



## **AGU Chapman Conference on Arsenic in Groundwater of Southern Asia**

**Siem Reap, Cambodia  
24–27 March 2009**

### **Conveners**

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- Scott Fendorf, Environmental Earth System Science, Stanford University, Stanford, California, USA, e-mail (fendorf@stanford.edu)

### **Co-Host**

The conveners and planning committee wish to thank the Royal Government of Cambodia, Ministry of Rural Development for their support of this Chapman conference.

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### Local Organizers

- Jan Willem Rosenboom, Water and Sanitation Program, World Bank, Phnom Penh, Cambodia, email (jrosenboom@worldbank.org)
- Mickey Sampson, Resource Development International, (Kean Svay, Kandal, Cambodia), email (mickey@rdic.org)

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Siem Reap, Cambodia  
24 – 27 March 2009**

**MEETING AT A GLANCE**

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**Monday, 23 March 2009**

0700h – 1400h	Pre-Conference Field Trip to Kandal Province
1600h – 1700h	Registration
1700h – 1900h	Ice Breaker Reception

**Tuesday, 24 March 2009**

0530h – 0830h	Buffet Breakfast ♦ Grandview Coffeehouse
0830h – 0900h	Opening Remarks
0900h	Session I
	Lunch ♦ Grandview Coffeehouse
	Dinner (On your own)
1900h	Poster Presentations
2000h	Oral Presentation
	Discussion and selection of posters

**Wednesday, 25 March 2009**

0530h – 0830h	Buffet Breakfast ♦ Grandview Coffeehouse
	Lunch
0700h – 1400h	<b>FREE TIME</b>
	Lunch ♦ Grandview Coffeehouse
1400h	Session II
	Dinner (On your own)
1900h	Poster Presentations
2000h	Oral Presentation
	Discussion and selection of posters

**Thursday, 26 March 2009**

0530h – 0830h	Buffet Breakfast ♦ Grandview Coffeehouse
	Session III
	Lunch ♦ Grandview Coffeehouse
	Dinner (On your own)
1900h	Poster Presentation
2000h	Discussion and selection of posters

**Friday, 27 March 2009**

0530h – 0830h	Buffet Breakfast ♦ Grandview Coffeehouse
	Session IV
	Lunch ♦ Grandview Coffeehouse
	Round Table Discussion
1800h	Press Conference
2000h	Buffet Dinner ♦ Poolside, Grandview Coffeehouse

# Program Overview

Sessions and events will take place at the Angkor Century Resort and Spa, Siem Reap, Cambodia. The Registration/Information Desk will be in the Lotus Ballroom foyer throughout the conference.

## MONDAY, 23 MARCH 2009

- 0700h – 1400h      Pre-Conference Field Trip – Kandal Province, Phnom Penh
- 1600h – 1700h      Registration ♦ Lotus Ballroom Foyer
- 1700h – 1900h      Welcome Reception ♦ Lotus Ballroom

## TUESDAY, 24 MARCH 2009

- 0530h – 0830h      Breakfast Buffet ♦ Grandview Coffeehouse
- 0830h – 0900h      Opening Remarks **JW Rosenboom, M Sampson**
- 0900h                **Session I – Biogeochemistry** ♦ Lotus Ballroom
- J Lloyd** *The Microbial Ecology of Arsenic Mobilizing Aquifer Sediments*
- Coffee Break ♦ Lotus Ballroom
- D Postma** *Mobilization of Arsenic and Iron from Red River Floodplain Sediments, Vietnam*
- B Bostick, B. Kocar** *Impacts of sulfur biogeochemistry on arsenic fate and transport in South/Southeast Asian Aquifers*
- Lunch ♦ Grandview Coffeehouse
- Dinner (On your own)
- 1900h                **Poster Presentations** ♦ Lotus Ballroom
- 2000h                **G Breit** *The geologic context of biogeochemical processes affecting arsenic in South Asia*
- J Hering** – Discussion and Selection of Posters

**WEDNESDAY, 25 MARCH 2009**

0530h – 0830h      Breakfast Buffet ♦ Grandview Coffeehouse

**0700-1400h      FREE TIME**

Lunch ♦ Grandview Coffeehouse

1400h      **Session II – Hydrogeology** ♦ Lotus Ballroom

**C Harvey** *Ponds, Fields, and Rivers - Sources of Water and Solute Loads to Aquifers in the Ganges Delta*

**M Stute** *Environmental Tracer Applications in Floodplain Aquifers with Elevated Arsenic Concentrations*

Coffee Break ♦ Lotus Ballroom

**S Benner** *Hydrologic Constraints on Arsenic Behavior, Observations From a Field Site in Cambodia*

**F Larsen** *Geological and Hydrogeological Processes Affecting the Distribution of Arsenic Ground Water Concentrations in Holocene and Pleistocene Aquifers in the Red River Flood Plain, Vietnam.*

Dinner (On your own)

1900h      **Poster Presentations**

2000h      **R Beckie** *The geochemistry of high- and low-arsenic groundwaters and their association with an in-filled abandoned channel at a Field Site in Gotra, Nadia District, West Bengal, India*

**W Burgess** – Discussion and selection of posters

**THURSDAY, 26 MARCH 2009**

0530h – 0830h      Breakfast Buffet ♦ Grandview Coffeehouse

0900h      **Session III – Vulnerability of low-As aquifers** ♦ Lotus Ballroom

**H Michael** *Is Deep Groundwater a Sustainable Source of Arsenic-Safe Water in the Bengal Basin? Management Insights from a Regional Modeling Analysis*

**Y Zheng** *Equilibrium and Kinetics of As Sorption to Bangladesh Gray and Orange Sediments Determined by Batch Experiments*

Coffee Break ♦ Lotus Ballroom

**D McKnight** *Reduced Humic Substances Promote Iron Reduction and Mobilization of Arsenic in Aquifers in Bangladesh*

**D Polya** *Arsenic mobilization into shallow groundwaters of southern Asia? where, when and why does it occur - evidence from organic, isotopic and bio- geochemistry*

Lunch ♦ Grandview Coffeehouse

Dinner (On your own)

1900h **Poster Presentations** ♦ Lotus Ballroom

2000h **S Fendorf, A van Geen** – Consensus

Discussion and selection of posters

<b>FRIDAY, 27 MARCH 2009</b>
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0530h – 0830h Breakfast Buffet ♦ Grandview Coffeehouse

0900h **Session IV – Open Questions and Mitigation** ♦ Lotus Ballroom

**A van Geen, S Fendorf** – Future Experiments

**KM Ahmed** *Groundwater Arsenic Occurrences in Bangladesh: Options for Management and Mitigation*

**M Berg, S Hug** *Predicting Groundwater Arsenic Contamination in Southeast Asia from Surface Parameters and from Geology at Depth*

Lunch ♦ Grandview Coffeehouse

1400h **A Smith** *Arsenic in Drinking Water Results in the Highest Known Toxic Substance Disease Risks*

**M Sampson** *Incomplete Arsenic-Removal by Iron-Amended BioSand Filters in Kandal Province, Cambodia*

**Round Table Discussion:** Drinking water options  
Discussion leader: **J W Rosenboom**

1800h **Press Conference** ♦ Lotus Ballroom

2000h Buffet Dinner ♦ Poolside, Grandview Coffeehouse

## Abstracts

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### **Groundwater Arsenic Occurrences in Bangladesh: Options for Management and Mitigation**

[\*K M Ahmed\*] (Department of Geology, University of Dhaka, Dhaka 1000, Bangladesh. ph:+880-2-9661920 Ex.7316; fax: +880-2-8615583; email: kmahmed@univdhaka.edu, kazimatin@yahoo.com)

Wide spread occurrences of arsenic in groundwater above the allowable limit for drinking water has emerged as a major public health issue in Bangladesh. The extent of the problem is severe in Bangladesh as many million people have been exposed to arsenic above the allowable limit. Intake through food chain has also been considered another major area of concern. Management of arsenic disaster in Bangladesh is a major challenge in the field of water supply, sanitation and irrigation. Current estimates show that about one third of the country's domestic drinking wells yield water above the Bangladesh national drinking water limit whereas more than half of the wells exceed the World Health Organisation provisional guideline value. Efforts have been made to manage the problem since its detection in 1993. However, the pace of mitigation is slow compared to the magnitude of the problem. There various different options for managing the problem. While planning arsenic management strategy, both drinking and irrigation water should be considered though the potable water warrants the top priority. It has been found in various parts of the country that arsenic safe groundwater can be abstracted from various depths if well sitting is done based on based on certain geological and hydrogeological criteria. Existing well testing data can also provide guidelines in delineating the safe depths. In general

there are safe aquifers at depths almost all over the country. However, there are certain constraints for deep groundwater development in specific geological provinces of the country. Current arsenic mitigation plan of the Government of Bangladesh puts emphasis on certain options without proper scientific validation. The current mitigation strategy needs to be revised giving emphasis on the options which are safe and sustainable. While doing this a review of the arsenic occurrence, distribution and mitigation is necessary in order to modify the action plan. The paper will present a review of the current situation and knowledge base and outline a revised mitigation strategy for sustainable management of water supply in Bangladesh.

### **Variability in Dissolved Arsenic in Shallow Aquifers Linked to Local Hydrology**

[\*Z Aziz\*] (Lamont-Doherty Earth Observatory of Columbia University, Palisades, NY 10964, USA, ph. +1-845-365-8412; fax +1-845-365-8154; e-mail: aziz@ldeo.columbia.edu); A. van Geen (avangeen@ldeo.columbia.edu); M. Stute (martins@ldeo.columbia.edu); B.C. Bostick (Benjamin.C.Bostick@dartmouth.edu); M.W. Rahman (mwrahman2002@yahoo.com); M. M. Rahman (moshiur\_848@yahoo.com); M.R. Huq (rezaul\_md@yahoo.com); K M Ahmed (Department of Geology, University of Dhaka, Dhaka 1000, Bangladesh; ph. +880-2-966-1920 Ext. 7316; fax +880-2-861-5583; e-mail: kazimatin@yahoo.com)

Time series of groundwater composition have shown that concentrations of As in groundwater of Bangladesh are by and large remarkably constant despite large seasonal variations in groundwater and river levels. Some temporal variations might be expected in particularly shallow aquifers, however, based on recent studies showing that local recharge can play a role in setting the spatial distribution of As. To explore the complex interactions between dissolved As levels in shallow aquifers and recharge, nests of three very shallow (6-9 m deep) monitoring wells were monitored bi-weekly over 2 years in three contrasting areas of Arai-hazar, Bangladesh. At control site Z, no vertical or temporal changes in groundwater chemistry or hydrology were recorded over the entire monitoring period: Eh ( $29 \pm 38$  mV), SO<sub>4</sub> ( $6 \pm 5$  mg/L), Cl ( $24 \pm 7$  mg/L), P ( $158 \pm 32$  ug/L), As ( $26 \pm 4$  ug/L) in the shallowest well and Eh ( $22 \pm 42$  mV), SO<sub>4</sub> ( $1 \pm 1$  mg/L), Cl ( $22 \pm 4$  mg/L), P ( $98 \pm 65$  ug/L), As ( $12 \pm 3$  ug/L) in the deepest well.

