m deep brown aquifers with low As (<10 µg/L), high Mn (2-5 mg/L), low Fe (<3mg/L), and high EC (2000-3000 µS/cm) dominated by Ca-Mg -Na-Cl with high Ca and Cl concentrations.

Drillers have traditionally used the transition from grey to brown sediments as an indicator for the depth from which safe drinking water can be obtained. However, in most of the tubewells of the studied area which are over 190 m deep, manganese exceeds the WHO-limit of 0.4 mg Mn/L by a factor 2-5 and the water is noticeably saline. Based on the water composition at various depths and a small survey in a 2.5×2.5 km<sup>2</sup> area, we recommended a depth range of 150-180 m for the construction of new DTWs and replacement of the wells over 180 m depth.

Pumping test showed that a clay-rich layer at 130 m has a relatively low hydraulic conductivity, which reduces the risk of contaminating the deeper aquifer with water from the shallow aquifer, as long as water is only abstracted by hand pumps

Several new DTW have since been installed in the recommended depth range.

Since the three types of water have distinctively different odors and tastes which might influence the acceptability and use of DTWs, we supplemented the hydrogeo-chemical study by a social acceptance study. In over 40 interviews conducted in households in the research area, it was found that the measured chemical parameters correlated with the taste and odor perceptions of the consumers and that the perceived water quality influences the acceptance of different mitigation options.

Deep tube wells overall are very successful in reducing exposure to arsenic. However, before installing larger numbers of DTWs in a new area, existing wells should be analyzed and monitoring wells should be installed where necessary, to find the optimal depth for water abstraction.

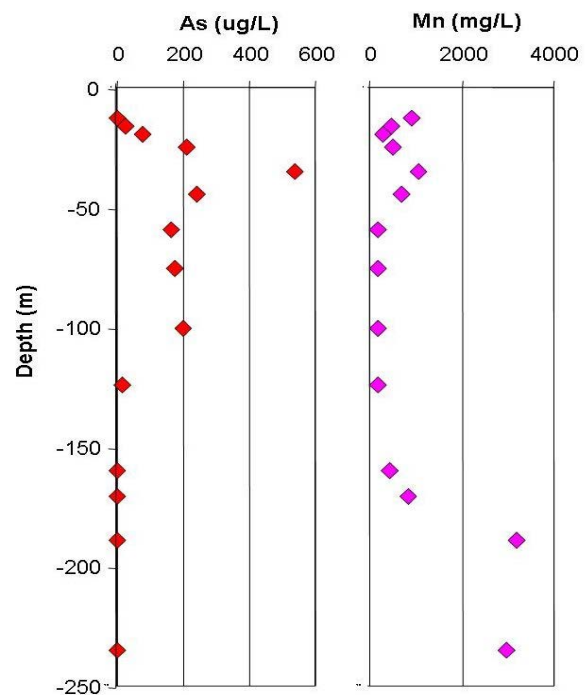


Figure 1. Arsenic and manganese concentrations as a function of depth in shallow and in deep monitoring tubewells East of Sreenagar, Munshiganj.

## Mobility of arsenic in aquifers: How to quantify arsenic adsorption to natural aquifer sediments?

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The prediction of arsenic mobility is vital to estimate flushing times for South East Asian Holocene aquifers by water with a low As concentration. The mobility of trace elements is often assessed from laboratory determinations of adsorption isotherms to natural sediments. For As, this approach is not trivial, because natural sediment from an As contaminated Holocene aquifer inevitably contains adsorbed As. To circumvent this problem push-pull tests have been applied by some authors. As a laboratory analogue to a push-pull test, we suspended samples of natural As-loaded sediment from the Red River delta in electrolyte solutions under anaerobic conditions. We then either removed initially adsorbed As by elutriation or added As by spiking the suspension with As(III) solution. Adsorbed As concentrations were then calculated by a mass balance.

Using the above method, Holocene sediment from a reduced As contaminated aquifer was found to possess roughly 10 nmol/g of initially adsorbed As in the form of As(III), i.e., after several steps of elutriation. Surface complexation models [1–3] predict that these 10 nmol As(III)/g must be adsorbed in competition with other ions, such as  $\text{CO}_3$ ,  $\text{PO}_4$  and silica. When the model surfaces were equilibrated in PHREEQC with a groundwater composition measured at the sediment sampling point, some hundreds (model dependent, 190 to 510) of nmoles sites per g sediment were needed to allow a surface coverage of 10 nmol As(III)/g. The result obtained by elutriation hence can be used to constrain the fitting of site density in surface complexation models.

When As(III) was added to the anaerobic suspension its disappearance from solution

indicated adsorption. The As(III) was released in subsequent elutriation steps indicating that the probable As(III) adsorption to the aquifer sediment was reversible.

The results from several As(III) additions and elutriation steps may be interpreted as points on an As(III) adsorption isotherm. Our preliminary result suggested an isotherm (Fig. 1) which was highly nonlinear up to an As(III) concentration of about 1  $\mu\text{M}$ , gradually approaching a maximum sorption of 15 nmol/g at a higher dissolved As(III) concentration. Potential pitfalls in this preliminary interpretation include the effect of non-linear competitive sorption which will be elucidated in on-going work.

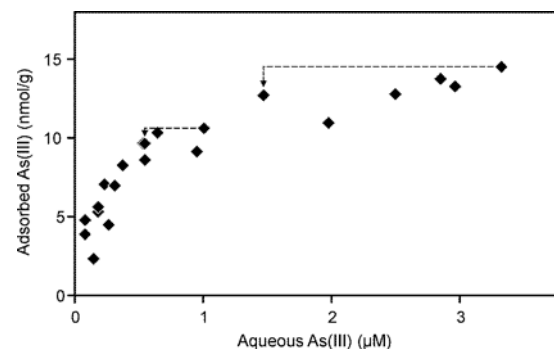


Figure 1. Preliminary results from elutriation/As(III) addition tests for a reduced Holocene aquifer sediment (five tests). Dashed lines indicate the desorption path between points obtained by an elutriation (desorption) step following an adsorption step.

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## Arsenic redox changes by reactive biogenic and abiogenic iron minerals

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Arsenic-contaminated environments (e.g. groundwater aquifers and rice paddies) affect about 1-2% of the world's population. Arsenic toxicity and mobility strongly depend on its interactions with iron minerals and humic substances via complexation but also via redox reactions. As(III) (arsenite) is generally considered to be more toxic and mobile than As(V) (arsenate). Understanding both microbiological but also chemical redox processes leading to As redox changes is necessary in order to predict the environmental behaviour of As.

In our experiments we quantified As(III) oxidation and As(V) reduction by abiotic Fe(III)-Fe(II) systems (e.g. goethite/Fe(II)) [1] as well as by Fe(III) minerals (e.g. ferrihydrite, magnetite and/or goethite) either precipitated by iron(II)-oxidizing bacteria or formed/reduced by iron(III)-reducing microorganisms. Speciation of dissolved and mineral-sorbed arsenic was determined by IC-ICP-MS and synchrotron based X-ray absorption spectroscopy techniques (XANES and EXAFS). Iron minerals were identified and characterized by Mössbauer spectroscopy, X-ray diffraction and electron microscopy. Our experimental results in particular showed that As(III) was oxidized by goethite/Fe(II) systems under anoxic conditions potentially explaining the occurrence of oxidized As, i.e. As(V), under reducing conditions in As-contaminated aquifers. Overall our results show that reactive iron mineral phases can lead to both As(III) oxidation and As(V) reduction depending on the geochemical conditions. These results suggest that microbial transformation of iron minerals can lead to arsenic redox changes and thus influence arsenic toxicity and mobility.

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## Modeling Dietary Intake of Arsenic in Drinking Water and Food: Impact on Human Health in Bangladesh

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Dietary intake of Arsenic (As) via contaminated drinking water and food is the major exposure pathway for people living in rural Bangladesh [1] where long-term ingestion of As mainly through water and rice causes adverse human health affects [2]. Since As groundwater contamination and the associated human health risk are potentially spatially connected, this research quantifies the spatial variability of As in the rural landscape in relation to As concentrations in drinking and cooking water, rice and other foods. The accurate estimation of dietary As exposure and the associated health risk required accurate estimation of diet and socio-demographic characteristics via a food frequency questionnaire (FFQ) and simultaneous field sampling and subsequent laboratory analysis of samples. Individual level average daily intake (ADI) of As, Hazard Quotient (HQ) and Cancer Risk were calculated using parameters appropriate to Bangladesh to quantify the impact of As exposure on human health. This involved integrating a number of complex databases in a single database through various SQL queries and relational database management system.

Total As in water and food samples were determined using ICP-MS. The mean As concentration in tubewell water was  $148 \mu\text{g L}^{-1}$  and ranged from 0 to  $969 \mu\text{g L}^{-1}$ . Spatial variation indicated that As concentrations were highly variable for water sources located even within close proximity (50 m) of each other.

A typical Bangladeshi adult diet consisted of a large volume of water ( $2.6 \pm 1.4 \text{ L day}^{-1}$ ), together with a large portion of rice ( $1494 \pm 776 \text{ g FW day}^{-1}$ ), vegetables ( $136 \pm 37 \text{ g FW day}^{-1}$ ) and dal ( $35 \pm 2 \text{ g FW day}^{-1}$ ) supplemented by irregular consumption of fish or meat. Dietary pattern analysis indicated

that, the rural diet was primarily reliant on water (53%) and cooked rice (31%) supplemented by smaller amounts of vegetables (3%), dal (1%), fish (1.5%), meat (1.5%) and other foods (9%). Excluding water from the rural diet resulted in consequential increases in contributions of cooked rice (66%), vegetables (6%), fish and meat (3% each) and dal (2%). A large proportion of the surveyed population (43%) were exposed to  $>50 \mu\text{g L}^{-1}$  As through drinking water on a daily basis. As concentrations in rice grain and cooked rice ranged from  $0.038 - 0.952 \mu\text{g g}^{-1}$  DW (n=180) and  $0.049 - 0.487 \mu\text{g g}^{-1}$  DW (n=180), respectively. The mean As concentration estimated in leafy (n=537), fruit (n=638), tuber (n=294) vegetables and herbs/spices (n=123) were  $0.027 \mu\text{g g}^{-1}$  FW,  $0.007 \mu\text{g g}^{-1}$  FW,  $0.048 \mu\text{g g}^{-1}$  FW and  $0.013 \mu\text{g g}^{-1}$  FW, respectively. Of all the vegetables considered (n=1592) only arum root (n=58) with an As concentration of  $0.027 \mu\text{g g}^{-1}$  FW was a significant contributor to As exposure but was rarely eaten in large amounts.

The ADI of As via direct ingestion of water and food was  $9.40 \mu\text{g kg}^{-1} \text{ BW day}^{-1}$  (n=1023), which was 4.5 times higher than the WHO's PMTDI level. The overall Hazard Index (HI) and cancer risk for life time exposure through water and food ingestion was 31.3 and  $8.7 \times 10^{-3}$  (n=1023), respectively indicating that both HI and cancer risk were significantly higher than acceptable guideline levels.

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## The use of bank infiltration from rivers as a means of reducing arsenic in abstracted groundwater, Nam Du well field, Vietnam

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Groundwater pumping from deep Pleistocene aquifers has been suggested as a means of reducing high arsenic contents in abstracted groundwater in SE Asia [1]. If this strategy is combined with pumping from bank infiltration schemes, infiltrated low arsenic surface water can potentially further contribute to a reduction of the arsenic content in the abstracted groundwater. In the Nam Du area in southern Hanoi, pumping from a Pleistocene aquifer has since 2004 been done from wells located in a line at a distance of 400 meter from the Red River [2]. However, the surface water can after infiltration receive arsenic, mobilized from Holocene sediments, when the water becomes anoxic [3].