At Site X, a strong vertical gradient in redox conditions and groundwater composition between the shallowest and deepest well is indicated by Eh ( $+134 \pm 64$  mV vs.  $-4 \pm 43$  mV,  $n=50$ ), P ( $47 \pm 38$  vs.  $1153 \pm 130$  ug/L,  $n=50$ ), As ( $3 \pm 1$  vs.  $230 \pm 24$  ug/L,  $n=50$ ), SO<sub>4</sub> ( $160 \pm 54$  vs.  $9 \pm 8$  mg/L,  $n=50$ ), and Cl concentrations ( $267 \pm 54$  vs.  $60 \pm 14$  mg/L,  $n=50$ ). Whereas the composition of groundwater at the shallowest and deepest well remained relatively constant over two years, considerably larger seasonal fluctuations were observed at the intermediate well (7.6 m):  $44 \pm 52$  mV in Eh,  $112 \pm 65$  mg/L in SO<sub>4</sub>,  $196 \pm 93$  mg/L in Cl,  $691 \pm 374$  ug/L in P, and  $15 \pm 11$  ug/L in As. Hydraulic head measurements indicate that these changes reflect a combination of changes in the direction of groundwater flow and mixing of groundwater from above and below 7.6 m depth. A non-conservative behavior of arsenic relative to its structural analogue phosphate, and the presence of arsenic

sulfides in the solid phase at this depth suggest that dissolved As is sequestered in sediments by the reduction of arsenate to arsenite followed by precipitation as arsenic sulfides in the presence of reduced sulfur. In this setting, the sequestration of As at the intermediate well significantly dampen seasonal variations that would be expected based on changes in groundwater level alone.

At Site Y, no sharp vertical gradient in aquifer properties was observed and neither were there any significant fluctuations in groundwater properties driven by the monsoon over the two year period: Eh ( $-8 \pm 35$  mV), SO<sub>4</sub> ( $85 \pm 54$  mg/L), Cl ( $115 \pm 55$  mg/L), P ( $994 \pm 102$  ug/L), As ( $45 \pm 7$  ug/L) in the shallowest well and Eh ( $-7 \pm 34$  mV), SO<sub>4</sub> ( $44 \pm 16$  mg/L), Cl ( $81 \pm 35$  mg/L), P ( $137 \pm 44$  ug/L), As ( $25 \pm 4$  ug/L) at the deepest well. However, the time series show a gradual decline of  $\sim 5$  ug/L per year in average As over the entire period at all depths. Relative hydraulic heads between sites Y and control Site Z and a broad trend of increasing downward hydraulic gradients at site Y parallel the declining average As. This suggests an enhancement of vertical recharge by irrigation pumping. Based on the observations at Site X, we postulate that enhanced recharge driven by irrigation pumping resulted in an enhanced supply of SO<sub>4</sub> and therefore removal of dissolved As by arsenic sulfide formation. These observations provide further evidence that recharge can occasionally drive seasonal and longer-term variations in groundwater composition including As in shallow aquifers of Bangladesh.

#### **Hydrologic Constraints on Arsenic Behavior, Observations From a Field Site in Cambodia**

[\*S.G. Benner\*] (Department of Geology, Boise State University, Boise, ID 83725, USA; sbenner@boisestate.edu; 208-426-3629; 208-426-4061); M.L. Polizzotto



(School of Earth Sciences, Stanford University, Stanford, CA 94305 USA), B.D. Kocar (School of Earth Sciences, Stanford University, Stanford, CA 94305 USA); M. Sampson (Resource Development International, Kien Svay, Kandal, Cambodia) S. Fendorf (School of Earth Sciences, Stanford University, Stanford, CA 94305 USA)

The hydrologic tools of mass balance, gradient driven flux, and flow continuity can provide rigorous constraints on arsenic behavior in groundwater. At a field site in Cambodia, where the shallow groundwater contains elevated arsenic concentrations, we have integrated these basic hydrologic tools within a numerical model to investigate the influence of groundwater flow on arsenic behavior. The dominant driver of groundwater flow at this site is hydraulic head differentials in the seasonal surface water levels of the Mekong River and the adjacent wetland systems that overlie the aquifer. While the relative elevations of these two water bodies invert semi-annually, the net annual hydraulic head gradient is from the wetlands to the river. Both the seasonal fluctuations and the net hydraulic gradient are manifested in the hydraulic head behavior for the aquifer; subsurface gradients invert seasonally and the net annual subsurface gradient is towards the river. The subsurface stratigraphy can be idealized as a two layer system, clay overlying sand, with the clay 2-10 m thick forming an aquitard overlying a sand aquifer that is approximately 60 m thick; this system extends approximately 5000 m outwards from the river. Application of the observed gradients in this flow media geometry (low hydraulic conductivity material overlying high conductivity material assembled as a long thin flow system) produces flow paths from the wetlands to the aquifer that are nearly vertical through the clay aquitard, while flow through the aquifer sands is nearly horizontal to the river. Such a flow system provides an optimal

setting for evaluating chemical changes along flow paths using vertically incremented sampling through the clay. Along these infiltration flow paths (over a 5-10 m distance), we observe universal increases in dissolved arsenic concentrations from the surface infiltrating waters ( $As < 10 \mu\text{g/L}$ ) to the aquifer ( $As > 500 \mu\text{g/L}$ ). Based on associated changes in aqueous and solid phase geochemistry, this arsenic release to the pore water is attributed to reductive dissolution of arsenic-bearing iron oxides at and below the depth of permanent saturation. In this presentation, we will discuss the uncertainties associated with this physical model, evaluate potential hydrological perturbations on this flow system and explore its relevance to arsenic behavior at other sites in Asia.

### **Predicting Groundwater Arsenic Contamination in Southeast Asia from Surface Parameters and from Geology at Depth**

[\*Michael Berg\*], Lenny Winkel, Manouchehr Amini, Stephan Hug, Annette Johnson (Eawag, Swiss Federal Institute of Aquatic Science and Technology, 8600 Dübendorf, Switzerland, michael.berg@eawag.ch); Pham Thi Kim Trang, Vi Mai Lan, Dao Manh Phu, Pham Hung Viet, Nguyen Van Dan, Nguyen Thi Ha (CETASD, Hanoi University of Science, Hanoi, Vietnam)

Arsenic contamination of groundwater resources threatens the health of millions of people worldwide, particularly in the densely populated river deltas of Southeast Asia. Although many arsenic-affected areas have been identified in recent years, a systematic evaluation of vulnerable areas remains to be carried out. In order to pinpoint untested areas at risk of groundwater arsenic concentrations, we produced a risk map by combining geological and surface soil parameters in a

logistic regression model, calibrated with 1756 aggregated and geo-referenced groundwater data points from the Bengal, Red River and Mekong deltas.

The model is based on three assumptions. First, sedimentary depositional environments are characterized by a unique combination of chemical, physical and biological properties and can serve as indicators (proxies) for chemical and physical conditions of the aquifers beneath the surface. Second, soil properties are proxies for present and past drainage conditions and they are also indicators of recent depositional environments. Third, soil textures, for example clay and silt, are proxies for the chemical maturity of the sediments, where clay is more mature than silt. An important factor in the development of soil textures is topography, which enables the delineation of areas where the model is applicable.

We show that Holocene deltaic and organic-rich surface sediments are key indicators for arsenic risk areas and that the combination of surface parameters is a successful approach to predict groundwater arsenic contamination. Predictions are in good agreement with the spatial distribution of known arsenic contamination but also indicate elevated risks in Sumatra and Myanmar where no groundwater data existed.

All the above is based on two-dimensional data (that is, surface maps). We are currently exploring avenues of three-dimensional predictions for the Red River delta, using a new set of regional geological maps at 1m depth intervals (surface to 100 m depth) in combination with As measurements from our groundwater survey of the delta area. Although, three-dimensional information could improve the performance of model, such data is generally not available at large scales and is technically difficult to be included in geostatistical modeling. Latest

results of this approach will be presented and compared with the predictions modeled entirely from surface parameters.

### **Impacts of Fluvial Geomorphic Processes on the Distribution of Groundwater Arsenic Contamination in the Mekong Delta**

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Arsenic contamination is a widespread but heterogeneous phenomenon in many large, sediment-laden deltas. Arsenic is released from sediments through the coupling of microbial decomposition of organic matter and reductive dissolution of arsenic-bearing iron minerals. In this work, we examine how fluvial processes impact the distribution of arsenic in the Mekong Delta of Cambodia. This dynamic region

changes rapidly in response to river stage, and erosion or deposition along active channels. The variation in depositional environment creates a number of unique geomorphic features, including scroll bars, avulsions, crevasse splays, and docked islands. Groundwater arsenic contamination is strongly correlated to these geomorphic features. The detailed characterization of transects of sediments, surface and ground water within these young geomorphic features suggest that they have several physical and chemical characteristics conducive to arsenic release. Organic matter quantity and quality differs in young features, as does their mineralogy. The wide variation in particle size from channel sands and gravels to fine-grained overbank deposits influences aquifer recharge and groundwater hydrology. Each of these factors impacts sediment redox chemistry, related arsenic release (or sequestration), and thus the distribution of groundwater arsenic. Such integrated approaches to identify affected areas are invaluable to identify sustainable groundwater sources in affected areas.

### **Characterizing Heterogeneity of Water-producing Sediments in the Bengal Basin – A Challenge in Assessing Aquifer Vulnerability**

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The variable composition of ground water in the Bengal Basin is partly the product of multiple depositional environments of aquifer sediments, temporally and spatially variable biogeochemical processes, and passage of water ranging from river water to sea water through the sediment. Implicit in these variations are the impacts of climate change, sea level, and more recently, human-induced land-use and hydrologic changes. Evaluation of the sustainability of ‘safe aquifers’ requires consideration of this complex framework and the implications it has for content of dissolved arsenic as well as iron, manganese, and salinity in the resulting ground water.

Within Bangladesh and West Bengal, India, potable water is produced from depths as little as a few meters to as great as 350 m; this interval is the product of more than 100,000 years of sediment deposition. Ground water from the upper 50 m of Holocene sediment varies in dissolved As, Mn, and Fe over 10s to 100s of meters. Deeper ground water (150-350 m) lacks As and varies in dissolved Fe, Mn, and TDS on the scale of a few kilometers. Such heterogeneity challenges the ability to predict the lateral uniformity of ground water within ‘aquifers’.

The distribution and abundance of arsenic in ground water in the Holocene sediment is consistent with equilibration of recently oxidized sediment buried in a chemically reducing environment. Although sediment deeper than 100 m has been suggested to be ‘flushed’ of its labile arsenic, it is more

likely that arsenic has been redistributed such that a substantial portion is retained in phases stable in the ambient geochemical environment. These environments include pyrite and other ferrous iron phases in chemically reduced sediment and crystalline ferric oxides in oxidized units. The degradation of water produced from 'safe-aquifers' can potentially result from flow of arsenic-rich water into the producing interval, and introduction of compounds that react with arsenic-containing minerals. Both mechanisms can be promoted by human induced and natural alteration of flow regimes and reactant supplies.

Laboratory experiments and field observations have shown that shallow 'safe aquifers' have a significant but finite capacity to remove arsenic and other reactants from solution. Thus, the sustainability of safe aquifers is affected by rates and volumes of ground water abstraction for domestic and irrigation purposes. Similar evaluation should be made for deep aquifers. Geochemical solute-transport modeling can be used to predict rates of 'safe aquifer' contamination; however, detailed hydrologic information is required to adequately define flow fields.