We are studying the surface-groundwater interactions, and the arsenic fluxes in the Holocene sediments, in the Nam Du well field. Groundwater abstraction is here done from the Pleistocene aquifer at depths of 47 to 65 mbs. Detailed studies have been conducted in the area between the river and the pumping wells. Based on a determination of the vertical downward hydraulic gradient, the hydraulic conductivities of the sand, seepage meter measurements in the bottom of the river [4], and numerical groundwater flow modeling, it has been estimated that approximately 30 % of the abstracted water is Red River water. This water is flowing through the Holocene aquifers and into the Pleistocene aquifer with a downward particle velocity between 8 and 30 m/yr.

The groundwater chemistry was studied from groundwater sampling in 11 short screened hand drilled boreholes, drilled few meters from

the river bank. These results show that arsenic now begins to build up in the groundwater from a depth of 20 mbs. The highest arsenic concentration of 1.8  $\mu\text{M}$  (135  $\mu\text{g/L}$ ) is reached at a depth of 30 mbs. This indicates that 6 years after the induced bank infiltration, the upper 20 meter of the Holocene sediments has been flushed, corresponding to a flushing rate of approximately 3 m/yr. With the same flow conditions, and a homogeneous distribution of mobilized arsenic, the Holocene aquifer sediments will be fully flushed within 6-8 years. The arsenic content in pumped water in the Nam Du well field should then be reduced. However, as the river water only accounts for around 30 % of the abstracted water, the arsenic content will still be high due to groundwater arsenic concentrations in the Pleistocene aquifer between 27 and 312  $\mu\text{g/L}$  (2). Optimization of the location of pumping wells and abstraction rates can potentially further reduce the arsenic content in abstracted groundwater.

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## Assessing Arsenic Adsorption Capacity of Natural Bentonite, Laterite and Zeolite

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Arsenic (As) contamination in drinking water becomes a serious problem for human health in several developing countries including India, Bangladesh, Pakistan, and Vietnam. The high concentration of As in water supplies has been linked to chronic health problems such as dermatitis, skin cancer, neurological effects, enlargement of liver, heart disease and internal cancers. Several techniques have been developed to remove arsenic from water. Adsorption, anion exchange, reverse osmosis and coagulation processes are some of the commonly used techniques. Since the majority of the people affected world-wide live in small communities, the tailored technologies must be economically feasible. In Vietnam, there are good resources of natural aluminosilicate minerals such as Bentonite, Laterite and Zeolite, which are well-known for their ion exchange capacities due to their high surface activities. The objective of the present study was to assess the potential and applicability of these natural minerals for removing both As(III) and As(V) present in drinking water.

In the present study, Bentonite, Laterite and Zeolite were used as natural absorbents for removing As(III) and As(V) in water with concentration ranging from 10 to 500 mg/l. The results showed that the As adsorption capacities of these minerals varied and were dependent on the forms of As such as As (III and V). In general, a greater amount of As (V) was adsorbed by these materials than As(III). The As (III) adsorption capacity of Bentonite was greatest and followed by Laterite and Zeolite. On the other hand, Laterite had higher capacity for removing As (V) than Bentonite and Zeolite, respectively. The initial testing concentrations of As (III and V) also affected the adsorption efficiency of the minerals. As such, Laterite appeared to be most efficient for removing As (III) at the initial concentration of

10-20mg/l (74-83%), and at 10-50mg/l (82-98%) for As(V). However, Bentonite had the greatest capacities for adsorbing As(III) (68-80%) and As(V) (70-90%) at the initial concentration of 10-20mg/l.

## Groundwater Arsenic Contamination and Mitigation Initiatives in Lowland, Nepal

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In lowland Nepal, groundwater arsenic contamination has become a public health problem. Almost half of Nepal's total population is living in 20 lowland districts and 90% of them are relying on groundwater as their major source of water for all domestic purposes including drinking. According to the blanket arsenic testing result of 1,120,912 groundwater samples as of July 2008, 7.5% samples were found with arsenic concentration above 10 ppb of WHO guideline value and 1.8% exceeded the national standard of 50 ppb [1]. The arsenic contamination in the districts varied from 0.0% to 12.3% in consideration to national standard. Surveys conducted in arsenic affected communities in seven districts have identified several hundred arsenicosis cases. The prevalence of arsenicosis was found on average 2.9%, which varied from 0.7 to 6.1% [2]. Government, national and international organizations have been collaboratively implementing arsenic mitigation programmes aiming to provide arsenic safe water options: Safe tubewell/Deep tubewell, Improved Dugwell, Arsenic Removal Filters and Rainwater Harvesting. Among different options, the users have preferred 'Kanchan<sup>TM</sup> Arsenic Filter' based on its performance, user friendliness, ownership and cost. However, inadequate awareness on arsenic and its health problems among the community people and lack of follow-up or monitoring of the provided options have largely restricted the continuous or effective use of above mentioned options. Future arsenic mitigation programmes should equally emphasize on awareness raising and capacity building at the local for preventing health damages through sustained use of safe water options.



Figure 1. Identified arsenicosis patient with keratosis on palms and soles.

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### Keywords:

Groundwater, Arsenic, Arsenicosis, Mitigation, Awareness, Lowland, Nepal



## Spatial Relationship Between Dissolved Arsenic and Other Groundwater Constituents Within the Village of Van Phuc, Vietnam

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The Van Phuc, Vietnam site is south of Hanoi and exhibits sharply contrasting aquifer As concentrations within a well-defined hydrological system that is ideal to study the interplay between the geochemistry and hydrology that affect As concentrations.

To properly characterize spatial variation at the site, it is necessary to understand the sorption processes that retain (or release) arsenic from sediments. Here we examine the relationship between dissolved As, iron, ammonium, sulfate, and other element and species in Van Phuc. Analyte concentrations reported here are based primarily on existing private tube wells using field kits, redox-sensitive electrodes, and ICP-MS.

The As concentrations in wells sampled in September 2010 was spatially heterogeneous (Figure 1). Most low-As wells were located in the northern portion of the study site, although low values were also found distributed throughout and in the southern portion of the site. Concentration ranges seem to parallel the river, though seem to roughly parallel to the modern river channel. While the nature of this distribution is not yet clear, it may reflect the fact that sampling is biased in populated areas and spreads parallel, rather than orthogonal to, previously identified gradients in As concentrations (identified in the map with black circles). Although the redox conditions were highly variable, the concentrations of ammonium, DOC, Fe(aq) and other species indicated that much of the area is at least moderately reduced, including areas that are low in As. Sulfate concentrations also varied considerably over the region, with most sulfate levels being quite low (<1 mg/L, with sporadic

concentrations exceeding 10 mg/L. Arsenic concentrations were usually low in water containing measurable sulfate, but no obvious relationship is apparent in the dataset, at least based on test kit data for sampled groundwaters. Similarly, neither well depth nor location, redox status, dissolved iron levels, or other measured concentrations are effective in themselves at describing As concentrations. Another round of private well sampling is planned in April or May 2011. Of particular concern from a practical point of view is the possibility that As concentrations might vary seasonally in low-As wells that are surrounded by high-As wells.

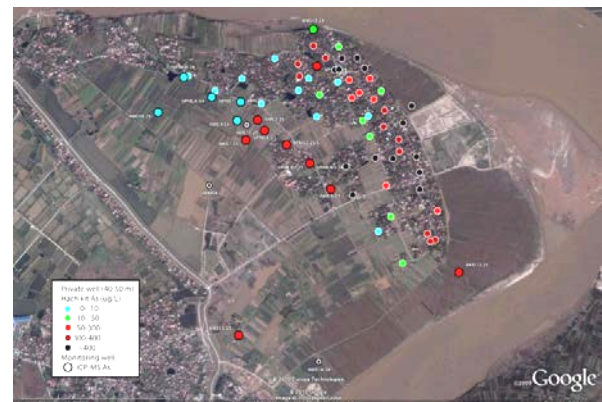


Figure 1. Van Phuc study area with sampled tubewells labelled based on their measured Hach test kit arsenic (white circles) or ICP-MS concentrations. The approximate width of the image is 3 km, and 15 km south of Hanoi, Vietnam.

## Adsorption and desorption of arsenic on Holocene aquifer sediments at Nam Du

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Because of groundwater abstraction close to the Red River at Nam Du, river water is infiltrating through the river bottom into the underlying Holocene aquifer. In contrast to the Holocene aquifer, the river water contains no arsenic. The infiltrating river water is therefore gradually leaching arsenic from the aquifer sediments. The downward groundwater velocity is about 30 m/yr [1] and since the Holocene sequence here is about 30 m thick [2], the sediments are being flushed by one pore volume each year. This setting is accordingly a natural analogue to a laboratory column experiment to study desorption and retardation of arsenic from Holocene aquifer sediments. The groundwater of the deeper part of the aquifer has about 1  $\mu$ M As(III) while As(V) is absent. However the upper 15 m is more or less free of As(III). Since groundwater abstraction in the area has been going on for 20 years, the retardation of As(III) is about  $(20 \times 30) / 15 = 40$ . The profiles for the groundwater contents of Fe, PO<sub>4</sub> and Si resemble that of As(III), even though PO<sub>4</sub> and Fe<sup>2+</sup> are slightly retarded compared to As(III) and Si, and these components are apparently also being leached from the sediments.

Laboratory experiments with adsorption and desorption of As(III) and As(V) on Holocene aquifer sediments were carried out. The experiments were carried out under completely anoxic conditions, using a sediment suspension in a serum bottle. The liquid phase was sequentially replaced and the amount of As adsorbed or desorbed was calculated from the mass balance. The results show that both As(III) and As(V) adsorb on the Holocene aquifer sediment and that adsorption of As(V) is much stronger than of As(III). Stollenwerk et al. [3] carried out similar experiments on oxidized Pleistocene aquifer sediments from

Bangladesh. A comparison of the two data sets shows them to be very similar, except that our Holocene sediments adsorb As somewhat stronger at higher concentrations. The similarity of As adsorption on oxidized Pleistocene aquifer sediment from Bangladesh with the reduced Holocene aquifer sediment from Nam Du is at odds with our common perception that As predominantly is adsorbed onto Fe-oxides which obviously are much more abundant in the oxidized sediment. Desorption experiments, following adsorption furthermore revealed that the arsenic binding mechanism to the sediment surface only is partially reversible and is also suggesting more complicated sorption mechanisms.

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## Radiocarbon Analysis of Microbial DNA and PLFA from Arsenic Impacted Aquifers in Bangladesh

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It is generally agreed that microbial respiration drives the release of arsenic from the sediment to water in drinking water aquifers throughout Southeast Asia. This microbial respiration requires organic carbon, and it is this source of organic carbon that is poorly constrained. It has been hypothesized that the carbon could be derived from: 1) young anthropogenic sources, 2) carbon deposited with the sediments, 3) carbon from organic rich peat lenses, or 4) older petroleum byproducts. However, no method is currently available to directly determine the source of organic carbon. In order to better constrain the source of organic carbon we developed a method to determine the radiocarbon signature of microbial DNA and phospholipids fatty acids (PLFAs) from groundwater samples. The radiocarbon signature of the DNA and PLFA will represent the source of organic carbon utilized by heterotrophic microbes. For DNA, the method includes filtering over 10,000 liters of groundwater onto a 0.2  $\mu\text{m}$  filter followed by DNA extraction and purification. For PLFAs the method includes filtering over 1,000 liters of groundwater onto a newly developed carbon free filter followed by PLFA extraction and purification. The DNA method enables us to collect, extract, and purify over 150  $\mu\text{g}$  of DNA with an absorbance at 260/280 > 1.8 and an A260/230 > 2; indicating pure DNA. The new method was utilized at Site F in the Lashkardi Village, Araihasar, Bangladesh. This site was chosen because sand extends to

the surface, recharge is rapid (0.5m/yr), and irrigation pumping occurs in the fields surrounding the village. The site therefore represents an area where rapid recharge of anthropogenic carbon might occur. DNA samples were analyzed from well F2 (11.1 m depth, 22.5 ug/L As), F4 (19.4 m depth, 183 ug/L As), F6 (25.4 m depth, 203 ug/L As), and F5 (56.8m depth, 1.04 ug/L As) along with controls of a blank filter, and *E. coli* grown on acetate, glucose, and LB media. PLFAs were also collected and analyzed from F6. No carbon was detected from the blank filter and the  $\Delta^{14}\text{C}$  of DNA from cells grown on acetate, glucose, and LB was similar to expected values. The  $\Delta^{14}\text{C}$  of DNA at 11.1m depth was  $-55.9 \pm 9.7$  (410  $\pm$  90 yrs), at 19.4m depth was  $-116.8 \pm 5.1$  (940  $\pm$  50), and at 25.4 m depth was  $-143.1 \pm 3.8$  (1185  $\pm$  40 years). The DNA is significantly older than groundwater ages and does not contain modern carbon but is younger than estimated sediment ages. This data eliminates petroleum byproducts and young anthropogenic carbon as sole sources of carbon for microbial respiration. We hypothesize that the carbon is either slowly transported downward and its velocity is retarded to that of groundwater or the carbon represents the mixing of a young and old source. Further utilization of this novel method should help to better constrain the carbon sources driving arsenic release in the shallow aquifers of Southeast Asia.

## Studies on the possibilities of Solidification/Stabilization of Arsenic Laden Iron Hydroxide Sludge

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Arsenic in groundwater is a concern to human health. In general iron based technologies are suggested/used for arsenic removal from water. These methods produce waste sludge which can be hazardous. This sludge needs to be disposed off in a manner that will not allow the adsorbed arsenic to leach out and contaminates the environment. Employing the sludge for some useful purpose could also be a sustainable long term solution. Through the work done here, an attempt was made to evaluate the options for solidification/stabilization of arsenic-iron hydroxide sludge using clay and cement as a binder. Efforts were made to evaluate the cause of leaching from the iron hydroxide sludge. It was seen that leaching of arsenic from the arsenic-iron hydroxide sludge under aerobic condition is mainly affected by pH, phosphate and silicate anions. Studies carried out revealed that leaching of arsenic is insignificant in the pH range of 2 to 8 in absence phosphate and silicate. However, about 14%, 41% and 46% As(tot) was seen to leach from the sludge in presence of 1 ppm, 2 ppm and 3 ppm of phosphate respectively at pH 8. Similarly, about 3%, 4% and 6% As(tot) was found to be leached in presence of 10 ppm, 20 ppm and 30 ppm silicate respectively. Under the above conditions, As(V) was found to be predominant in the leachate. Under anaerobic environment, leaching of arsenic was found to be about 17% in 42 days and As(III) in the leachate was around 65%.

Clay was found to be effective for stabilization of arsenic-iron hydroxide sludge in the solidified form. Arsenic co-precipitates with iron hydroxide and a process of cementation occurs between these two substances [1]. Arsenic laden sludge was mixed with clay in different proportions (up to 30% of the weight of the brick) for making bricks in a commercial

brick kiln. Leaching of arsenic from the bricks was found within the USEPA prescribed regulatory limit of toxicity characteristic (TC) i.e. 5 mg/L. From engineering point of view, bricks containing up to 15% sludge was found satisfying the Class 10 brick (designated as first class) category of IS 1077: 1992. Brick mixed with 20-25% sludge met the Class 7.5 brick category (designated as 2<sup>nd</sup> class brick) of IS 1077:1992 and 30% sludge containing bricks found in the category of 3<sup>rd</sup> class brick from strength point of view.

Cement can also be used for stabilizing the sludge in solid matrix form before disposal into landfill site. Experimental analysis of solid matrices of various combinations indicated that 75% sludge could be mixed with cement. The TCLP results of cement stabilized sludge were found within the USEPA prescribed regulatory limit. Maximum compressive strength achieved by the cement sludge matrices containing 75% sludge was 0.74 MPa and minimum was 0.55 MPa after 28 days of curing, which is sufficiently above the required compressive strength of 0.35 MPa for landfill.

Based on the study it seems that arsenic laden sludge can be disposed off by mixing with clay to form bricks or encapsulated with cement for disposal into landfills.

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## Importance of aquifer structure to release arsenic into groundwater via convergent groundwater flow in a recharge zone in Sonargaon, Bangladesh

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Sonargaon, located at the boundary between Pleistocene terrace and Holocene flood plain, is one of highly arsenic polluted groundwater areas in Bangladesh. Although the most arsenic polluted groundwater was found in stagnant groundwater condition in this country, the highest arsenic polluted groundwater (1.2 mg/L max.) appears in a recharge zone of Holocene aquifer in our study area of Sonargaon. Such a situation must be suitable for observation of the very early stage of arsenic contaminated groundwater formation. Thus, arsenic concentration and residence time of groundwater were studied in relation to the depth and structure of arsenic contaminated groundwater aquifer.

Drilling survey of the aquifer sediments revealed that the Holocene and Pleistocene aquifers directly contacted at about 40 m depth due to lack of aquitard clay layer beneath the highest arsenic contaminated groundwater area. The previous study also showed that another highly arsenic contaminated groundwater area was at the similar geologic structure of the aquifer<sup>1)</sup>. Thus, the aquifer structure, i.e., direct contact of Holocene and Pleistocene aquifers, is essential for high arsenic concentration of groundwater.

Based on the data of <sup>3</sup>He/<sup>4</sup>He ratio and CFCs, groundwaters having contrastive arsenic level recharged at two different periods present in the Holocene aquifer; one is the As-free groundwater recharged before 1970 and the other containing As >1 mg/L recharged after 1990's. Concentration of the arsenic is dependent on the mixing ratio of the two groundwaters.

The arsenic concentration increases with depth in the Holocene aquifer from 100-200 µg/L at

5m depth to >800 µg/L at 10 m depth. Most active release of arsenic occurs in 5-10 m depth at the center of recharge zone, and the arsenic concentration does not change below that depth.

Combining with the above observation facts, schematic model can be drawn as in Figure 1. The arsenic is released into groundwater in the upper half of Holocene aquifer in association with convergent groundwater flow toward the depression of the aquifer bottom, at where the underlying Pleistocene aquifer contacts. Highest arsenic contaminated groundwater gives the age <20 years. Thus, the release of arsenic started at early 1990's, probably when irrigation pumping from the Pleistocene aquifer rapidly increased in the area.

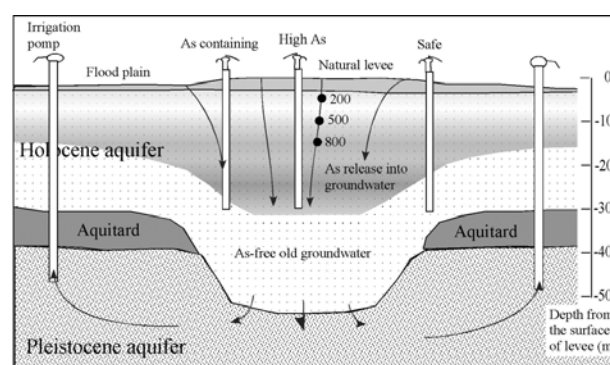


Figure 1. Schematic model of arsenic contaminated groundwater formation in a recharge zone of Sonargaon, Bangladesh. Attached figure on dot gives concentration of Arsenic in the pore water in mg/L. Arrows indicate groundwater flow direction.

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## A to Z development of a biosensor based microfluidic unit able to perform continuous monitoring of arsenic in groundwater

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Contamination with arsenic is a recurring problem in both industrialized and developing countries [1]. Of particular concern is the contamination of potable water sources by arsenic in Southeast Asia (Bangladesh, Vietnam). In order to provide alternative measurement tools for detection arsenic contamination, our group has developed a number of bioassays with so-called reporter bacteria [2,3]. These bacteria synthesize an easily measurable protein (such as green fluorescent protein, GFP) in response to arsenic. The response is proportional to the amount of arsenic applied to the cells.

The goal of the overall project is to miniaturize the arsenic bioassay and fit in a stand-alone portable unit. The unit should consist of an easy and cheap device by which samples could be continuously measured for arsenic in the field. The central reaction element is formed by small cavities ( $15000 \mu\text{m}^2$ ) in a microfluidic chip holding several hundreds of bacterial reporter cells from which the combined fluorescence can be quantified [1].

The project is articulated in three major areas. First, the optimization of the bioreporter genetic circuit to obtain stronger signals, lower background, lower detection limits and a broader operational range. To increase the sensitivity we deleted the chromosomal arsenic detoxification system (*arsRBC*). To enhance the signal and the operational range new reporter circuits have been designed with different configurations of the regulator and promoter elements that drive expression of the reporter gene.

The second area concerns the design and production of the microfluidics systems, including channels, valves, filters and operational protocols that altogether should

compose the stand-alone microfluidic core. This core should be autonomously able to preserve the bioreporter and perform multiple measurement cycles, each of which is composed by mixing of sample with the bioreporter cells, stacking of the cells into its microcavity and washout after the measurement is done.

The third area concerns the miniaturization of the electronic interface to excite the GFP, collect the emitted fluorescence from the cells and produce the instrument's read-out.

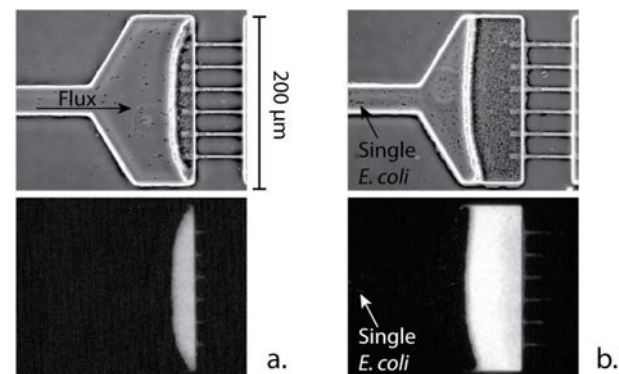


Figure 1. Picture of the filter and of the microcavity in which the cells are accumulated. Panel a. phase contrast (top) and fluorescence (bottom) images of cells induced per 60 minutes with  $8 \mu\text{g/l}$  of arsenite, panel b. same experiment then panel a. but after 180 minutes.

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## Multi-scale modeling of physical and chemical effects on arsenic transport to deep wells in the Bengal Basin

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Low-arsenic deep groundwater is a promising alternative to As-contaminated drinking-water wells in the Bengal Basin. Thousands of deep wells have already been installed; most are As-safe, but some have As concentrations above health guidelines. The occurrence of As in deep groundwater and the sustainability of currently low-As resources depend on the physical and chemical characteristics of the aquifer system. Geology, hydrology, and pumping determine physical flowpaths, and the chemical properties of aquifer sediments and reactions determine porewater As concentrations. We use groundwater flow and solute transport models on the basin scale (500x500km) to assess flowpaths and As concentrations in deep wells for a range of physical and chemical conditions. Alternative pumping depths and rates, effective hydrogeologic properties, and a range of sorptive properties (retardation) are considered. Regional-scale analysis of flowpaths [1] and As concentrations indicates that restricted pumping at depth, on the order of the current domestic pumping rate with some future increase, is essential to limit downward migration of As from shallow contaminated regions, even in areas where deep sediments sorb As.