### **Processes of Arsenic Accumulation within Holocene Alluvium of Kandal Province, Cambodia: Implications for Land Use**

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Samples of ground water from Holocene sediments in the Kandal Province of Cambodia contain as much as 1000 mg/L arsenic. These high concentrations are attributed to the reductive dissolution of ferric oxyhydroxides coating detrital grains within buried sediment. Detrital organic matter is considered to be responsible for establishing reducing conditions evident in the high contents of dissolved organic carbon, ammonium and, locally, methane. In addition, ammonium in the high-arsenic ground water has δ<sup>15</sup>N values of 2.8 to 4.8 per mil, values consistent with anaerobic release of organically bound nitrogen in peat accumulations (2.3 to 3.7 per mil) within the study area.

Analyses of sediment exposed in excavations and along river banks revealed that, in addition to release from sediment, arsenic has accumulated locally in diagenetic pyrite and secondary goethite. Samples of peaty sediments contained 10 to 500 ppm arsenic; analyses of pyrite in these sediments found up to 0.6 wt.% As. In oxidized sediment, arsenic accumulates to levels of 40 to 450 ppm through assimilation into neoformed ferric oxyhydroxides. The organic-rich and oxic sediments act as natural filters capable of removing dissolved arsenic from contaminated ground water, although the rate of accumulation relative to ground water transport remains unknown.

Sediments with natural arsenic enrichments should be considered in the management of arsenic contaminated areas to minimize disruptions that might destabilize the arsenic-containing phases. Land-use change in Kandal province is evident in excavation and dispersal of peaty sediments, burial of aerated sediment, and drainage of wetlands. These modifications could result in local 'hot-

spots' of arsenic contamination even in areas with no prior arsenic contamination as arsenic-rich phases are destabilized. In addition, disruption of the natural accumulation processes could result in a sustained increase in ground water arsenic concentrations where flow paths cross the disrupted sediments.

### **Provenance and Travel Time of Groundwater Pumped from 'Arsenic-safe' Depths in the Aquifer System of Southern Bangladesh: Sources of Uncertainty and Implications for Security of Supply**

**[\*W G Burgess\*]** (Department of Earth Sciences, University College London, London WC1E 6BT, UK; ph. +44 (0) 207-679-7820; fax +44 (0) 207-387-1612; e-mail: [william.burgess@ucl.ac.uk](mailto:william.burgess@ucl.ac.uk); M A Hoque (Department of Earth Sciences, University College London, London WC1E 6BT, UK; ph. +44 (0) 207-679-2364; fax +44 (0) 207-387-1612; e-mail: [m.hoque@ucl.ac.uk](mailto:m.hoque@ucl.ac.uk))

Security, in relation to arsenic content, of groundwater pumped from depth in southern Bangladesh is a function of borehole catchment and time of travel from the recharge provenance. Borehole catchments in layered sedimentary systems are sensitive to basin geometry, hydrostratigraphy, anisotropy, sources and styles of recharge and the imposed pumping regime. Representation of these factors in models involves uncertainty on account of limitations of knowledge and data, and limitations inherent in the modeling process. These uncertainties have been investigated for a 5000 km<sup>2</sup> region of SE Bangladesh, using data from 11 petroleum exploration lithological logs to 1700 m, 600 lithological logs and 12 geophysical logs to a depth of up to 350 m, and sensitivity analysis of boundary conditions. A range of aquifer representations has been applied to a series

of models, consistent with these data. Model outcomes may be compared with independent determinations of groundwater age, and are used to demonstrate the scale of uncertainty in the implications for security of supply.

### **The Interplay of Microbiology and Nanoparticle Chemistry in Arsenic Mobilization**

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The distribution pattern of arsenic concentrations in the Ganges Delta region is heterogeneous and there are numerous As hotspots in Bengale. In this work, we examine how field work combined with microbiological, chemical and spectroscopical observation impact the distribution of arsenic in asian deltas, and demonstrates the importance of hydrogeochemical characteristics

(groundwater flow and recharge) of an aquifer in the release of As to groundwater. Our study site is located along the Hooghly River, 60 km north of Kolkata City, near the city of Chakdaha, in India West Bengale. The spatial distribution pattern of As is patchy with areas containing groundwater that is high in As ( $>200 \mu\text{g L}^{-1}$ ) found in close vicinity to low As ( $<50 \mu\text{g L}^{-1}$ ) groundwaters (within 100 m). The river Hooghly, which forms the NW boundary of the study site, shows dual behaviour (effluent and influent during pre- and post-monsoon periods, respectively), complicating the site hydrogeology. The observed groundwater flow lines tend to be deflected away from the high As portion of the aquifer, indicating that groundwater movement is very sluggish in the As-rich area. This leads to a high residence time for this groundwater package, prolonging sediment–water interaction, and hence facilitating groundwater As release.

Mn and Fe concentrations are found to fluctuate with depth. These fluctuations are shown to be, via solubility of solid carbonate phases, mostly by local  $\text{PCO}_2$ , i.e. by respiration of microorganisms such as the dissimilatory iron reductive bacteria (DIRB). We investigated DIRB dissolution of As(V) rich "ferrihydrite", and developed a biogeochemical kinetic and equilibrium model to simulate aqueous- and solid phase X-ray diffraction and X-ray absorption observations. The main conclusions drawn from the model are the following. (1) As(V) is not reduced during the first incubation month characterized by high Eh values, but rather re-adsorbed onto the ferrihydrite surface, and this state remains until arsenic reduction is energetically more favorable than iron reduction. (2) the decoupling of Fe and As release is controlled by the solubility of the nano-sized initial As-rich ferrihydrite sub particles and (3) the release of As during

the second month is due to its reduction to the more weakly adsorbed As(III) which cannot compete against carbonate ions for sorption onto ferrihydrite.

The identity of the weekly As adsorbing secondary Fe(II) rich solid phases formed in this process is the topic of an intense debate in the literature. Analysis of the As, Mn and Fe fluctuations observed with depth in our field site show groundwater to be always at equilibrium with siderite, carbonate green rust and rhodochrosite ( $\text{MnCO}_3$ ). However a separate Mössbauer spectroscopic study performed on analogue anoxic formations, shows these (and other Fe(II) rich species such as Fe(II) rich clays) to be extremely sensitive, even to exposure to air at room temperature just the time necessary to record the Mössbauer spectra. These Fe(II) rich phases are therefore systematically underestimated in mineralogical studies which do not include drilling under nitrogen and transport in liquid nitrogen, conditions seldom encountered in field studies. Therefore the accurate identification and size characterization of Fe(II) secondary phases formed in the field (phyllosilicates, magnetite, carbonate, oxycarbonate and sulfides) as well their solubility and As affinity are urgently needed in order to correctly model the widespread heterogeneity in groundwater arsenic contamination.

### **Modeling Shallow Groundwater Flow in an Arsenic-Impacted Aquifer at a Field Site in Gotra, Nadia District, West Bengal, India**

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The geological surveys of India and Canada have established a field research site in the village of Gotra, West Bengal, in order to investigate the occurrence of elevated arsenic concentrations in local groundwater. The village is located in the Bengal Delta Plain, approximately 55 km north-east of Kolkata and 17 km east of the river Hooghly. It is situated on a natural levee forming the northeastern, concave, bank of an arcuate abandoned river channel which has been dammed into a string of small ponds. Another series of ponds, excavated for building material, borders the village to the northeast where the levee gives way to lower-lying ground used for vegetable and rice cultivation.

The site is relatively unique in that repeated surveys of groundwater chemistry in domestic wells have revealed a sharply-defined zone of high arsenic, approximately 80m wide, extending sub-parallel to the trend of the abandoned channel. The zone is characterized by highly reducing conditions with elevated alkalinity, iron, ammonium and phosphate. The purpose of the groundwater modeling exercise is to establish a sound hydrogeological framework for interpreting this geochemical pattern. More specifically, modeling is used to determine the hydrogeological significance of contrasting pond types (abandoned

channel versus excavated) as sources of aquifer recharge, and to assess their potential as sources of organic carbon driving the reductive process associated with high arsenic concentrations.

Based on subsurface information from 17 boreholes and surface geomorphology, the shallow geology of the site is interpreted as a meander-belt fluvial fining-upwards sequence approximately 25m thick overlying undifferentiated alluvial deposits. The sequence consists of grey, fining-upward, point-bar sands capped by oxidized, silty levee or crevasse splay deposits and a soil layer. The point bar sands are the shallowest permeable unit and they represent the aquifer most commonly tapped by villagers for domestic purposes. Hydraulic conductivities, measured by slug tests, are in the range of  $5E-04$  m/s. Silty levee deposits form a leaky confining layer over the northeastern portion of the study area. However, towards the abandoned channel, the point-bar sands thin as overlying, low-conductivity ( $K = 9E-08$  m/s) channel-fill deposits thicken. These deposits, which consist of dark, organic-rich, clayey silts, form an asymmetric plug in cross-section, and reach a maximum thickness of 22m in the thalweg of the abandoned channel. The highest observed groundwater arsenic concentrations ( $500 \mu\text{g/L}$ ) are encountered in the aquifer adjacent to the string of ponds that mark the final course of the abandoned channel.

A conceptual model of the shallow groundwater flow system is developed from the hydrostratigraphy and hydrographs obtained from a network of instrumented piezometers. It is implemented in a transient, 3D numerical (MODFLOW) model calibrated to piezometric data and constrained by mass balance calculations and lines of evidence from conservative tracers and stable isotopes. The model is designed with a discretization grid appropriate for

investigating the relatively short-scale and shallow flow paths in the aquifer affected by arsenic contamination. It provides an internally-consistent, quantitative, hydrogeological context for interpreting the observed geochemical front in light of seasonal variations in the groundwater flow regime and the effects of irrigation pumping. Results of the modeling study show that not all ponds are equal as sources of recharge and organic carbon, despite similarities in their water chemistry. Although high-arsenic groundwaters were recharged in ponds, the source of organic carbon is demonstrated to be in the underlying channel-fill sediments.

**The geochemistry of high- and low-arsenic groundwaters and their association with an in-filled abandoned channel at a Field Site in Gotra, Nadia District, West Bengal, India**

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Since 2004, the Geological Surveys of India and Canada in collaboration with the

University of British Columbia have been investigating naturally occurring arsenic in groundwater at a field site near the village of Gotra, West Bengal, India. The site is located in a classical fluvial-deltaic depositional environment and with an in-filled abandoned channel located between relatively low permeability flood-plain deposits to the south and west and higher permeability point-bar deposits to the north and east. The distinguishing feature of the site is that groundwater with high concentrations of arsenic (> 50 ppb) is found in the aquifer below and proximal to the in-filled channel and is separated by a sharp transition zone of less than 30 m width from groundwater with lower concentrations of arsenic to the north and east. Shallow wells completed in the low-permeability soft, gray silty-clay channel fill within 5 m from the edge of a pond show unambiguously that the arsenic is released within the channel fill and is moving vertically downward into the aquifer sands where most domestic wells are completed. Water proximal to another pond away from the channel is not associated with high arsenic. All geochemical indicators point to organic-matter driven reductive release processes. Indeed, groundwater with high arsenic is associated with high phosphate, low sulfate, high ammonia, high alkalinity, abundant methane, high dissolved organic carbon and PCO<sub>2</sub> between 10-1.2 and 10-0.7 bars. The degree of super-saturation with respect to vivianite and siderite increases with arsenic concentration. Sediments contained solid-phase arsenic concentrations of 1 to several ppm As in sandy zones up to 20 ppm As in finer-grained channel material. In vertical profiles, sediment arsenic peaks did not coincide with dissolved-arsenic peaks although the highest dissolved and sediment arsenic was observed near the surface. The sediment geochemistry showed that solid-phase arsenic was strongly correlated with solid-phase iron, manganese and the metals copper, nickel,



chromium and to a slightly lesser extent zinc. The correlation was stronger in the low-dissolved-arsenic zone than in the high-dissolved-arsenic zone. There was a poor correlation between solid-phase arsenic and sulfur, although any correlation could have been masked by the high solid-phase sulfur detection limits.

### **Estimating Long-Term Trends of Arsenic Accumulation in Irrigated Paddy Soils in Bangladesh: A Mass Balance Approach**

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In Bangladesh, groundwater is extensively used for irrigation of dry season Boro rice. Due to often high arsenic (As) concentrations in irrigation water, approximately 1360 tons of As were estimated to be transferred to arable soils in Bangladesh each year (1). Potential accumulation of As in paddy soils may have adverse effects on rice yield and quality and consequently human health.

We studied the fate of As in paddy fields in Munshiganj, where Boro rice is grown since the early 1990's under irrigation with water containing ~ 400 µg As L<sup>-1</sup>. We found that irrigation leads to spatially heterogeneous As input into paddy fields. Soil As contents are highest in topsoils and decrease with increasing distance from the point where the irrigation water enters the field. On the field site the growth season is followed by intense monsoon flooding and soil As is variable over the year, increasing during irrigation and decreasing during monsoon. These high spatiotemporal As variations complicate the reliable assessment of long term trends. First estimates suggested that As input may partly be counteracted by As loss through irrigation water percolation and/or As diffusion into monsoon floodwater (2, 3).

In order to assess the potential for long-term As accumulation, we measured soil As contents in an individual field with high spatial and temporal resolution (38 soil cores, 4 sections down to 40 cm, 7 sampling campaigns over 3 years (4x after monsoon, 3x after irrigation)). We will discuss the results from these sampling campaigns with respect to seasonal As fluxes and the As accumulation potential in paddy fields.

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## **Role of Agricultural Practices in Mobilization of Arsenic From Sediments to Groundwater**

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Arsenic contamination in groundwater is posing a major health threat to global human population. The problem is especially severe in many South Asian countries like West Bengal (India), Bangladesh, Vietnam and Cambodia. Careful observation shows a striking similarity between all the affected areas of South Asia that follow similar agricultural practice i.e. traditional paddy cultivation method. In this method, harvested crop is

cut from the middle of the stem and the remaining half of the stem and roots are ploughed back for the next cultivation. This activity leaves a considerable amount of organic matter in the paddy field, which during monsoon starts decomposing and subsequently leads, among others, to the formation of organic acids. Organic acids thus produced percolates down with rainwater and on their way to the groundwater table reacts with the mineral surfaces and modifies their sorption behaviour. In the present work, a study has been made to investigate the role of organic acids produced in the paddy field in mobilizing arsenic from sediments to groundwater. For this purpose, column experiments on a 9 meter deep soil profile, collected from a paddy field in West Bengal have been conducted. In the column filled with the material from the uppermost 3 meters of the soil profile results indicate a significant mobilization of arsenic from the very beginning of the experiment when leached with a solution containing 100 mg/L of indigenous organic acids. At depths between 3 to 9 meters the sediments become coarser with increasingly larger grain size dominated by sand fraction that apparently acts as sorption media for arsenic. In the column filled with this material, the release of arsenic during six weeks of the experiment increases gradually in parallel with the decrease of the redox values and the availability of binding sites for adsorption. In a control experiment, using tap water without addition of organic acids no significant release of arsenic could be observed during the same time interval. The results of these experiments may be helpful in better understanding of arsenic release mechanism especially in the South Asian countries which have similar agricultural practices, climate and sediment type (deltaic).

## **The Cause of Severe Arsenic Contamination in Bangladesh**

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Biogeochemists have puzzled over the mechanisms that cause high arsenic concentrations in the groundwater of Bangladesh since the severe health effects of contaminated drinking-water wells were first publicized. To describe all of the biogeochemical processes that lead to high arsenic concentrations with certainty would require tracking sediment-water interactions along a flow path from recharge to contamination ? an endeavour that would require the detailed level of hydrogeologic characterization only supported in economically developed countries. However, by combining physical understanding of groundwater flow, with isotopic tracers and detailed chemical characterization of both recharge water and groundwater, we demonstrate that recharge from constructed ponds leads to high arsenic concentrations at a site in Munshiganj, Bangladesh. We show that labile organic carbon that enters the aquifer through pond sediments promotes arsenic mobilization from aquifer minerals, and that the resulting high concentrations of arsenic are distributed through the aquifer by groundwater flow. Three-dimensional numerical simulations of groundwater dynamics demonstrate that recharge from ponds excavated during the last century is drawn laterally through the aquifer at the depth of peak arsenic concentrations by irrigation withdrawals. Isotopic tracking of groundwater sources supports these results, and laboratory experiments show that pond recharge contains biological degradable organic carbon, whereas the organic carbon in recharge through agricultural soils is recalcitrant. Furthermore, likely reaction pathways suggest that the interaction of

pond recharge with aquifer sediments results in the chemical composition observed in arsenic-contaminated groundwater. These findings have a number of implications that are important for water management. First, arsenic concentrations will likely shift over decades, the time-scale of groundwater circulation and land-use change, so monitoring programs will need to extend over this time-scale. Second, our results support Michael and Voss's recent suggestion to place drinking water wells below irrigation wells because the hydraulic barrier induced by the irrigation wells can prevent recent local surface water recharge from reaching drinking-water wells. Third, the results emphasize the importance of understanding how land-use changes can affect water quality. Changes, such as the extensive excavation of ponds and widespread adoption of groundwater irrigation, can alter groundwater chemistry by changing patterns of groundwater flow as well as the biogeochemical input to aquifers.

## **Water Resources Quality (WRQ): Risk Assessment and Mitigation for Inorganic Contaminants in Groundwater**

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As a sustainable source of safe drinking water, groundwater has many advantages over surface water, most notable its natural protection from the pathogens that are a leading cause of child mortality in developing countries. As tragically illustrated in South and Southeast Asia, however, consumption of groundwater can also pose health risks due to exposure to geogenic contaminants. These risks are

real and their impact on exposed populations must be acknowledged, but they can also be managed. The WRQ approach promotes the development of risk awareness through use of GIS-based maps of the probability of occurrence of the geogenic contaminants arsenic and fluoride. In locations where groundwater containing geogenic contaminants is a necessary component of the drinking water supply, WRQ focuses on risk mitigation by water treatment for arsenic and fluoride removal. (\*WRQ team at Eawag: C.A Johnson (coordinator) K. Abbaspour, M. Berg, E. Hoehn, S. Hug, H.J. Mosler, K. Mueller, H. Yang, [http://www.wrq.eawag.ch/index\\_EN](http://www.wrq.eawag.ch/index_EN) )

### **Study on geochemical changes of bank infiltration in Red River floodplain aquifer - Case study at Dan Phuong, Ha Tay**

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With the supposition that the artificial recharge of high-arsenic groundwater by non-arsenic river water could be a feasible strategy to produce low-arsenic groundwater for human consumption in the Red River floodplain, the pumping infiltration experiment was installed throughout rainy season (July to October) to investigate the geochemical changes during this process. After 33 days of pumping, electric conductivity (EC) of groundwater reduce significantly from about 780 $\mu$ S/cm to 350 $\mu$ S/cm (compare to EC of river water is ~200  $\mu$ S/cm), other

chemical parameters such as alkalinity, As(T), As(III), Fe(II), Mn, Na, K, Ca, Mg, NH<sub>4</sub><sup>+</sup>, CH<sub>4</sub> also reduced from 8.8mM; 232 $\mu$ g/L; 188  $\mu$ g/L; 10.8; 0.4; 3.9; 3.3; 111.5; 31.7; 0.5; 2.3 mg/L to the lowest point at the 33rd day with the concentration is 3.5mM; 160.8 $\mu$ g/L; 141.9 $\mu$ g/L; 4.2; 0.2; 2.7; 2.1; 47.8; 12.6; 0.3; 0.38 mg/L. The mixing fraction, calculated based on EC, showed that when river water level was highest, groundwater was recharged by 69.4% of river water on average. It means that, the major changes in water chemistry of groundwater caused by mixing with the river water infiltrated to the adjacent aquifer. However the whole process can be very complex due to the redox processes, the dissolution and precipitation of minerals such as FeS, CaCO<sub>3</sub>, etc.

### **Arsenic and Manganese Concentrations in Deep Tubewells in Munshiganj, Bangladesh**

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Deep tubewells are installed in many regions in Bangladesh to avoid arsenic contaminated groundwater from shallow tubewells. The necessary depth to reach 'arsenic-free' water is dependent on the local stratigraphy. In the district of Munshiganj, where over 80% of the shallow tubewells are affected by more than 50 µg/L As, deep tubewells are typically screened at 180-230 m depth. In two small surveys in Sreenagar Upazila, we found As concentrations below 10 µg/L in almost all deep tubewells, but Mn concentrations reached 1-5 mg/L (greatly exceeding the WHO guideline value for Mn of 0.4 mg/L) in most deep tubewells around Sreenagar town. To obtain more detailed information about the deeper aquifers, we installed monitoring tubewells down to 230 m depth, at a location ca. 1 km east of the town of Sreenagar. The transition from gray Holocene to brown Pleistocene sediments was observed at 170-190 m. As concentrations peaked at around 30 m depth with over 500 µg/L and concentrations of around 200 µg/L extended down to 100 m. Below 130 m, As concentrations were lower than 20 µg/L. Mn concentrations were below 0.5 mg/L down to 180 m, but then rose sharply to over 3 mg/L from 180-210 m. If planned pumping test show that water from 160-180 m depth (slightly above the Pleistocene sediments) can be pumped for household use without the risk of contamination with shallow water, deep tubewells screened in this depth range could provide water with low As and Mn concentrations in this region.

### **Arsenic Removal Technologies in Bangladesh: an Interim Progress Report**

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The Government of Bangladesh through its Environmental Technology Verification programme has granted provisional approval to four arsenic removal technologies. These include three household level filters (ALCAN, READ-F and SONO) and one community plant (SIDKO). As part of a broader evaluation, nearly 20,000 filters have been distributed to arsenic-affected households since 2007, and more than 50 community plants have been constructed. Water quality of the source wells and treated water has been monitored by NGO workers, and a social assessment is underway. Preliminary monitoring results are presented which show that in most cases the household and community filters are able to remove arsenic for at least one year. In some parts of the country arsenic breakthrough has occurred earlier, this seems to be mainly due to a more challenging water matrix, though in some cases physical damage to the filter caused during transport and installation has led to filter failure.

### **In situ Removal of Arsenic: Column Studies**

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By injecting aerated water into an aquifer which contains elevated levels of dissolved

Fe(II), localized oxidizing conditions can be created. Fe(II) is then oxidized in situ, creating fresh ferric surfaces which can subsequently adsorb Fe(II), allowing low-Fe water to be abstracted for some time. A series of column experiments using goethite-coated sand were conducted to simulate this process, and to determine if in situ treatment could simultaneously remove Fe(II) and As(III). Retardation factors for O<sub>2</sub>, Fe(II), and As(III) were estimated by measuring the number of pore volumes at which 50% breakthrough occurred. Experiments were conducted at pH 7.0, 7.5, and 8.0, and simulated using a geochemical model.

The observed retardation of oxygen, iron and arsenic was in good agreement with theory.