Factors occurring on scales smaller than can be represented in the basin-scale model can have important effects on flow and transport. The large-scale model considers homogeneous hydraulic conductivity across the basin, with heterogeneities represented as vertical anisotropy. Pumping is evenly distributed (though spatially varying), as would occur from closely-spaced, low-yield handpump tubewells. The potential effects of these simplifications are considered for a location within the basin where the flow direction is nearly vertically downward, an area vulnerable

to As contamination from the surface. Smaller-scale models, 60x60km, were populated with a geostatistical representation of hydraulic conductivity modeled based on driller log data [see 2]. Boundary conditions produce a vertical hydraulic gradient consistent with that of the basin-scale model. Deep domestic wells were represented individually to explore effects of high-capacity municipal wells. Simulations indicate that geologic heterogeneity greatly increases variability in flowpaths and the time to As breakthrough in deep wells. The amount of drawdown in the aquifer, which may prevent the use of deep wells in some areas, is also highly variable, controlled primarily by local hydraulic conductivity. The effect of individual rather than distributed pumping wells is smaller than that of geologic heterogeneity on this spatial scale.

Results of this study confirm previous findings that deep groundwater should be used only for domestic supply, with irrigation water obtained from other sources. The results also indicate the importance of small-scale effects, thus local field studies are essential for assessment of feasibility and variability across the basin. The geologic and chemical heterogeneity of the basin and the uncertainties associated with large-scale analyses support regular monitoring for arsenic and other contaminants.

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## Communication between low- and high-arsenic aquifers in Araihsazar, Bangladesh and its role in the failure of deep aquifer community wells

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The installation of deeper aquifer community wells has been one of the major As mitigation strategies followed by Bangladeshi government and NGOs. In Araihsazar upazila, we installed 51 community wells between 2001-2003, four of which failed to provide groundwater (GW) that meets the Bangladeshi drinking water standard of 50 µg/L As. Some of the failures have been attributed to cracked pipes, but others might have occurred due to the flow of shallow GW along the well casing or, on a slightly broader scale, through the aquifers and leaky confining units. The disconcerting possibility of pumping-induced intrusion of high-As GW into deeper aquifers has been addressed by basin-wide hydrological models that use representative, but homogeneous, parameters. However, as hydrogeologic conditions across the Bengal basin vary, site-specific studies are necessary to assess the extent to which a local low-As aquifer might fail due to the shallow GW intrusion, and to provide general guiding principles for similar analyses at other locations.

The site of one of our failed community wells was selected for such studies. The initial well was installed in the middle of a 30m-thick intermediate-depth aquifer, separated from the water table aquifer by ~10m of silty clay, and underlain by ~7m of hard, plastic clay. After the well failed 18 months later, it was reinstalled deeper within the same aquifer, yet failed again in <1 year. It was finally replaced by a deeper aquifer well (safe to date) installed under the hard clay layer. Pumping from isolated sections of the initial well pipe (to check for cracks) indicated no leakage anywhere above the screen. Drill cuttings, collected after the second well failure, showed elevated levels of leachable As in the sediments located near the screens of the two failed wells. These observations led to a hypothesis that a broader leakage from overlying contaminated aquifer might have played a role in the interm. depth community well failures, thus the site was prepared for pumping tests to establish hydraulic properties and connectivity of the high- and low-As aquifers.

Lithologs from 6 boreholes located within a 70m radius from the initial community well showed that local stratigraphy was contiguous across the site, and X-ray fluorescence profiles of the total sediment As, Fe, and Mn also indicated that sediment at equivalent depths was laterally uniform. Three pumping wells were installed in Dec. '10 / Jan. '11, as well as 18 observation wells screened at strategic depths and grouped in 4 spatial clusters across the site. These were sampled for basic water quality before and after a series of 8 to 48 hour long pumping tests. Pumping was carried out from wells screened across the entire vertical extent of either the shallow or interm. aquifer, as well as from isolated sections of the latter to check for its anisotropy.

Water levels were ~1m higher in the shallow than in the interm. aquifer, and pumping from one aquifer did not induce measurable drawdown in the other, both observations implying a degree of hydraulic separation between the two aquifers. On the other hand, drawdown in the confined (interm.) aquifer reached equilibrium within 12 hours, the rather short time indicating that GW might be leaking through the silty clay. Preliminary results also indicated that high-As GW is *not* present widely across the site at the depth of well failures (middle and lower section of the confined aquifer). However, GW from the upper section of the aquifer (right below the silty clay) had elevated levels of NH<sub>3</sub>, Fe, and As, source of which could potentially be from above. Alkalinity, conductivity, pH, and T indicated that the interm. aquifer is otherwise rather uniform, and the low observed anisotropy ( $\leq 10$ ) could allow a fair amount of vertical flow within the aquifer. Further analyses of the water samples and drawdown data will offer clues to the reason for community well failures at the site, and serve as a benchmark for the comparison of local and larger-scale studies.



## Hydrochemical characteristics and redox facies delineation of low arsenic aquifers in South-eastern Bangladesh

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High levels of arsenic (As) in the sedimentary aquifers comprising the Holocene Meghna floodplain deposits have posed a significant health risk to the inhabitants of Matlab, Bangladesh (Fig. 1a). Previous studies in the region [1] suggest that groundwater composition and redox conditions are strongly related to the color of the sediments. Thus, this study has been carried out within the Sustainable Arsenic Mitigation (SASMIT) project in Matlab to provide guiding tool for the local drillers for targeting low-As aquifers. The specific aims were delineate depth specific low As aquifers through 2D-lithostratigraphic modeling and to ascertain the replicability of the emerging sediment color concept elsewhere in areas with similar hydrogeological settings.

Both the sediment and groundwater samples were collected from the SASMIT installed piezometer nests during pre-monsoon (March), 2009. A four step process has been developed to assign colors to the collected sediment samples: i) assigning color in the field; ii) assigning Munsell color codes for all collected sediment samples with the help of a Munsell soil color chart; iii) correcting field observed colors with respect to Munsell color codes; and iv) distributing all 60 field observed colors to 4 broad colors [1] viz. black (B), off-white (OW), red (R), and white (W) considering local driller's visual perceptions.

Three aquifers (Af1, Af2, Af3) intervened by two aquitards (At2, At3) have been identified in the study area (Fig 1b). The shallow aquifer (Af1) extending up to a depth of about 40 to 50 meters b.g.l. consisting of black sediments is characterized by mainly Ca-Mg-HCO<sub>3</sub> water-type and water-level fluctuation of about 3-4 m. The intermediate aquifer (Af2)

comprising red/off-white/white sediments underlying At2 is characterized by primarily Na-Ca-Cl water-type. Groundwater from black group of sediments represent a highly reducing environment contains high aqueous concentrations of As, Fe<sup>2+</sup>, NH<sub>4</sub><sup>+</sup>, HCO<sub>3</sub><sup>-</sup>, PO<sub>4</sub><sup>3-</sup>

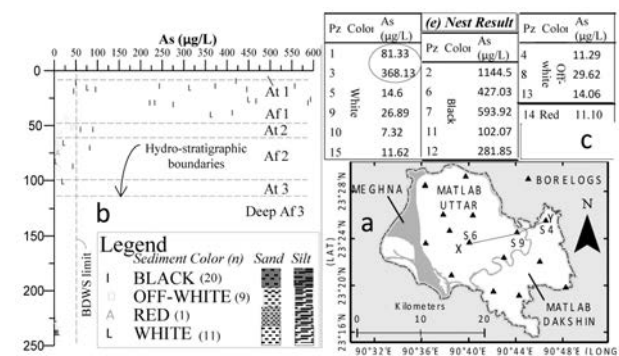


Figure 1. a) Location of piezometric nests in Matlab; b) As vs. depth; c) As in piezometers

and DOC as well as low SO<sub>4</sub><sup>2-</sup> and Mn<sup>2+</sup>. The red/off-white/white group of sediments, show an opposite trend, thus representing a less reducing condition (Fig 1c). A very strong to good correlation between DOC with HCO<sub>3</sub><sup>-</sup>, As<sub>tot</sub>, Fe<sub>tot</sub>, NH<sub>4</sub><sup>+</sup>, and PO<sub>4</sub><sup>3-</sup> and A<sub>stot</sub> with HCO<sub>3</sub><sup>-</sup>, Fe<sub>tot</sub>, and NH<sub>4</sub><sup>+</sup> within the black group of samples indicate that, oxidation of organic matter is driving all the redox reactions and thereby releasing As in solution. In the case of red/off-white groups of samples with low organic content, all the correlations are poor. Depth-specific spatial distribution of lithofacies indicates that installation of wells at a depth of about 70 m b.g.l. anywhere in the SE part of the study area would most likely yield low As groundwater.

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## Mobilization of sorbed and co-precipitated As from biogenic Fe(III) (hydr)oxides by the Fe(III)-reducer *Shewanella oneidensis* MR-1

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Mobile arsenic in arsenic-contaminated groundwater and soil in South-East Asia enter the human food chain directly or indirectly via plants and animals. This can have a vast impact on the health of many people. Consequently, research has focused on the geochemical and biogeochemical processes leading to both mobilization (release) and immobilization (removal) of arsenic from aquifers and soil. Recent studies by Hohmann *et al.* [1] demonstrated that Fe(II)-oxidizing bacteria can efficiently immobilize arsenic in aqueous systems. By forming biogenic Fe(III) (oxy)hydroxides consisting of mixtures of ferrihydrite, nano-goethite and goethite, these microorganisms form co-precipitates of Fe(III)(hydr)oxides and arsenic and additionally arsenic can sorb to the surface of the biogenic mineral phases. However, the co-existence of Fe(II)-oxidizing with Fe(III)-reducing bacteria in the environment could result in efficient and rapid redox cycling of Fe by re-reduction of biogenic Fe(III) hydroxides. This could lead either to a dissolution of the Fe(III) minerals causing a release of the bound arsenic or alternatively to the formation of secondary Fe mineral phases [2] and an immobilization of arsenic.

In this study, we followed the reduction of biogenic arsenic-bearing Fe(III) minerals (mixtures of ferrihydrite, nano-goethite and goethite) by the Fe(III)-reducing strain *Shewanella oneidensis* MR-1 (Fig. 1). We then compared As (im-)mobilization during reduction of these biogenic Fe(III) hydroxides to As (im-)mobilization from chemically-synthesized Fe(III) minerals that contained sorbed and co-precipitated arsenic. Additionally, we determined chemical redox changes of aqueous and solid phase arsenic due to the formation of reactive Fe(II) species

using IC-ICP-MS and synchrotron based X-ray absorption spectroscopy techniques (XANES and EXAFS). The resulting iron minerals were identified and characterized by X-ray diffraction, Mössbauer spectroscopy and electron microscopy. First results show that arsenic is only partially remobilized during microbial reduction of biogenic Fe-As-co-precipitates and that the remaining arsenic is bound either to the non-reduced goethite or to the newly formed Fe(II) carbonate and phosphate minerals phases.

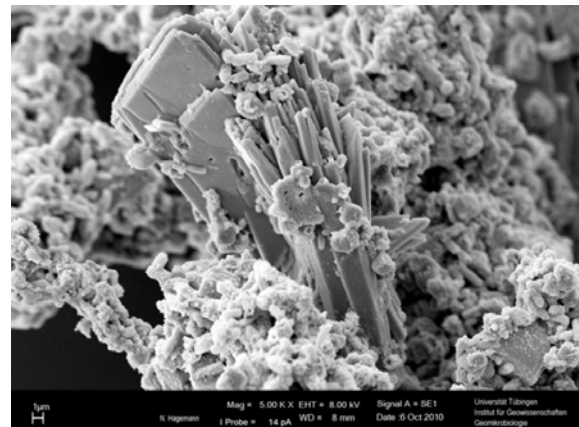


Figure 1. SEM micrograph of an Fe(III) mineral phase containing arsenate at a 250:1 Fe:As mass ratio after microbial Fe(III) reduction.