Iron retardation during abstraction phases increased with increasing pH, and matched stoichiometric mass balance calculations from oxygen retardation during injection phases. Duplicate columns showed good agreement. Geochemical modeling predicts that retardation factors should increase with increasing treatment cycle numbers, as sediments become increasingly coated with fresh ferric surfaces. This 'ripening effect' was observed at pH 8.0 only.

Arsenic retardation showed less pH dependence, and a ripening effect was seen at pH 8.0 only. However, substantial retardation was consistently noted the first time Fe(II) and As(III) were co-injected on the column; this is interpreted as an electrochemical effect, as adsorbed Fe(II) increases the surface potential. This effect did not persist in subsequent cycles, indicating that the product of Fe(II) oxidation is different from the goethite originally present.

Mass balance calculations, as well as independent batch experiments, indicate

that goethite has a substantially higher capacity for Fe(II) than for As(III).

These experiments suggest that in situ treatment is a promising approach for obtaining safe drinking water from aquifers containing elevated levels of dissolved arsenic and iron.

### **Geochemistry of Arsenic during Groundwater Discharge in the Ganges-Brahmaputra-Meghna Delta**

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Shallow groundwaters in the Ganges-Brahmaputra-Meghna Delta (GBMD) are frequently elevated in arsenic and iron. The large hydraulic gradient between shallow groundwater and rivers at the onset of dry season drives the flow from groundwater to rivers, but little is known regarding the fate of arsenic during discharge. Sporadic sedimentary As enrichment up to hundreds to thousands mg/kg in the shallow subsurface found along the Meghna Riverbank from Northeastern Bangladesh (25 °N) to the

Bay of Bengal (22.5 °N), is associated with zones of discharge. This accumulation of arsenic suggests a plausible mechanism of trapping of As by a natural reactive barrier consisting of freshly precipitated Fe minerals formed at the redox boundary between reducing groundwater and oxic river water during discharge.

To ascertain this hypothesis, shallow sediment core (n=14) and pore water profiles (n=7) were collected at sites along the Meghna River to ~ 7 m depth in January 2006 and Oct-Nov 2007 for geochemical analysis. Groundwater discharge rate is  $6.1 \pm 1.8$  cm/d based on seepage meter (n=19) deployed in Oct-Nov 2007. Depth profiles of sediment Fe(II)/Fe(II+III) ratios and pore water dissolved oxygen and Fe concentrations indicate that there is a redox transition zone from anoxic to suboxic from ~2 m depth to the surface. Sediment As enrichment up to ~700 mg/kg is closely associated with this redox transition zone. Concentrations of groundwater Fe, As, and P decreased significantly along the flow path from the upland shallow well groundwater to riverbank pore water, and finally to river water, while the decreases of concentrations of major cations are much less. This indicates immobilization of groundwater As and P coupled with Fe at the point of discharge. Transects of sediment cores and high-resolution depth analysis of sediment indicate that the arsenic enrichment zone in the riverbank is vertically thin, only 5~20 cm in a number of cores, but is wide horizontally spanning a length of 10-15m from the river shore. Arsenic speciation in sediment determined by X-ray absorption spectroscopy (XAS) is dominated by mixed As(III) and As(V) with on average,  $23 \pm 23\%$  and  $68 \pm 20\%$  of total As, respectively. In pore water, > 90% of dissolved As in shallow groundwater is in the form of As(III). This suggests that dissolved As (III) is partially oxidized during or after trapping. Ferrihydrite, which commonly forms from

the rapid oxidation of Fe(II) at neutral pH, is the dominant Fe mineral in Meghna Riverbank sediment enriched with As by XAS.

### **Arsenic contamination in ground water samples of Rajnandgaon district, Central India**

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Studies were carried out on ground water samples (n = 50) collected near Rajnandgaon district (21N06 81E08) of newly formed Chhattisgarh state of Central India for the determination of arsenic. The concentration of arsenic in the study area was found to be in the range of 10 – 800  $\mu\text{g L}^{-1}$ . The median ( $\mu\text{g L}^{-1}$ ) and standard deviation of the metal in ground water samples was calculated and found to be 159.5 and ( $\pm$ ) 233.02, respectively. The high variation in the range and standard deviation of the concentration of arsenic in ground water samples was recorded may be due to wide variation in their natural availability in soil, scavenging potentiality, chemical forms, solubility etc. The industrial emission (burning of coal in steel and thermal power plants in the region) strength with wide range may also be contributing factor in the statistical variations of the metal concentration in ground water samples. The toxic form of arsenic i.e. As (III) and As (V) were also found to be present in the analyzed samples, predominantly. The sources of

arsenic in the study area may be due to rock weathering which in turn leaching the ground water samples with contributions of atmospheric depositions. The people living nearby the study area may be affected from diseases related with arsenic pollution i.e. keratosis, melanosis, skin cancer etc.

### **Spatial Variation of Arsenic in Groundwater in the Rural Landscape of Bangladesh and the Impact on Human Health**

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Arsenic (As) contaminated groundwater commonly extracted through tubewells is widely used for drinking and identified as major As exposure pathways to the population that live in the rural areas of Bangladesh. Since As groundwater contamination and the associated human health risk are potentially spatially connected, this research assesses and quantifies the spatial variability of As concentrations in the rural landscape in relation to As concentrations from drinking and irrigation water sources. Arsenic contamination and human health risk were treated as spatial phenomena and methodology was developed to analyze and visualize the spatial variability of As

contamination and risk. To achieve this goal tubewell water, together with plant and soil samples, from rural household and irrigation fields were collected and subsequently As determination was carried out using ICP-MS. Laboratory determination of As concentration shows that the overall mean As concentration in tubewell water across the landscape was 148  $\mu\text{g L}^{-1}$  and ranged from 0 to 969  $\mu\text{g L}^{-1}$ . Analysis of As water surfaces indicated that As concentrations were highly variable for water sources located within close proximity (50 m) of each other

To identify spatial variability and patterns of As contamination across the landscape, geostatistical techniques were applied to the As concentration database to create concentration surfaces. Geostatistical interpolation was of limited value for As concentration surfaces due to inherit high spatial variability in groundwater As concentrations even over short distances (< 50 m), but did indicate some trends and patterns of As concentration in groundwater that varied between thanas. To identify the causes of spatial variability of As concentration in tubewell water the depth-concentration relationship was investigated. While there was no significant linear relationship between tubewell depth and As concentration ( $r^2 = 0.11$ ), the negative correlation ( $r = -0.34$ ) exhibited between tubewell depth and As concentration, indicated that As concentration did tend to decrease with increasing tubewell depth. The frequency of exceedance of the Bangladesh drinking water guideline value (50  $\mu\text{g L}^{-1}$ ) was related to reported tubewell depth and indicated a peak when the tubewell depth was around 18.7 m. A small number of tubewells exceeded the Bangladesh guideline of 50  $\mu\text{g L}^{-1}$  at lower depth and also at depths above 70 m suggesting that both shallow and deeper tubewells could be solutions to alleviate As exposure from water. Spatial analysis of As concentration



in water sources also indicated that the current Bangladesh drinking water guideline of 50  $\mu\text{g L}^{-1}$  underestimates the risk of As exposure and hence a large fraction of the population and their water sources would not be targeted for the remediation measures using this guideline.

This investigation was further extended by identifying the relationship between water-soil-plant (vegetables) As concentration using GIS. Distance-concentration-impact analysis indicated that there was no direct correlation between water As and surface soil As concentrations in the same location in the landscape. However, a positive linear correlation ( $r = 0.4$ ) was observed between As concentration in groundwater and rice grain, but no similar relationship was observed between As concentration in groundwater and vegetables ( $r = -0.1$ ).

### **Measuring and Simulating the Near-Surface Biogeochemical and Hydrologic Processes Governing Arsenic Transport in the Mekong Delta, Cambodia**

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Weathering of As-bearing rocks in the Himalayas has resulted in the transport of sediments down major river systems such as the Brahmaputra, Ganges, Red, Irrawaddy, and Mekong. Groundwater in these river basins commonly has As concentrations exceeding the World Health Organization's recommended drinking water limit (10  $\mu\text{g/L}$ ) by more than an order of magnitude. Coupling of hydrology and biogeochemical processes underlies the elevated concentrations of As in these aquifers. In particular, the spatial distribution As within sediment profiles must be examined to ascertain sources and sinks of As and to predict future patterns of contamination in evolving aquifers. We therefore performed a comprehensive analysis of near-surface and aquifer biogeochemistry within an As-afflicted field area south of Phnom Penh, Cambodia, bounded by the Bassac and Mekong Rivers and comprising approximately 50 km<sup>2</sup>. Biogeochemical profiles of aqueous constituents including As, Fe, and DOC coupled with detailed hydrologic measurements illustrate that As is released within near-surface (<12 m) sediments within oxbow features.

To fully elucidate the biogeochemical mechanisms of near-surface sedimentary As release, we used a number of field, laboratory, and spectroscopic measurements. Based on these measurements, we assess the thermodynamic potential for As, Fe, and S reduction to transpire—the major processes influencing As release and mobility. Our results illustrate that sediments (0-12m deep) within oxbow and interior wetland environments are seasonally inundated, exhibit saturated conditions throughout the year, and possess appreciable quantities of As-

bearing Fe-(hydr)oxide and organic carbon—conditions conducive for the mobilization of As through As(V) and As-Fe-(hydr)oxide reduction. Ensuing reductive mobilization of As from As-bearing Fe (hydr)oxides results in its migration to the underlying sandy aquifer (>12 m deep). Near-surface As release is linked to widespread aquifer contamination with reactive transport modeling; simulations calibrated with biogeochemical and hydraulic field data demonstrate that continuous release from near-surface sediments delivers sufficient quantities of As to propagate widespread, elevated As concentrations within the aquifer for centuries to millennia.

**Geological and Hydrogeological Processes Affecting the Distribution of Arsenic Ground Water Concentrations in Holocene and Pleistocene Aquifers in the Red River Flood Plain, Vietnam.**

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Geological and hydrogeological processes affecting concentrations of arsenic (As) in Holocene and Pleistocene aquifers in the Red River flood plain in Vietnam have been studied both on a regional and a local scale. The geology was investigated using geophysical methods and drilling of exploratory boreholes. The hydrogeology was studied using: (i) water sampling in monitoring boreholes in a 45 km transect across the southern and central part of the delta, (ii) time-series of hydraulic head distributions in surface waters and aquifers; (iii) the stable isotope composition of rain, surface and ground water, and (iv) numerical ground water modeling. Results show relatively high As ground water concentrations in the shallow Holocene aquifers and lower concentrations in underlying Pleistocene aquifers.

The major mobilization of As to ground water seems to occur in the Holocene sediments, with the reduction of As-contaminated Fe-oxides controlled by natural organic matter degradation as the controlling geochemical process. An estimated mobilization rate of As from the Holocene sediments of 14 µg/L/year is comparable with estimated release rates from a previous Bangladesh study of As release from similar aquifer sediments. Through most of the year, the ground water flow in the shallow Holocene aquifers is controlled by a regional flow towards the main rivers, whereas during the monsoon, the river water stages rises up to 6 m and stalls the regional ground water flow. In this high water stage period, the interaction between the surface waters and shallow aquifer system is highly dynamic with a succession of gaining and losing phases through high permeable layers adjacent to the rivers. A mass balance based on the numerical ground water flow modeling, and average As ground water concentrations, suggests that As is exported with the ground water from the Holocene aquifers to the rivers, where

is seems to be re-precipitated in bottom sediments. Compared to the pool of As present in the aquifers sediments, the flux of As into the rivers is small (0.01 %) and a timescale of thousands of years is envisaged before the Holocene sediments become depleted in As.