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## Potential Impact of Rice Field Water Management Schemes on Arsenic Concentrations in Bangladeshi Wells

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In Bangladesh, groundwater-irrigated rice fields are an integral part of the country's hydrologic and geochemical system. Pumping for rice field irrigation has decreased the residence time of water within the arsenic-contaminated aquifer and increased the amount of surface water recharge drawn into the aquifer [1]. This surface recharge evolves into groundwater with variable arsenic contents; recharge from ponds evolves into high arsenic groundwater while recharge from rice fields evolves into low arsenic groundwater [2]. The fields themselves act as net sinks of arsenic from the shallow aquifer, receiving arsenic in irrigation water and returning arsenic-free water back to the aquifer [3]. Therefore, the role of groundwater-irrigated rice fields within the arsenic-contamination problem is complex. They directly remove arsenic from shallow aquifer and indirectly promote the evolution of high-arsenic groundwater. This complexity suggests that any rice field management schemes that alters irrigation pumping or field recharge rates will alter arsenic concentration patterns within the aquifer. Field management schemes, including intermittent irrigation (i.e., alternate wetting and drying) [4] and sealing the raised boundaries around fields (bunds) [5,6], are often promoted based solely on their water-saving potential. In Bangladesh, efforts are underway to evaluate the impact these schemes have on arsenic loading and chemistry in field soils [3,7]. However, no consideration has been given to the complex role that fields play with respect to aquifer contamination.

Here we utilize an existing, three-dimensional, seasonal groundwater flow and conservative transport model [2] to evaluate the potential for rice field management schemes to shift arsenic concentration patterns in the shallow aquifer. Specifically, we investigate the adoption of

alternate wetting and drying (AWD) and bund sealing, and track how these schemes alter the relative proportion of water in existing domestic wells that evolved from different recharge sources. We assume that an increase in the proportion of water originating from ponds results in an eventual increase in arsenic concentrations. The results clarify the sensitivity of current arsenic concentration patterns to rice field management practices and highlight the potential for future contamination of currently clean, shallow domestic wells.

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## **Arsenic contamination in ground water in Viet Nam and it's adverse affects to public health**

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The investigation of arsenic contamination in ground water and its affects on public health have been conducted in 8 provinces of the Red River Delta 2008 - 2010. The results showed that :

- 77,6% of tube wells with arsenic readings surpassing 50  $\mu\text{g/L}$ , a half of them have arsenic concentration higher than 100  $\mu\text{g/L}$ . Arsenic contamination in ground water is severe in Ha Nam (74,5%), Nam Dinh (63,2%), Vinh Phuc (47,3%), Ha Tay (46,7%). Despite using the sand filtration unit, arsenic content in drinking water is still high, only 36,5% of filtrated water samples were fit for Vietnamese standard (10  $\mu\text{g/L}$ ).

- The prevalence of disease related to arsenic affects such as neuropathy (64,7%), abnormal sensation (19%), cardio-vascular disease (32,8%), skin hyperkeratosis (3,6%), pigmentation changes (4,6%), cancer (4,1%). The average arsenic concentration in the urine and hair samples of exposed persons was statistical higher than those of people in control group  $p < 0.05$ . There were 60 cases (1,62%) suspected of arsenicosis among 3700 persons that have been medically examined.

The authors recommended the following measures for preventing massive endemic arsenicosis in Vietnam :

- To improve IEC activities on arsenic contamination in ground water and arsenic removal technologies as well as adverse affects of arsenic on health.
- To expand investigation on arsenic contamination in Vietnam to identify contaminated areas and support for appropriate arsenic removal technologies.
- To take periodic medical examination in arsenic contaminated areas for early identification of arsenicosis cases to improve health status of patients and prevent massive endemic arsenicosis.

## Mobilization of Arsenic in groundwater in the southern Hanoi city (Viet Nam) as studied by isotopic and related techniques

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16 samples of surface and groundwater from the monitoring network and ponds around the wells in the Thanh Tri district has been taken and analyzed for the water chemistry including major ions, As content, tritium activity,  $d^{13}C$  in DIC,  $d^2H$  and  $d^{18}O$  to elucidate the mobilization of As constituent in groundwater of the study area. The isotopic composition of groundwater indicates that the water in that area is recharged from the local meteorological and the Red River's water sources. The mean residence time of the groundwater should be before 60'ies of the past century as its  $^3H$  activity ranged from LOD of the analytical technique (0.4 TU) to 2.1 TU only implying that As would not be related to its recent application. The concentrations of As in the water samples is weakly correlated with those of  $Fe^{2+}$  ( $R^2=0.08$ ) but it strongly did with the concentrations of bicarbonate that  $R^2 = 0.80$ . Thus, bicarbonate seems to liberate As adsorbed on hydrous ferric oxides (Hfo) into water through the displacement mechanism. The surface adsorption-desorption of As could be proven by a strong correlation between As and Mo concentrations ( $R^2=0.77$ ). The bicarbonate formation in groundwater was thought to be, partly, due to the bio-mineralization of natural organic matter (NOM) by bacteria to form  $CO_2$  followed by the dissolution of calcite and/or biotite present in the sediments. A strong correlation between As and ammonium concentrations ( $R^2=0.67$ ) is an evidence for the NOM bio-mineralization. Additional evidence for the NOM bio-mineralization was found in a close relationship between  $d^{13}C$  and the concentration of bicarbonate in water ( $d^{13}C, ‰ = 7.59 * \ln[HCO_3^-] - 25.67, R^2 = 0.78$ ). Therefore, the mobilization of As in

groundwater of bicarbonate type in the Holocene aquifer in the southern part of Hanoi city seems not only due to the reductive dissolution of the constituent from Hfo but the displacement of As on the Hfo by bicarbonate also should be considered.

## Arsenic contamination of water, dust and soil in central India

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Arsenic in Indian subcontinent is becoming an increasing concern to human health due to exposure of several millions of populations through drinking water, contaminated food, dust, etc. In central India, the rural population residing over  $\approx 500$  km<sup>2</sup> is severely affected with arsenic poisoning (1-2). In the present work, the arsenic contamination pattern of groundwater, dust and soil samples of the Ambagarh Chauki, Rajnandgaon, CG, India (20°43'9"N & 80°44'7"E) are described.

The water, soil, dust and ash samples were collected in years, 2010-11. The analytical techniques: TXRF, ICP-AES, AAS, IC and ion selective electrode were used for the analysis of As and F<sup>-</sup> in the water is summarized in Table 1.

Table 1. As and F<sup>-</sup> levels in ground water

S. No.	Tube well	F <sup>-</sup> , mg l <sup>-1</sup>	As, $\mu$ g l <sup>-1</sup>
1	Bharĭ khurda	4.5	220
2	Bharĭ khurda	3.7	217
3	Kaudĭ kasa	5.7	510
4	Kaudĭ kasa	10.0	419
5	Kaudĭ kasa	19.5	985
6	Kaudĭ kasa	24.0	179
7	Arajkund	11.0	208
8	Arajkund	15.0	489
9	Kaudĭ kasa	12.0	376
10	Kaudĭ kasa	16.0	315
11	Kaudĭ kasa	8.7	620
12	Sansaytola	19.3	575
13	Sansaytola	12.0	826
14	Sansaytola	23.2	148
15	Dhadĭtola	14.0	906
16	Joratarāĭ	7.4	721
17	Jadutola	8.3	805
18	Mangatola	14.6	587
19	Mangatola	25.4	795
20	Sangali	27.0	210

The content of As, Na<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>, organic carbon (OC) and carbonate carbon (CC) in the 20 groundwater samples

were ranged from 0.15 – 0.99, 16 – 80, 11 – 73, 22 – 138, 14 – 195, 14 – 84, 116 – 412, 20 – 10730 and 148 – 945 mg l<sup>-1</sup> with mean value of 0.51 $\pm$ 0.12, 38 $\pm$ 8, 30 $\pm$ 8, 62 $\pm$ 14, 69 $\pm$ 20, 40 $\pm$ 9, 286 $\pm$ 39, 2001 $\pm$ 1024 and 506 $\pm$ 118 mg l<sup>-1</sup>, respectively. The mean content of total As in the 20, 14, 6 and 3 soil, rhizospheric soil, dust and ash were found to be 585 $\pm$ 130, 1644 $\pm$ 758, 235 $\pm$ 78 and 458 $\pm$ 755 mg kg<sup>-1</sup>, respectively. High arsenic content in the environment (i.e. water, soil, dust and ash) of the Kaudikasa area, Rajnangaon, Chattiasgarh, India is observed. The arsenic occurrence in this region is associated with high content of metals i.e. Al (9.5 $\pm$ 1.5%), K (4.5 $\pm$ 0.5), Ca (3.5 $\pm$ 1.2), Ti (4.4 $\pm$ 0.5%), Mn (8.4 $\pm$ 1.6) and Fe (37.9 $\pm$ 4.2%). A higher content of all elements (except Ti, V and Mn) present in the rhizospheric soil. At least 3-folds higher arsenic is associated in the rhizospheric soil. All ground water samples are found to be contaminated with As and F<sup>-</sup> beyond permissible limits of 10  $\mu$ g l<sup>-1</sup> and 1.5 mg l<sup>-1</sup>, respectively.

The arsenic content in the soil of this region is found to be several folds higher than the tolerance levels of 10 mg kg<sup>-1</sup>. The health problems in the population of Koudikasa are observed mainly due to exposure of the contaminated water, food, dust, etc.

### Acknowledgement

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## Arsenic and trace elements in paddy and agricultural soils and fish pond sediments in the Mekong River basin, Cambodia

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For the first time, the concentrations of arsenic and other trace elements in paddy soils (Kandal n = 8; Kampong Cham n = 8), agricultural soils (Kandal n = 6; Kampong Cham n = 6) and fish pond sediments (Kandal n = 6; Kampong Cham n = 6) were simultaneously investigated in the Mekong River basin of Cambodia. Chemical measurements of Aqua Regia digestate of soils and sediments using inductively coupled plasma spectrometry revealed that the concentrations of As, Cd, Rb, Se, Ag, Tl and U in paddy soils in Kandal were significantly higher than those in Kampong Cham. However, there were not significant regional differences in Ba, B, Ga, Pb, Mo and Zn concentrations in paddy soils. As concentration in paddy soils in Kandal ranged from 3.07-26.36 mgAs/Kg with median of 9.04 mgAs/Kg and mean of  $12.86 \pm 10.43$  mgAs/Kg (mean  $\pm \sigma$ ) while it was found  $\leq 0.93$  mgAs/Kg in Kampong Cham. Similarly, As, Pb, Tl and U concentrations in agricultural soils in Kandal were significantly higher than those in Kampong Cham. There was not significant difference in concentrations of Ba, B, Cd, Ga, Mo, Rb, Se, Ag and Zn in agricultural soils between two provinces (t-test,  $p < 0.05$ ). The mean concentration of arsenic in agricultural soils in Kandal was  $6.15 \pm 0.98$  mgAs/Kg (mean  $\pm \sigma$ ) with a range from 5.20-7.48 mgAs/Kg and median of 5.84 mgAs/Kg whereas it was observed  $\leq 1.64$  mgAs/Kg in Kampong Cham. Inversely, concentrations of Cr, Co, Cu and Ni in paddy and agricultural soils in Kandal were significantly lower than those in Kampong Cham (t-test,  $p < 0.05$ ). Although there were not significant regional difference in As, Ba, B, Cr, Co, Cu, Ga, Pb, Mo, Ni, Se, Ag, Tl, U and Zn concentrations in

fish pond sediments, the concentrations of Cd, Rb and Ag in fish pond sediments in Kandal were higher than those in Kampong Cham (t-test,  $p < 0.05$ ). The mean concentration of arsenic in fish pond sediments in Kandal was  $6.28 \pm 1.18$  mgAs/Kg (mean  $\pm \sigma$ ) with a range from 4.19-7.67 mgAs/Kg and median of 6.34 mgAs/Kg whereas a range of arsenic in fish pond sediments in Kampong Cham was from 2.10-8.72 mgAs/Kg with a mean of  $4.62 \pm 2.34$  mgAs/Kg (mean  $\pm \sigma$ ) and median of 4.24 mgAs/Kg. This study suggests that paddy and agricultural soils in Kandal are of potentially contaminated with arsenic, resulting in low grain yield and high risk of arsenic exposure, if groundwater irrigations are continuously applied for agricultural practices. In addition, indigenous aquatic species may be at risk of accumulating arsenic and other trace elements in their bodies. Therefore, further research is needed to conduct risk assessment of arsenic intake through individual daily diets.