Observed low As groundwater concentrations in the Pleistocene aquifers have been ascribed to a reduced reactivity of the organic matter in these older sediments and in addition to a originally lower content of organic matter in these fluvial deposits. Localized elevated As ground water concentrations in the Pleistocene aquifers could therefore be controlled by natural or pumping induced downward flow from the Holocene aquifers into the underlying Pleistocene aquifers. Observed stable isotopes compositions ( $^{18}\text{O}/^{16}\text{O}$  and  $2\text{H}/1\text{H}$ ) and As concentrations from these studies seem to confirm such a flow control on the As ground water distribution in the Pleistocene aquifer, but it still need to be proven whether this is a widespread phenomenon. Where high As containing ground water is flowing down into Pleistocene aquifer, sorption of As to sediment surfaces could reduce the As concentrations in the water.

### **Isotopic Tracing of Ground-Surface Water Interaction and its Role in Arsenic Release in West Bengal, India**

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Arsenic in groundwaters utilised for drinking, cooking and irrigation in many parts of southern Asia is adversely affecting the health of tens of millions of people. It is widely accepted (although not universally held) that this arsenic is of natural origin and that it is mobilised under

reducing conditions via the microbially mediated reductive dissolution of Fe(III) phases. This process is driven by the consumption of organic matter (OM). However, the nature and provenance of this OM utilized by these microbes remains a subject of intense debate. Harvey et al (2002) have suggested that that modern OM, drawn in to reducing aquifers from surface water bodies following the extensive pumping of shallow groundwater over the last few decades, has accelerated the rate of the arsenic release process. If this is shown to be the case, then it would have profound implications for management of groundwater resources in Southern Asia.

We present here data collected from a field study site in Chakdaha, West Bengal, where massive groundwater abstraction has been proceeding for decades. Tritium,  $^{14}\text{C}$  and noble gas data provide key constraints on groundwater ages and provenance, whilst  $\text{d}18\text{O}$ ,  $\text{dD}$ ,  $\text{d}13\text{CDIC}$  and  $\text{d}13\text{CDOC}$  provide key complementary information with which to determine the relative importance of surface water contributions to the groundwater and the nature and provenance of organic carbon present in the aqueous phase. This data directly addresses the issue of the role of surface waters and hence the source of OM in promoting arsenic mobilisation.

### **Arsenic-Humic Substances Complex in Groundwater of the Chianan Coastal Plain, Taiwan**

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Groundwaters from deep aquifers (60-300m) in southwestern Taiwan are high in concentrations of arsenic (As) and humic substances (with molecular weight larger than 500 Dalton). Previous studies showed that arsenic can be complexed with dissolved humic substances, but the existence of As-humic substances complex in the Chianan groundwater has not been confirmed. Therefore, we analyzed the contents of dissolved organic carbon (DOC), arsenic, major ions, and total alkalinity of 22 groundwater samples from the plain. Moreover, the percentage of complexed arsenic in 13 samples was further determined by ultrafiltration methods. Analysis results obtained show that DOC and arsenic concentrations range from 3.8 to 45.9 mgC/L and from 0.02 to 1.01 mg/L, respectively. A distinct positive correlation was found between arsenic and DOC concentrations.  $\text{Na}^+/\text{Cl}^-$  molar ratios are essentially the same as seawater, but  $\text{SO}_4^{2-}/\text{Cl}^-$  molar ratios are not, reflecting the occurrence of sulfate reducing reaction. Besides, the values of total alkalinity increase with DOC concentrations, suggesting that DOC and DIC resulted from microbial metabolism of sedimentary organic carbon (SOC). Ultrafiltration analyses showed that almost all arsenic (more than 90%) of all but one samples analyzed were found to be retained in the dissolved organic matters which have the molecular weight greater than 500 Dalton, demonstrating that most arsenic was complexed with humic substances.

## **The Microbial Ecology of Arsenic Mobilizing Aquifer Sediments**

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The contamination of groundwaters, abstracted for drinking and irrigation, by sediment-derived arsenic, threatens the health of tens of millions worldwide. Using the techniques of microbiology and molecular ecology, in combination with aqueous and solid phase speciation analysis of arsenic, we have used microcosm and axenic culture-based approaches to provide evidence that anaerobic metal-reducing bacteria can play a key role in the reductive mobilization of arsenic in sediments collected from aquifers in West Bengal and Cambodia. The critical controls on these activities will be described, including the role of organic matter in promoting arsenic-mobilizing respiratory processes, alongside the diversity of organisms involved in mediating these transformations. The impact of other competing anaerobic processes, including sulfate reduction, on arsenic speciation will also be discussed in the context of mitigating arsenic mobilization.

These biogeochemical processes have been investigated using culturing experiments and stable isotope probing (SIP) techniques in combination with functional gene analysis, to identify the active fraction of subsurface microbial communities responsible for mobilizing arsenic. Using SIP we have shown that the introduction of a proxy for organic matter (including <sup>13</sup>C-labelled acetate and other electron donors) stimulated As(V) reduction in sediments collected from a Cambodian aquifer that hosts arsenic-rich groundwater. This was accompanied by an increase in the proportion of prokaryotes closely related to the dissimilatory As(V)-reducing bacteria *Sulfurospirillum* NP-4

and *Desulfotomaculum auripigmentum*. As(V) respiratory reductases genes (*arrA*) closely associated with those found in *Sulfurospirillum barnesii* and *Geobacter uraniireducens* were also detected in active bacterial communities utilising <sup>13</sup>C-labelled acetate in microcosms. Thus, this SIP study suggests a direct link between inputs of organic matter, and the increased prevalence and activity of organisms which transform As(V) to the potentially more mobile As(III) via dissimilatory As(V) reduction.

### **Relationship between Sediment Depositional Age and Groundwater Arsenic Levels in Cambodia.**

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Arsenic contamination in groundwater is associated with regions of rapid change within the deltas of southern Asia. These

areas are unique in that such deltas contain regions of rapid deposition, erosion, and, as a result, there are numerous lateral unconformities that complicate their stratigraphy, which result in a complex relationship between sediment age and groundwater arsenic levels. While these areas of extensive arsenic contamination appear to be quite young based on landscape position, there is little information about the absolute age of sediments, or the role of sediment deposition rates and age on the expression of groundwater arsenic. Here, we measure maximum sediment ages using Pb-210, Cs-137 and other atmospherically-derived radionuclides, and to establish the recent depositional history of different landscape surfaces. We find extreme heterogeneity in sediment ages, with many areas experiencing little or no significant deposition immediately adjacent to areas with rapid deposition. In isolated cases associated with areas of groundwater contamination, the presence of excess Pb-210 at depths of >10 m indicates that sediment deposition is both very recent and extensive. We attribute the presence of excess lead at these depths to channel migration and rapid infilling during subsequent flooding episodes. Despite the presence of excess Pb-210 in some environments, there are several limitations to using this methodology for the characterization of depositional rates in these environments, most notably extensive sediment redistribution, which dilutes radionuclide activities with relatively old sediments, and non-steady state conditions, which limits the accumulation of atmospherically-derived radionuclides at the soil surface.

**Biotite and its chemical weathering as a primary source and formation mechanism of arsenic contaminated groundwater in the Holocene aquifer in Bangladesh**

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The formation mechanism of arsenic contaminated groundwater via microbial reduction and dissolution of iron oxyhydroxides/oxides hosting arsenic must be reconsidered based on the geochemical data set of groundwater and cored sediments from the boundary between contaminated Holocene and uncontaminated Pleistocene aquifers in Sonargaon, Bangladesh.

The major chemistry and oxygen and hydrogen isotope ratios of the groundwater in the studied area suggest that highly arsenic contaminated groundwater was recharged from narrow areas around each wells during the late rainy to early dry seasons. Major cation composition of the

groundwater is determined by the reaction with detrital minerals especially feldspars and biotite. Nitrogen stable isotope ratios of ammonium, which was believed to be a product of microbial activity in reducing aquifer condition, indicate the chemical fertilizers such as urea as the source of ammonium.

The sediments were taken from the surface and shallow depth around unsaturated and saturated zones of unconfined groundwater and cored through arsenic contaminated Holocene aquifer (10 to 30 m depth) to uncontaminated Pleistocene aquifer (>45 m depth) up to 90 m depth. Arsenic concentration of all the studied sediments is <12 mg/kg except one (50 mg/kg), and gives the well positive correlation to the concentration of aluminum, iron and magnesium, and XRD peak intensities of mica (muscovite and biotite). Abundant biotite, which were partly altered to be hydrobiotite and not coated with iron oxyhydroxides/oxides, is included in the Holocene aquifer sediments comprising fine to medium sand. The separated biotite fractions contained 10~50 mg/kg arsenic. Those facts indicate that the biotite is a primary source of As in the studied sediments.

The above facts strongly support the hypothesis that the arsenic contamination occurs associating with vertical infiltration of surface water, promoting chemical weathering of detrital minerals including arsenic-bearing biotite, into the aquifer along outside of well pipes and/or holes of abandoned well due to excess use of well water.

Arsenic accumulation in the surface and shallow sediments, in which the decomposition of basic minerals and iron hydroxides formation would occur in association with changing surface and groundwater level and following redox condition, were not observed in the studied area; i.e., organic matters and

silicates/sulfides, but not iron hydroxides/oxides, are the abundant host phases of arsenic. Microbial activity would play an important role to be demobilized and detoxicate arsenic as producing organo-arsenic species, since the arsenic in organic phases increases and that in silicate/sulfide phase decreases with decreasing levels of arsenic contamination of groundwater of the areas.

### **Reduced Humic Substances Promote Iron Reduction and Mobilization of Arsenic in Aquifers in Bangladesh**

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Humic substances are heterogeneous organic compounds that can act as electron shuttles in the microbial utilization of labile dissolved organic matter, enhancing the rates of electron transfer to iron oxides in anoxic sediments. This redox cascade can influence overall metal cycling in the environment, as sorbed metals are released through reductive dissolution of iron oxides. The redox active moieties in humic substances have quinone-like properties and their redox state can be characterized by electron spin resonance and

fluorescence spectroscopy. In the Ganges Brahmaputra Delta of Bangladesh, a greater understanding of iron-oxide reduction in shallow groundwater is a priority because this process drives arsenic mobilization in water supplies used by millions of people. We used fluorescence spectroscopy to characterize the dissolved humic substances in several surface waters and groundwater from Bangladesh and modeled the spectra using parallel factor analysis (PARAFAC). In general the surface water contained oxidized humic substances and high concentrations of labile DOM, as indicated by protein-like peaks in the fluorescence spectra. In contrast, in shallow groundwater where iron and arsenic concentrations are high, humic substances were in a reduced state and labile DOM was less abundant. These results suggest that a humic-enhanced electron shuttling cascade contributes to iron reduction and arsenic mobilization in the Bangladesh groundwater system.

### **Is Deep Groundwater a Sustainable Source of Arsenic-Safe Water in the Bengal Basin? Management Insights from a Regional Modeling Analysis**

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Groundwater containing unsafe concentrations of dissolved arsenic is produced from shallow depths by domestic and irrigation wells in the Bengal Basin aquifer system. Deeper groundwater, nearly universally low in arsenic, is a potential source of safe water, but an understanding of the sustainability of the supply is critical for management of the resource. Unsustainable deep pumping would induce vertical flow of water from



shallow depths, with associated transport of dissolved arsenic on a timescale of management, contaminating the wells and destroying the deep resource. Sustainability assessment requires an understanding of the groundwater flow system and its potential response to changes in pumping rates and depths, achieved through large-scale hydrogeologic analysis and flow simulation.

Results from groundwater modeling, in which the Bengal Basin aquifer system is represented as a single aquifer with higher horizontal than vertical hydraulic conductivity, indicate that this anisotropy is the primary hydrogeologic control on the natural flowpath lengths, and despite extremely low hydraulic gradients due to minimal topographic relief, anisotropy implies large-scale (tens to hundreds of kilometers) flow at depth. Other hydrogeologic factors, including lateral and vertical changes in hydraulic conductivity, have minor effects on overall flow patterns. However, because natural hydraulic gradients are low, the impact of pumping on groundwater flow is overwhelming; modeling indicates that pumping has substantially changed the shallow groundwater budget and flowpaths from predevelopment conditions.

Three pumping scenarios were considered as possible future management options within the high-arsenic region, with associated sensitivity analysis. The scenarios are (1) deeper pumping for both irrigation and domestic supply, (2) deeper pumping only for domestic supply while maintaining shallow pumping for irrigation, and (3) deeper pumping for domestic supply without groundwater irrigation. Analysis indicates that limiting deep pumping to domestic supply only (scenarios 2 and 3) may provide a sustainable source of arsenic-safe drinking water to more than 90% of the arsenic-impacted region over a 1000-year

timescale. This insight may assist water-resources managers in alleviating one of the world's largest groundwater contamination problems.

### **Field Study of Arsenic Adsorption in Low-Arsenic Aquifers of Bangladesh by Simulating Shallow Groundwater Intrusion**

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Deeper, mainly Pleistocene, aquifers currently provide a safe source of drinking water for Bangladesh due to their ubiquitously low arsenic concentrations. However, evidence exists that downward hydraulic gradient is developing between the high As, shallow Holocene aquifer and the low As aquifer around Dhaka as a result of increased pumping from deep wells. Increasing exploitation of deeper aquifers raises concerns about the possibility of leakages of shallow groundwater on smaller scale around pumping wells, and on larger scales in areas where clay aquitard is thin or completely absent. In order to simulate the intrusion of shallow groundwater, four injections of ~1000 L of high As groundwater were performed in the deeper aquifer at our research site in Arai-hazar. Deep groundwater with additions of ~200

□g/L As(V) or As(III) was used for two of the injections, while the other two were performed with unaltered high As shallow groundwater from two different depths.

As(V) added to deep groundwater adsorbed more rapidly than As(III), with 50% of As removed in 1.5 and 4 hours, respectively. Shallow groundwater As generally seemed to follow the adsorption patterns of As(III), aside from the slower initial rate observed with high P groundwater. We considered As adsorption to proceed like a first order reaction, which yielded fast adsorption kinetics for the first 6-12 hours post injection, followed by a lower rate of adsorption up to 2 days. After 2 days, a slow rate of desorption occurred as the ambient low-As water was drawn towards the wells. This simple approach does not, however, account for the complexity of a single well injection-withdrawal experiment with incomplete mixing within the affected volume and with a contaminant that has a high partitioning coefficient ( $K_d$ ). A numerical model was constructed instead to account for the role that As retardation and flow patterns play in the observed adsorption, thus effectively separating kinetic and equilibrium aspects of the breakthrough curves.

Overall, the performed experiments demonstrated fast kinetics of As adsorption onto deeper aquifer sediments and confirmed their high  $K_d$  in situ. The results appear favorable to continued use of these aquifers as a sustainable source of drinking water. However, further studies are necessary to assess the capacity of these sediments to adsorb As from a prolonged leakage of shallow groundwater.

### **Temporal Indicators of Hydrochemical Processes Including Cation Exchange in Arsenic Contaminated Groundwater of Nawalparashi, Nepal**

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The Nawalparashi district of Nepal lies in the headwaters of the South Asian arsenic crisis region. Strong heterogeneity in groundwater arsenic distribution is characteristic of this area for uncertain reasons. This study investigates the role of localized hydrologic differences in generating that heterogeneity by affecting the hydrochemical environment and arsenic mobility.

Six nested piezometer stations were established to monitor water levels, major cations and anions, arsenic, iron and phosphate on a monthly basis. Three river points were also monitored for hydrochemical parameters and two were also monitored for discharge. Based on water level variations and monsoon response these observation wells can be categorized into two groups. One group (Group A) has the greatest and quickest monsoon response, representing wells at depths less than 30 m. Other group (Group B, consisting of wells having around 50m depth) has a delayed and subdued response to monsoon. Each multi-level site exhibits a downward hydraulic gradient.

All wells have bicarbonate-dominated water. Group B has sodium-dominated bicarbonate whereas most of Group A has calcium-dominated bicarbonate water. The highest sodium to calcium ratio is

observed in Group B, strongly suggesting a cation exchange process is active in intervening clays. Six out of eight wells in Group A and one out of two wells in Group B have arsenic greater than WHO guideline value of 10 ppb in all time series data. Arsenic was below detection limits in the river points. Total dissolved solids (TDS) in all wells declined to an almost uniform value of 650 ppm by monsoon end, indicating thorough flushing. TDS then increases steadily in shallow zones during the dry season up to about 1000 ppm which is probably due to poor sanitation. Considerable variability is observed in major cations/anions, arsenic and water levels and their relationships remain uncertain. Lack of correlation between Arsenic and Sulphate indicates that Pyrite oxidation is not the cause for Arsenic release. Good correlation between Arsenic and Phosphate shows that Phosphate is not exchanged for Arsenate. Arsenic exhibits good correlation with bicarbonate and total iron indicating that reductive dissolution of ferric oxyhydroxides is the cause for Arsenic release in the wells having Arsenic greater than WHO guideline values.

**Geological Controls on Groundwater Arsenic: New Insights from a Field Site at Gotra, Nadia District, West Bengal, India**

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Groundwater arsenic hotspots exhibit a patchy distribution throughout the Bengal Delta Plain which straddles the state of West Bengal, India, and adjacent Bangladesh. Reasons for the small-scale spatial variability of groundwater arsenic concentrations are still not well understood. However, investigations by the Geological Surveys of India and Canada at a field site in the arsenic affected village of Gotra, Nadia District, West Bengal, are shedding new light on the geological controls that determine the pattern of groundwater arsenic contamination in a meandering fluvial depositional environment. Measurements of arsenic in over fifty domestic tube-wells and piezometers have delineated sharply defined high and low arsenic zones which can be related to aquifer geology.

The village of Gotra is located on a natural levee adjacent to an abandoned river channel. The subsurface geology is characterized by two 60m undisturbed cores and fifteen “hand flapper” boreholes of 30m from which only samples of fine-grained sediment could be recovered. The deposits of the Bengal Delta Plain consist of a thick sequence of fluvio-deltaic sediments of Quaternary age characterized by successions of sand, silt and clay with subtle variations in color, grain size, and to some extent, mineralogy. Generally, the lithologies intersected in the boreholes consist of approximately 25m of grey, coarse-to-fine grained Holocene sediments underlain by brownish grey sediments tentatively dated as Pleistocene. The sediment mineralogy is dominated by

quartz, chlorite, mica (muscovite) and smectite.

In the village area, the shallow Holocene sediments represent a classic meander-belt fluvial fining-upward sequence. Subsurface information and the curvature of the abandoned channel indicate southwesterly migration of point-bar deposits which underlie the low-lying cultivated area northeast of the village. The point-bars consist of thick grey medium-to-fine sands capped by brownish oxidized silts likely representing crevasse splay deposits. Beneath the levee, the point-bar sands start to thin and are overlain by channel-fill deposits which thicken as the abandoned channel is approached. Being the shallowest transmissive unit, the point-bar sands form the aquifer most often tapped by villagers although arsenic contamination is clearly related to proximity of the abandoned channel. The channel-fill deposits consist of very fine-grained, dark-grey, organic-rich sediments that reach a maximum thickness of 22m beneath the remnant ponds marking the final course of the abandoned channel. The highest sediment arsenic concentrations (26 ppm) are associated with the finest-grained (> 10% clay) and organic-rich (Corg up to 1.8% weight) of these sediments. Laterally, the channel incised earlier Holocene flood plain deposits consisting of thinly-bedded, dark, organic-rich silts and clays with peat and gastropod horizons. The base of the meander-belt fluvial sequence is generally at around 28m bgs and is marked by a hard clayey paleosol layer containing calcrete (kankar) and woody debris. The upper portion of the layer is grey-blue in color transitioning to oxidized brown in its lower half. The layer grades downward in brown silty sands, and, at 35-37 m bgs, into a fine-to-medium grained unit known as the "Orange Sand" aquifer. This unit is being promoted as an immediate target for safe potable groundwater. It is underlain by brownish-grey silty sands which are

tapped by deeper irrigation wells. Although ubiquitous locally, the paleosol and "Orange Sand" are discontinuous and appear to have been incised by the younger Holocene sequence in the channel vicinity. There, the grey Holocene sediments are immediately underlain by the brownish-grey sands and they are found to contain moderate levels of dissolved arsenic.

An understanding of the sedimentology and stratigraphy of the study area has established a clear spatial linkage between groundwater arsenic contamination in the shallow Holocene aquifer and fine-grained, organic-rich sediments filling an abandoned fluvial channel. This understanding has also led to the identification of the "Orange Sand" aquifer that may provide a readily accessible safe groundwater resource on the short term. Finally, these investigations point to the significance of the low-permeability paleosol layer in protecting the quality of groundwater in deeper aquifers.

### **Coupled Hydrologic and Biogeochemical Processes Controlling Arsenic in Cambodian Groundwater**

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Tens of millions of people in South and Southeast Asia routinely consume groundwater that has unsafe arsenic levels. Arsenic is naturally derived from eroded Himalayan sediments, and is believed to enter solution following reductive release from solid phases under anaerobic conditions. However, the processes governing aqueous concentrations and location of arsenic release to pore water remain unresolved. This uncertainty is partly attributed to a poor understanding of groundwater flow paths altered by extensive irrigation pumping in the Ganges-Brahmaputra delta, where most research has focused. Accordingly, we have established a field area on the minimally disturbed Mekong delta of Cambodia and conducted routine groundwater and surface water sampling in order to constrain natural flow paths and arsenic distributions.

Within our field area, water is cycled from the Mekong River to inland wetlands and ponds, then through near-surface clays to the underlying sand aquifer and back to the river. Dissolved chemical concentrations vary spatially and temporally and are dominantly influenced by flow paths and sediment interactions. In particular, arsenic on floodplain sediments is released during the transition from aerobic to anaerobic conditions; while arsenic may be released from aquifer sediments, arsenic gradients along flow paths indicate that the greatest quantities of arsenic are liberated at the near-surface. Owing to similarities in geologic deposition, aquifer source rock and regional hydrologic gradients, our results represent a model for understanding pre-disturbance conditions for other major deltas in Asia. Furthermore, the

observation of strong hydrologic influence on arsenic behavior indicates that release and transport of arsenic are sensitive to continuing and impending anthropogenic disturbances.