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## Spatial and Temporal Variations in Groundwater Chemistry from an Arsenic-Contaminated Area of Cambodia

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Use of groundwater for drinking water is increasing in Cambodia, but knowledge about this resource is lacking. Consequently, groundwater use often results in health risks. In particular, the occurrence of high concentrations of arsenic has slowly poisoned tens to hundreds of thousands of people, and, as in other parts of South and Southeast Asia where similar conditions exist, the causes for and distribution of arsenic in groundwater are not completely understood. In an effort to better understand spatial and temporal geochemical patterns, we have conducted routine groundwater and surface water sampling from a well-characterized field area in the Upper Mekong Delta of Cambodia [1] as well as an adjacent region where an arsenic-free Pleistocene aquifer outcrops at the surface.

Groundwater arsenic concentrations in aquifer and shallow wells vary considerably across the field area and span a range of 0 to 1300  $\mu\text{g L}^{-1}$ . Wells with As < 10  $\mu\text{g L}^{-1}$  are shallow wells (< 12 m depths) screened in surficial clay layers (not productive for domestic use) or tap Pleistocene aquifers. Aqueous arsenic concentrations do not correlate with solid-phase concentrations, which are at background levels (< 5 mg/Kg) in the aquifer sands and only slightly higher (< 12 mg/Kg) in surficial clays. Arsenic concentrations are highest below inland ponds and trend downward towards the Mekong River. The highest DOC, ammonium, DIC, phosphate, and ferrous iron concentrations are also found immediately below ponds, although the spatial distributions differ slightly in other areas throughout the profile. These chemical indicators suggest enhanced biological activity at recharge zones.

Seasonally-shifting hydraulic gradients and surface water chemistry lead to temporal variations in aqueous concentrations,

particularly at reservoir boundaries. Recharge zone pore water arsenic concentrations are highest when steep downward gradients induce water flow into the underlying aquifer, indicative of reductive arsenic release from shallow surficial sediments. Within near-surface porewater,  $\text{Fe(II)}_{\text{aq}}$  concentrations follow arsenic, while  $\text{SO}_4^{2-}$  concentrations are inversely correlated, suggesting changing redox conditions. Within aquifer discharge zones, temporal variations in groundwater chemistry reflect the importance of groundwater movement on geochemistry. Arsenic concentrations are highest during the dry season, when flow is from the aquifer to the river; concentrations drop when the river is flowing into the aquifer. Trends in arsenic are positively correlated with  $\text{NH}_4^+$  and negatively with  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{SO}_4^{2-}$ . The rapid response of arsenic (and other dissolved parameters) to shifting hydraulic gradients highlights the mobility of dissolved arsenic within the reducing groundwater.

Our results support the model that arsenic fate and transport within the surface and subsurface is controlled by coupled hydrological and biogeochemical processes, including liberation from sediments at recharge zones and transport by groundwater through the aquifer. Importantly, as has recently been demonstrated in other parts of South and Southeast Asia [2], arsenic-free wells from Pleistocene aquifers remain vulnerable to future contamination.

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## The application of surface complexation models to assess arsenic mobility in aquifers

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Surface complexation models, the generalized two layer model for ferrihydrite [1], the CD-MUSIC model for goethite [2] and a model fitted onto sorption data for a Bangladesh Pleistocene aquifer sediment by Stollenwerk [3] were used to explore multicomponent adsorption and desorption processes, given the composition of pristine groundwater and the measured amount of adsorbed As(III). The results of all three models show As to be a minor component on the surface complex underpinning the importance of competitive adsorption, including the bulk water composition, particularly PO<sub>4</sub>, Si, HCO<sub>3</sub> Fe(II) and pH, and the performance of the model used. The models for ferrihydrite and goethite produced surprisingly different results. The ferrihydrite model favors As(III) over As(V) and has bicarbonate (52 %) and silica (27%) as the main competitors for surface sites while PO<sub>4</sub> surface species only constitute 5%. For goethite, however, the CD-MUSIC model calculates a greater affinity for As(V) over As(III) while 51% of the sites are occupied by phosphate, with Fe(II) complexes as the second most important species (28%) – both silica and bicarbonate cover less than 1%. In the CD-MUSIC model for goethite all As(III) sorption is through a combined As(III)-Fe(II) complex which is not found in the ferrihydrite model. The model derived from Pleistocene aquifer sediment data resembles the goethite model most. As for goethite, the surface affinity for As(V) is much stronger than for As(III). Phosphate is again the most important ion competing for surface sites with 41%, while bicarbonate complexes are insignificant. On the other hand, silica complexes cover 18% of the surface sites and in this respect it resembles more the two layer ferrihydrite model.

Sensitivity analysis was carried out by varying different parameters in model runs. In the near neutral pH range, both the CD MUSIC and the Stollenwerk model predict that small changes in pH may strongly affect the amount of adsorbed As(III) while this is not the case in the Dzombak and Morel model. The competition of PO<sub>4</sub> with As for sorption sites is strong both in the goethite and in the Bangladesh sediment models while it is minor in the ferrihydrite model. However, while in the Bangladesh sediment model the PO<sub>4</sub> concentration strongly affects both the adsorption of As(III) and As(V), it only affects As(V) in the CD MUSIC model for goethite because As(III) sorbs as a combined As(III)-Fe(II) complex. And in this case As(III) adsorption also becomes a function of the Fe(II) concentration.

The three models were used to model field data from a forced gradient experiment where water from the Red River, low in As, PO<sub>4</sub> and Si, intrudes a river bank aquifer. Compared to conservative mixing of river and groundwater, the field data showed desorption of As, Si and PO<sub>4</sub> from the sediment. Modelling the field data, the Stollenwerk model for the Bangladesh aquifer sediment was found to perform superiorly as compared to the models for ferrihydrite and goethite.

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## Arsenic porewater dynamics and As uptake by rice in intermittently and continuously flooded paddy fields in Bangladesh

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Arsenic-contaminated groundwater is widely used to irrigate dry-season rice (*boro*) in Bangladesh. This has greatly improved food security but is leading to increased As levels in soils and rice and may cause As-induced yield reductions in the long term. Owing to the gradual accumulation of As in paddy soil [1,2], the adverse effects of groundwater irrigation may also extend to monsoon rice (*aman*) cropped under rain-fed or naturally flooded conditions. Since As concentrations and speciation in soil porewater are strongly influenced by redox conditions, irrigation management during the dry season and the water regime prevailing during the monsoon may significantly influence As uptake by *boro* and *aman* rice, respectively.

Here we present data from field studies in Munshiganj and Jessore Districts (Bangladesh), in which As porewater dynamics and plant As uptake were assessed in relation to water management during crop growth.

At the field site in Munshiganj, we studied porewater dynamics of As, Fe, P, Si in a *boro* field irrigated according to local practice, in which flooding was intermittent. During early rice growth, As porewater concentrations reached up to 500  $\mu\text{g L}^{-1}$  and were dominated by As<sup>III</sup>, but As release was constrained to the lower portion of the soil above the plow pan. In the later part of the season, soil conditions were oxic throughout the depth range relevant to rice roots and porewater concentrations only intermittently increased to  $\sim 150 \mu\text{g L}^{-1}$  As<sup>V</sup> following irrigation events [1]. Our results suggest that intermittent irrigation, currently advocated in Bangladesh for water-saving

purposes, may be a promising means of reducing As input to paddy soils and rice plant exposure to As.

To further substantiate these findings we assessed porewater dynamics in relation to As uptake by *aman* rice in two fields in Jessore District, in which rain-fed *aman* is cropped in rotation with groundwater-irrigated *boro*. The fields were maintained continually and intermittently flooded, respectively, by supplementing rainfall with pond water irrigation when necessary. We here compare As contents in *aman* straw and grain collected along spatial soil As gradients in both experimental fields and discuss these in conjunction with time series of soil porewater profiles obtained 2, 4, 7 and 8 weeks after the onset of the controlled water regimes.

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## Mortality risks from arsenic in drinking water ... what water concentration is “safe”?

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Risk assessments for arsenic in drinking water have usually focused on linear extrapolation of cancer risks [1]. Based on such estimates, we recommended that the situation concerning arsenic in drinking water in Bangladesh should have been declared a public health emergency [2]. Recently, two large prospective cohort studies in Bangladesh reported mortality from all causes in relation to arsenic in drinking water [3, 4], both claiming increases in mortality with arsenic water concentrations as low as 10-49 ug/L. These findings suggest a markedly supra-linear dose-response relationship and, if valid, would indicate that the risk assessments conducted in the past with linear extrapolation have grossly underestimated risks. The implications of this would be that water concentrations in the range of 10-49 ug/L, and—by extrapolation—even lower water concentrations, would be associated with major increases in mortality. Here we assess the validity of the findings from these two mortality studies, focusing on exposure assessment and mortality outcomes, and conclude that the apparent increase in mortality with water concentrations in the range 10-49 ug/L are probably the result of inherent biases in each study, in particular due to exposure misclassification. However, even with linear extrapolation, risks are unacceptable for water concentrations of 50 ug/L, and the long-term goal should be to find water sources containing less than 10 ug/L. Nevertheless, in the short-term, sources containing less than 50 ug/L are a distinct improvement compared to continuing high exposures [5]. Since many people continue to drink water containing well in excess of 50 ug/L, arsenic in drinking water should still be thought of as a public health emergency in many Asian countries where such exposures are prevalent.

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# Spatial modelling of groundwater-arsenic-attributable morbidity and mortality in Cambodia

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Agencies involved in protecting the public from detrimental health end-points attributable to the chronic usage of hazardous arsenic-bearing groundwaters for drinking, cooking and/or irrigation require quantitative information about the magnitude and spatial distribution of such risks [1]. We present here such risk maps for Cambodia, one country where significant groundwater arsenic-attributable health risks are becoming increasingly visible [2-4].

GIS & geostatistics have been used to develop hazard & risk maps, the latter based upon combining hazard, exposure & age- & gender-dependent dose-response data for various arsenic-attributable sequela. A regression kriging (RK) approach following that of Rodriguez-Lado [5] was used to model the spatial distribution of groundwater arsenic hazard. The distribution obtained is broadly similar to obtained previously [5]. Dose-response relationships for “arsenicosis” (defined for the purposes of this study as either the development of hyperpigmentation or of keratoses), skin cancer and internal cancers were based on the equations of Yu [6].

Other than substantially lower risk relative to hazard in key urban areas, the risk maps show very similar trends to the hazard map. Combining available spatially-resolved population data has enabled estimates of peak annual disease burden to be estimated viz. 58,000 cases of arsenicosis, 2,000 cases of skin cancer and 5,700 cases of internal cancers; with annual excess (i.e. arsenic attributable) deaths of 400 for lung cancer.

Comparison to data from the Global Burden of Disease study suggests that, at present estimated rates of exposure, chronic exposure to groundwater-derived arsenic in Cambodia

may ultimately contribute over 20 % of the overall annual mortality due to lung cancer.

There is considerable uncertainty in several parameters utilized in this study, in particular the distribution of exposures and the dose-response relationships, both generally and with specific application to the various sub-groups of the Cambodian population. Considerable further work is required to refine these models.

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## **Arsenic mobilisation and anthropogenic ammonium sources in the groundwater in the Nam Du well field, Red River, Hanoi, Vietnam**

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Arsenic enrichment and increasing concentrations of ammonium in the deep groundwater aquifer in the Red River delta in Vietnam are the two major issues concerning drinking and groundwater quality in the Nam Du area, south of Hanoi city. The Nam Du well field is situated on the bank along the Red River in order to facilitate induced infiltration. The area receives surface water with a high load of nutrients and organic matter from the Hanoi sewage system, and is subject to recently increased groundwater extraction from the Pleistocene aquifer system. Several studies performed in the area have found concentrations of As highly exceeding the WHO-guideline of 10  $\mu\text{g/L}$  and  $\text{NH}_4$  concentrations often exceeding 5 mg/L and up towards 30 mg/L. We have so far carried out two field campaigns in the area in 2006 and 2007. The main conclusions were that (i) the distribution of As is highly variable but the zones with the highest concentrations of As are near the Red River in the Holocene aquifer and just down gradient from this in the Pleistocene aquifer, (ii) the sediments within the aquifers are considered to be the source of the As, where the Holocene aquifer is believed to act as the main source of As into the Pleistocene aquifer as reduced As-rich groundwater from the Holocene aquifer is flowing downwards due to the downward gradient, and (iii) two different processes appear to take part in the As mobilisation process. (Holocene aquifer: reductive dissolution of FeOOH and the release of adsorbed As and in the Pleistocene: mobilisation of adsorbed As due to competition from  $\text{HCO}_3$  ions for surface sites on FeOOH). The reducing conditions in the

aquifer will maintain the high ammonium concentrations. The isotopic composition of the ammonium ions and peat combined with the pattern of groundwater flow implies that the ammonium ions are not derived from the peat. Human activities, such as farming or release of sewage water are more likely explanations of the high ammonium ion concentrations. The objective of a new field investigation in the area during April and May 2011 will focus on the age distribution and mixing of waters from different aquifers and surface water bodies to try to verify earlier results and resolve where the main arsenic and ammonium contributions originates. Knowledge of groundwater age in wells, i.e. travel times in the groundwater system enhance the understanding of the flow system and can explain the changes of groundwater quality and pollution concentration. There is a great bene-fit of groundwater dating as existing groundwater quality data becomes more valuable as a reanalysis and may reveal trends that couldn't have been revealed without the knowledge of recharge times of the groundwater samples. The use of the following methods for age determination of groundwater will enhance the understanding of recharge age and mixing of waters of different ages within the aquifer: dissolved CFC gases, tritium level from in-growth method from groundwater samples, and tritogenic helium ( $3\text{H}/3\text{He}$  ratio), krypton-85, helium-4, argon and neon taken from a gas diffusion sampler. The results from the field work will be presented during the Hanoi conference 2011.

## The Influence of Flow Patterns and Recharge Sources on Groundwater Arsenic Concentrations in Van Phuc, Vietnam

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The village of Van Phuc, Vietnam offers a unique opportunity to study the influence of groundwater flow patterns on arsenic concentrations. Van Phuc is located 15km south of Hanoi within a meander bend of the Red River. Groundwater arsenic concentrations range from <10 to ~500 ug/L in local wells, with a distinct spatial pattern existing in the distribution of arsenic concentrations. The wells high in arsenic primarily tap grey sandy aquifers along the riverbank whereas most of the wells low in arsenic are associated with orange sands located further inland. With three sides of Van Phuc bounded by the Red River, the setting is well suited to hydrogeologic characterization. To this end we have recorded river stage and groundwater heads from a network of wells.

Using these data, in conjunction with logs of aquifer lithology we constructed and calibrated a transient, three-dimensional groundwater flow and solute transport model. Oscillating river stage forces groundwater flow on two time-scales, tidal and seasonal, and the recorded aquifer response on both time-scales enables more accurate calibration of the model than either time-scale alone. River water recharges the aquifer as the river rises from its annual low stage to its peak stage and aquifer water discharges to the river as the river falls from its peak stage. Modeled movement of recharge through the aquifer indicates that the region of high groundwater arsenic coincides with the area of aquifer experiencing river water inflow.

To characterize the solute load carried by inflow from the river we collected pore water samples from the riverbed during the period of rising river stage, when the river recharges the

aquifer. Although the river water is low in arsenic, pore water in the river sediments has high arsenic concentrations after flowing through less than a meter of sediment, with the highest measurement of 825 ug/L surpassing any measurement from the aquifer. These high concentrations of dissolved arsenic in recharge from the river could explain the high arsenic concentrations found in wells, although the solute load carried by the river water likely continues to react with aquifer sediment as it is transported through the aquifer.

These findings are important from a groundwater management perspective. Groundwater withdrawal to supply Hanoi creates northward flow in Van Phuc, potentially drawing high-arsenic water originating from river inflow into the low-arsenic areas of the aquifer. The effect of Hanoi pumping on the net movement of river recharge is crucial to determining the future migration of arsenic contamination within Van Phuc, and more generally areas with juxtaposed high and low As groundwater. Current modeling is directed towards answering this question and determining if areas of Van Phuc currently low in arsenic are vulnerable to future contamination.

## Defining the controlling factors of organic carbon and iron (hydr)oxide reactivity on arsenic release in Mekong Delta sediments

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Drinking of arsenic-contaminated groundwater has led to the chronic poisoning of tens of millions of people throughout the large deltas of S/SE Asia. Under the anaerobic conditions of these deltaic sediments, microbially driven oxidation of organic carbon coupled to the dissimilatory reductive dissolution of arsenic-bearing iron (hydr)oxides causes the transfer of arsenic from the solid to the aqueous phase. The reactivity and quantity of organic carbon and arsenic-bearing iron (hydr)oxides dictate the rate of arsenic release from soil/sediment to pore-water. Methods exist for quantifying the reactivity of iron (hydr)oxides, although they have been applied sparingly for predicting arsenic release; however, no widely-accepted method exists for quantifying organic carbon reactivity. Moreover, methods are lacking for measuring the reactivity of organic carbon and arsenic in the field. Here we developed proxies for the reactivity of organic carbon and arsenic in Mekong Delta sediments in Cambodia. The reactivity of organic carbon and As-bearing iron (hydr)oxides were examined along two contrasting sediment profiles: 1) a (near) permanently flooded wetland having sustained anaerobic conditions with co-burial of organic carbon and arsenic bearing sediment and 2) a seasonally flooded wetland experiencing aerobic-anaerobic cycles and less carbon input [1]. Samples were retrieved through successive excavation from the surface to 12 m depth. Incubations of fresh sediment with sterile, anoxic groundwater medium (pH 7.1) were initiated in the field immediately upon sediment collection under nitrogen atmosphere. Prior to sediment addition, eleven treatment additions to the groundwater medium were performed in triplicate: 0.1, 1, and 10 mM glucose, 6.67 mM lactate + 10 mM acetate + 10 mM ethanol, 0.035 and 0.35% Fe<sup>3+</sup> (w/w) (as As-loaded goethite), 3.5% Fe<sup>3+</sup> (both as As-loaded goethite and as As-loaded

Al-substituted ferrihydrite), 10 mM glucose + As-loaded goethite (3.5% Fe<sup>3+</sup>), 10mM glucose + As-loaded Al-substituted ferrihydrite (3.5% Fe<sup>3+</sup>), and no amendment. Each of the eleven treatments had an abiotic counterpart achieved by antibiotic addition. Iron (hydr)oxide addition alone did not stimulate arsenic or iron(II) release at both sites (Figure 1). In contrast, high rates of organic carbon (e.g., glucose) alone increased aqueous arsenic and iron(II) concentrations, suggesting organic matter reactivity governs the arsenic release rate in these sediments. The addition of organic carbon and iron hydr(oxides) together released iron(II), but not arsenic, suggesting the added iron (hydr)oxides sequestered any liberated arsenic. We then couple the incubations with detailed chemical (spectroscopic and microscopic) analysis of the As-bearing iron (hydr)oxides and organic matter. Collectively, these measurements allow parameterization of key sediment reactivity essential for spatial and temporal prediction of arsenic fate.

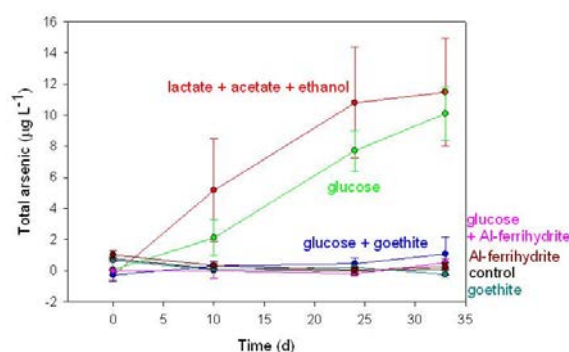


Figure 1. Arsenic release ( $\mu\text{g L}^{-1}$  per gram dry sediment) from inner wetland sediment at a 10 cm depth as a function of time in response to various organic carbon and iron(hydr)oxide treatments.

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## On organic matter reactivity and sediment age as controls on the groundwater arsenic concentration- Part 1

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In the Dan Phuong area, a transect of groundwater sampling wells was installed extending from very young sediments close to the river [1] to older sediments at the floodplain margin. Near the river, the groundwater arsenic concentration was up to 6  $\mu\text{M}$  while near the floodplain margin the As concentration decreased to less than 2  $\mu\text{M}$ . The reactivity of sedimentary organic matter was determined by radiotracer methods as the rate of methanogenesis by both reduction of  $\text{CO}_2$  and fermentation of acetate.  $\text{CO}_2$  reduction was found to be the far dominant process with rates of up to 3 mM C/yr near the river, decreasing to about 0.15 mM C/yr near the floodplain margin. Also determined by radiotracer method was the rate of acetate oxidation which in the absence of sulfate, nitrate or  $\text{O}_2$  is a good indicator for the rate of Fe(III) reduction. The rates are again highest near the river, up to 0.13 mM C/yr decreasing 0.03 mM C/yr at the floodplain margin. Clearly the groundwater arsenic concentration is correlated to the reactivity of the organic matter.

At each location, sediment leaching experiments were carried out to determine the speciation of iron and arsenic in sediments. The extractants were 0.5M  $\text{NaHCO}_3$  at pH 8.5, 10 mM Ascorbic acid at pH 3, HCl at pH 3 and 0.2M  $\text{NH}_4$ -oxalate buffer + 0.1M ascorbic acid, pH 3.  $\text{NaHCO}_3$  releases adsorbed Fe but is insignificant. Ascorbic acid reduces ferrihydrite, lepidocrocite and poorly crystalline goethite, while ascorbate+oxalate also reductively dissolve stable Fe-oxides like hematite and well crystalline goethite. HCl at pH 3 mobilizes easily dissolvable phases like siderite and vivianite [2]. The extractions were done in parallel. Most Fe is extracted by ascorbate+oxalate and the lowest concentration is found near the floodplain margin. Near the

river the sediment still contains ascorbate reducible Fe, not dissolvable in HCl, as was also found in the river mud [2]. Further inland, the two fractions become equal indicating the formation of a Fe(II) phase and complete removal of easily reducible Fe(III).

Overall, the sediment arsenic content decreases strongly going from the river to the floodplain margin. Most sedimentary arsenic is associated with well crystalline Fe-oxides like hematite and goethite that can be reduced by ascorbate+oxalate but not by ascorbate alone. Again the HCl extractable As is considered to be present in carbonates, phosphate or other easily dissolved phases. Near the river, the HCl extractable As is significantly lower than ascorbate As indicating some As to be present in reactive Fe-oxides. However, further inward, the two fractions are the same, suggesting the absence of As in a easily reducible phase, and presence of a large fraction of reduced As in a easily dissolved phase.

Going from the river to the floodplain margin the groundwater arsenic content decreases as the organic matter reactivity decreases together with Fe-oxide bound arsenic. An intermediate Fe(II)-As(III) phase accumulates but is eventually also leached out.

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## Part 2 of - On organic matter reactivity and sediment age as controls on the groundwater arsenic concentration - modelling

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As described in part 1 [1] of this contribution, data have been gathered from very young sediments close to the Red River [1] to older sediments at the floodplain margin. The purpose of the modeling presented here is to try and combine the observations presented and discussed in part 1 [1]. The observations comprise vertical profiles of groundwater chemistry, point information on sediment chemistry and rates of methane production and acetate oxidation as well as sediment and groundwater ages and the implied flow rates. Three separate 1D models over depth, are set up for the three sites described in part 1 [1]. The models attempt to describe the observed changes in groundwater chemistry occurring as the water moves forward and downward in the aquifer. Since the observations are from the saturated zone where flow is not vertical, the 1D approach implies the assumption that infiltrating water chemistry is constant in time and upstream of the observation point and that variations in sediment chemistry are found as homogenous layers upstream of the observation point. Given the land use and erratic nature of the sedimentation in a meandering river system this is certainly a simplification.

A 1D model for the site nearest to the river has been published [2], however in order to have a consistent set of models the data was remodeled as described below. Constant rates of the organic matter oxidation and compositions and stabilities of the included minerals are used for a given layer. Because the modeling described in [2], of the presumably most dynamic site indicated that sorption processes were not so important for the As distribution, they are not included in the modeling presented here, which all in all implies that the models represent a quasi-steady-state of the three systems.

The inputs used in the 1D models derived from the observations are : a flushing solution, that is a modified version of a solution from the top of the measured vertical groundwater chemical profile and an Fe:As:P ratio for the Fe-oxide being reduced, thereby releasing the As. The As/Fe ratio is derived from the ascorbate + oxalate sediment extracts presented in [1]. The parameters used to fit the models are: the rate of organic matter oxidation at a given depth, the C:N:P ratio of the organic matter, the Fe:P ration and solubility of the Fe-oxide and the saturation index of minerals that speciation calculations on the groundwater chemistry have indicated as being relevant. The minerals used are the As and P bearing Fe-oxide, calcite, siderite, Fe-sulfide, MnHPO<sub>4</sub>, and vivianite. The specified saturation indexes, work as chemical boundary conditions, constraining how the model chemistry develops over depth. Still, the system is very sensitive to e.g. the rate of organic matter oxidation and the solubility of the Fe-oxide. In fitting the models, the As concentration was used as a primary goal because this, in the setup, with a constant As/Fe ratio of the Fe-oxide and no sorption, tracks the amount Fe-oxide reduction. The fitted rate of organic matter oxidation, compares favorably with the directly measured rates of methane production and acetate oxidation.

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## Characteristics of an arsenic “hot spot” with anomalously high phosphate and dissolved organic carbon in Bangladesh groundwater

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Shaharasti is one of half-dozen upazillas in Bangladesh where, according to BGS/DPHE data, the average As concentrations in groundwater range between 200 and 500 µg/L and the average phosphate content exceeds 2 mg/L P. The proportion of villagers with lesions attributable to As is also particularly high in Shaharasti; the area was therefore selected for a vitamin E and Se supplementation trial to mitigate the effects of past As exposure. As part of this intervention, UNICEF provided several thousand household-level As removal systems because there were initially no low-As wells in the area. In 2008, the Alcan and Read-F filters were found to be generally effective several months after deployment (effluent  $\leq 50$  µg/L in 54 out of a subset of 58 sampled units), a high proportion of SONO filters did not perform, even after proper re-installation in 2009 (effluent  $> 50$  µg/L in 17 out of 49 units). The elevated P content of influent water ( $3.3 \pm 1.4$  mg/L P;  $n=49$ ) may contribute to the poor performance of the SONO filters, but the influent water contained even more extreme concentrations of dissolved organic carbon that could have inhibited As removal (DOC  $45 \pm 5$  mg/L;  $n=49$ ).

We returned to the area to collect sediment and install a nest of monitoring wells in December 2010. We were relieved to find that deep ( $> 200$  m) low-As community wells had been installed in many affected villages since our previous visit and that they seemed to be used for drinking and cooking by all surrounding households. Three months into the dry season, a striking feature of the area was the concentration of filled ponds and standing water in many of the surrounding fields. The suggestion of impeded drainage due to the low permeability of local sediment was confirmed

by drilling. The upper 40 m were dominated by silt and clay, with only 4 intervals of grey sand totaling 15 m in thickness. Concentrations of As were the highest in the shallowest sand interval tapped by two monitoring wells (740-750 µg/L at 10-15 m) and, unfortunately, also by surrounding household wells ( $740 \pm 190$  µg/L As;  $n=8$ ). Although Fe and P concentrations in shallow groundwater were also elevated, they were actually highest in a deeper grey sand interval where the As concentration was somewhat lower (5.2 mg/L, 6.0 mg/L, and 270 µg/L for Fe, P, and As, at 33 m respectively). The pronounced yellow color of the groundwater was consistent with high DOC levels.

Total concentrations of As in the sands measured by X-ray fluorescence ranged from 1-3 mg/kg, about half of which was extractable with 24 hours in 1 M phosphate at pH 5. Batch adsorption experiments set up in the field in a glove-bag flushed with N<sub>2</sub> using fresh sediment cores and ambient groundwater pumped from the monitoring wells indicate K<sub>d</sub>'s of 1-2 L/kg after 30 days, and little saturation at groundwater concentration up to 10,000 µg/L. Synchrotron X-ray spectroscopy of sediment preserved in glycerol right after collection indicates a predominance of As-sulfides ( $65 \pm 10\%$ ;  $n=3$ ) relative to adsorbed As(III;  $23 \pm 1\%$ ) or As(V;  $12 \pm 3\%$ ), despite low dissolved S concentrations in groundwater within the shallowest, high-As aquifer ( $0.15 \pm 0.03$  mg/L;  $n=10$ ). Whereas the local stratigraphy and DOC are unusual, our results don't as of yet indicate any obvious feature that unambiguously explain the origin of this “hot spot” in groundwater As. <sup>3</sup>H-<sup>3</sup>He and <sup>14</sup>C sampling of the site is scheduled for late April 2011.

## Phosphorus interference in colorimetric determination of arsenic in environmental samples

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Spectrophotometry has become the standard method for arsenic (As) determination because of its simplicity, precision, and low cost. The well-known ascorbic acid method by Murphy and Riley initially developed to measure phosphorus (P) in water has been modified over the years to measure soluble As concentrations in aqueous systems. However, phosphorus pentoxide ( $P_2O_5$ ) forms blue-colored compounds with molybdenum and therefore, can significantly interfere As ( $As_2O_5$ ) measurement. For As measurement, arsenic pentoxide is much more easily reduced than phosphorus pentoxide and thus it is possible to eliminate the influence of arsenic in the determination of phosphorus, but not vice versa. Consequently, the methods given in the previous papers can be used for the determination of arsenic only in solutions free from phosphorus pentoxide.

Recently, the malachite green spectrophotometric method has recently been used to determine phosphorus concentrations in water and soil solutions. This method has several advantages over the widely used ascorbic acid method developed by Murphy and Riley due to its sensitivity, and stability upon changes in heating, reagent addition or reaction time. It is proposed that if As (III) and As (V) do not form blue colored compounds with the malachite green dye, the As content in solution can be determined by the difference between the mixed (As+P) absorbance in the ascorbic method and the color absorbance in the malachite green method. The objective of this study was to

investigate the interference of P in colorimetric methods for accurate determination of As in aqueous systems.

Arsenic (V) solutions were prepared from  $Na_2HAsO_4 \cdot 7H_2O$ . These As solutions were further spiked with different amounts of P ranging from 0.1 to 5 ppm. The As concentration in samples determined by ascorbic and malachite green methods were compared with As concentrations analysed by inductively-coupled plasma mass-spectrometry (ICP-MS) (detection limit of As at < 1 ppm). The results showed that the interference of P occurred in samples with P concentration greater than 0.5 ppm. It therefore can be concluded that the use of malachite green methods did not overcome the P interference when determining As in samples with high P concentration.

## The application of Fe-Mn binary oxide (FMBO) in the system of micro-flocculation and filtration for arsenic removal in groundwater

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Bivalent iron (Fe(II)) and bivalent manganese (Mn(II)) anions are often present along with arsenic (As) in groundwater [1]. Additionally, the Fe removal systems in waterworks can be used to remove As from drinking water, which are also correlated with the two primary removal mechanisms of adsorption and coprecipitation [2]. Previous studies also indicate that As removal during Fe hydroxide precipitation is directly correlated with the total Fe concentrations and the oxidation of arsenite (As(III)). In order to enhance the As removal efficiency, chemical agents such as Fe salts and oxidants were added into the Fe removal system to increase the Fe concentrations and enhance the oxidation of As(III). However, little data exist on the capability of As removal in pilot-scale or full-scale applications to reduce As on a sustained basis with the addition of chemical agents.

In this pilot-scale study ( $Q=48 \text{ m}^3/\text{d}$ ,  $V=10 \text{ m}^3$ ), in-situ formed Fe-Mn binary oxide (FMBO), which has both oxidative and adsorptive capabilities [3], was added into the system of micro-flocculation and filtration (backwashed every 48 h) to evaluate the improvements of As removal and other water characteristics. The results showed that the As removal was enhanced considerably by adding FMBO. With the average As concentration of about  $40 \mu\text{g/L}$  in the effluent, the As(tot) concentrations ranged from  $12.8$  to  $23.2 \mu\text{g/L}$  in the effluent without the addition of FMBO. After in-situ formed FMBO was added, the average effluent As(tot) concentration decreased to approximate  $6 \mu\text{g/L}$ . On the other side, it is noticeable that the FMBO addition also improved other water characteristics. The average Fe concentration decreased from  $0.17 \text{ mg/L}$  to  $0.07 \text{ mg/L}$ , and the average Mn

concentration decreased  $0.06 \text{ mg/L}$  to and  $0.01 \text{ mg/L}$ , respectively. It may be due to the species changes of Fe/Mn elements in the groundwater. Though the enhancement of turbidity removal was not obvious after adding FMBO, the micro-particle numbers in the effluent were sharply decreased. Furthermore, based on the results of pilot-scale study, demonstration engineering facilities were set up and put into operation to remove As in a groundwater plant. The treatment capability has achieved to be as high as  $200,000 \text{ m}^3/\text{d}$ , and the effluent As concentration was consistently less than  $10 \mu\text{g/L}$ .

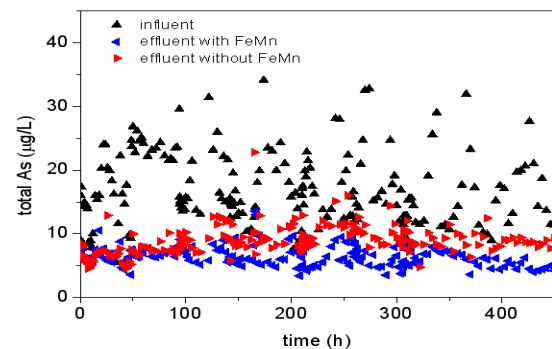


Figure 1. the effluent As concentrations in the demonstration engineering operation

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**Installation of well screen at the Van Coc site of the School Transect of the VietAS project.** After the borehole has been made by water jetting, the hole is open for a very short time due to a very thin mud cake formed by the natural clay content of the Red River sediments. Because the time is so short, the entire screen and casing is assembled into one long string, which is then rapidly inserted immediately after the water jetting equipment has been retracted. Critical as it is – everyone around participates on the ground, in the trees and on the wall. Wells down to >40 meters can be screened and cased in this fashion.