### **Arsenic mobilization into shallow groundwaters of southern Asia ? where, when and why does it occur - evidence from organic, isotopic and biogeochemistry**

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ph. +44 161 275 3935; fax +44 161 306 9361; e-mail: david.vaughan@manchester.ac.uk); B Van Dongen (School of Earth Atmospheric and Environmental Sciences, University of Manchester, Manchester, UK M13 9PL; ph. +44 161 306 7460; fax +44 161 306 9361; e-mail: bart.vandongen@manchester.ac.uk); Key questions still to be comprehensively addressed regarding the origins of arsenic-bearing groundwaters in southern Asia include: (i) in a local context, where does arsenic mobilization take place - does it occur predominantly within the bulk of such reducing aquifers or is mobilization in narrow zones of high redox gradients more significant?; (ii) when does arsenic mobilization take place in relation to sedimentation history?; (iii) why does mobilization occur? , and in particular what is the role of various types of organic matter, including exogenous organic matter, to controlling the rates of Fe(III) and As(V) reduction considered by some to be critical steps in transfer arsenic from the sediment to the aqueous phase? . the timing of arsenic mobilization in relation to sedimentation history; (ii) the location of arsenic mobilization with respect to the distribution of saturated sediments and redox zones? (iii) the source of organic matter (OM) utilized during the reduction of Fe(III) and/or As(V) during these processes; and (iv) the provenance of arsenic-bearing groundwaters.

We summarise here organic, isotopic and bio-geochemical evidence, obtained over the period 2002-2008 by the group at Manchester and our collaborators, that speaks to these issues. In particular, we provide organic geochemical evidence for the widespread occurrence of natural petroleum in arsenic-bearing shallow groundwater systems in southern Asia, both in Ganges Delta and in the Mekong Delta. The significance and implications of this association? and in particular whether or not it is likely to be causal rather than a

function of the nature of the tectonic environments in which such aquifers are found - are discussed. We further report stable isotope, organic geochemical and radiocarbon data that addresses the issue of the relative importance of labile surface OM to accelerating arsenic mobilization. Lastly we present a discussion of the relative importance of bulk aquifer and narrow high redox gradient zones to overall observed groundwater arsenic budgets in these aquifers.

### **Mobilization of Arsenic and Iron from Red River Floodplain Sediments, Vietnam**

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Sands and muds, transported by the Red River, have been deposited on the floodplain. In these sediments, aquifers and aquitards developed which gradually became anoxic and released arsenic to the groundwater. If this scenario is correct, then we must expect to find differences in the chemical composition and the mineralogy of river and aquifer sediments as well as in their ability to release arsenic. We have used a broad suite of methods to investigate this matter, starting with mineralogy and traditional sequential extraction schemes, followed by time dependant extractions with ascorbic acid and HCl at pH 3, the determination of the reactivity of the Fe(III) pool and finally incubation of unamended and amended sediments.

The iron oxides in the Red River sand and mud, as determined by Mössbauer spectroscopy, consist mainly of goethite with subordinate amounts of hematite while less stable iron oxides like ferrihydrite are absent. The goethite present in the mud has a distorted and poorly crystalline structure. The reactivity of the iron oxides, as determined by time dependant ascorbic acid leaching, shows for the sand a reactivity corresponding to goethite while the mud contains a pool of Fe(III) with a reactivity comparable to that of ferrihydrite. Reductive dissolution of iron oxides by ascorbic acid readily releases both As(V) and As(III) from river sand and mud and particularly from the mud the release of arsenic is high. Sediment incubations, unamended and with added acetate, both release Fe and As. Again the release of arsenic is strongest from the mud, while the addition of acetate has no effect and the process is therefore not carbon limited. The river mud apparently both contains reactive Fe-oxide, high in As, as well as reactive organic carbon and can therefore be a powerful source of arsenic when deposited on the floodplain

The aquifer sediments from the oxidized and reduced zone also contain goethite and hematite, but here relatively more hematite is present. The oxidized sediment releases Fe, but little As, by reductive dissolution with ascorbic acid while almost nothing is released by HCl. For the reduced aquifer sediment the reversed pattern is observed. HCl readily releases Fe and As and nothing more comes out with ascorbic acid. Apparently a Fe(II) phase like siderite is present in the reduced sediment which dissolves in HCl. The experiments did run for 3 days and during this time the reduced aquifer sediment did not to release much As by reductive dissolution of iron oxides. However sediment incubations that did run for 45 days did release some As and Fe while the addition of acetate to the incubations did strongly stimulate As and

Fe release. These results indicate a continued potential of the aquifer sediments to release arsenic which is limited by the reactivity of the sedimentary organic matter.

### **Groundwater As Gradients in a Shallow Aquifer of Bangladesh: The Role of Local Adsorptive Equilibrium**

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The hydrological and geochemical factors that regulate the partitioning of sediment and groundwater As in an incompletely flushed aquifer system is the focus of this study. Using a three dimensional array of monitoring wells, temporal changes in

hydraulic gradient and groundwater chemistry have been investigated in Pach Gao Char Para village, 24 km northeast of Dhaka since December 2006. Monitoring wells were installed in the sandy, raised village and in adjacent agricultural fields covered with silty clay bordered by a small stream. Dissolved As concentrations increase from less than <5 to 500 ug/L over the 300 m distance separating the village and the stream. There is a strong redox gradient across this distance indicated by with low dissolved Fe and high SO<sub>4</sub> in the village and high Fe and low SO<sub>4</sub> towards the stream, respectively. Solid phase P-extractable arsenic concentrations vary less than ten-fold over the same distance, from 0.4 to ~ 4 mg/kg, without showing any systematic spatial trend. Head measurements over the entire area show that annually-averaged groundwater flow leads from the village towards the stream. However, the hydraulic gradient reverses, and flows from the stream towards the village, between the peak of the dry season and the onset of the monsoon.

The large gradient in groundwater As that is unaccompanied by a systematic gradient in P-extractable As in the sediment suggests that either the sediment plays a minor role in regulating groundwater As through adsorptive equilibrium or that the sediment-groundwater partitioning coefficient (K<sub>d</sub>) decreases along the flow path. New results from batch adsorption and push-pull experiments show that the later is the case. Batch experiments indicate that the K<sub>d</sub> declines from about 30 to 1 L/kg from the village towards the stream, a range that is broadly consistent with the range determined from the field data. Push-pull experiments conducted in the fields to simulate the intrusion of groundwater indicate a rapid adsorption or desorption, depending on the direction of the perturbation, with some form of re-equilibration achieved within 2 days. The observed decrease in K<sub>d</sub> may be linked to



the increasing reducing state of the amorphous Fe coatings (from 0.5 to 0.9 Fe(II)/total Fe extractable by HCl) along the transect, the input of sulfate with recharge within the village, or a combination of both.

These observations suggest that groundwater As concentrations are determined by the “upstream” groundwater concentrations and the local adsorption partitioning ( $K_d$ ) of the sediment. Whereas this partitioning regulation does not specify how As is initially mobilized, it provides a framework for understanding how interaction with the sediment affects groundwater As concentrations during transport in sedimentary aquifers. Our goal is to represent the likely evolution of As in groundwater of the study area into the future by combining these observations with a simple groundwater flow model.

### **Leaching Kinetic Rate of Arsenic Bearing Minerals in the Ganges Delta Basin Subsurface Sediments: An Estimation Approach**

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In the recent decades subsurface groundwater aquifers in the Ganges delta

basin has severely been affected with the elevated Arsenic (As) contamination caused by the naturally occurring regional hydro-chemical phenomena. This As is supposed to get leached from the interface of the saturated-unsaturated zone sediment with the potential interaction of the natural leaching agent such as  $\text{HCO}_3^-$  which may essentially be evolved under the microbial degradation of the highly carbon contained sediments. The rate at which such leaching reaction can be occurred was attempted to figure out in this study. To estimate the reaction rate  $K_r$ , brown clay samples containing  $28.4 \mu\text{g/g}$  As, extracted at the depth of 10 m from the targeted aquifer of the South-Western Bangladesh were subjected to undergo closely controlled monitored leaching test for the time period of 7, 13, 23 and 29 days until the equilibrium conditions for the respective experimental run varying in mixing speed had been reached. Distilled water enriched with  $\text{Na}_2\text{CO}_3$  (0.01M) was the leaching solution and the sediment-liquid ratio of 1:10 was maintaining in a suspension by employing a mechanical mixer. Based on the relationship between computed reaction rate and the linear form of the mechanical mixer speed, a linear regression equation ( $R^2 = 0.94$ ) was obtained that could predict the field based reaction rate,  $K_r = 7.03 \times 10^{-13}$  /sec when field obtained infiltration velocity through the clay,  $5.34 \times 10^{-5}$  cm/sec was used. Rainfall infiltration getting interacted with the brown clay may also be assumed to do potential leaching in its course of transport through the aquifer sediments. The laboratory estimated  $K_r$  value is nearly consistent with that of the in-situ one  $5.25 \times 10^{-15}$  /sec which was again computed based on the moles of minerals obtained from inverse mass-balance modeling, contact reaction time taken from the C14 data, the BET measured specific surface area, porosity, particle density and the abundances of the minerals estimated from XRD data. This findings might help to explain the time span that is required for

the accomplishment of the As desorption from the source mineral essentially at the contaminated sediment which can further be incorporated into the vertical As transport code for assessing the vulnerability of the successive aquifers.

**Regional Groundwater Model:  
Contribution to Numerical Modeling of  
Arsenic Transport in Mekong Delta  
Aquifer, Cambodia**

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Arsenic contamination of the Mekong delta located at the southern part of Cambodia is recently identified as a serious groundwater crisis. More than one million people are living under the threat of arsenic polluted groundwater, which ranges the arsenic concentration between 100-1000 ppb. A systematic numerical study is inevitable to understand the flow and transport of arsenic in this region. In this study, we highlight the comprehensive groundwater flow simulation in regional scale. A two dimensional groundwater flow model and a groundwater recharge model are coupled to simulate the groundwater flow of the selected area of 26,600 km<sup>2</sup>. The fluctuations of river water elevations are coupled to the model to make it more realistic. The result demonstrates that; in the north-western

part, mountainous areas supply the groundwater to the Tonle Sap River in all seasons, while in Mekong delta, groundwater elevations raised higher than river water in Bassac and Mekong River in dry season and vice versa in rainy season. This study promotes the knowledge of groundwater recharge areas and the condition of groundwater environment in the polluted region. Arsenic transport model under redox condition considering biogeochemical processes will be conducted in next phase of our research.

**Arsenic Remobilization from Paddy  
Soils During Monsoon Flooding in  
Munshiganj/Bangladesh**

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Bangladesh relies strongly on groundwater resources, often containing high concentrations of arsenic (As), for the irrigation of dry season rice (boro). Since accumulation of As in paddy soils may adversely affect rice yield and quality, understanding the processes determining retention and release of As from paddy soils is crucial. Monsoon flooding strongly attenuates As accumulation in the topsoil of rice fields, but the underlying mechanisms and their relative quantitative importance remain unclear. Here we present data from paddy fields near Sreenagar (Munshiganj, Bangladesh) which show that As was reductively mobilized and released into the overlying floodwater throughout the duration of monsoon flooding. As concentrations in topsoil porewater increased over time, reaching values of up to 1160  $\mu\text{g L}^{-1}$  at 3-7 cm depth after 16 weeks of flooding. The floodwater column was either vertically well-mixed exhibiting As concentrations between 5 and 20  $\mu\text{g L}^{-1}$  over a height of 1-2.7 m, or characterized by distinct gradients of decreasing As concentrations with increasing distance from the soil. On days of limited vertical mixing, As concentrations ranged between 40-120  $\mu\text{g L}^{-1}$  in floodwater 2.5 cm above the soil.

Based on vertical As concentration gradients measured in topsoil porewater and the accumulation of As in floodwater over time, we estimate that between 55 and 250 mg  $\text{m}^{-2}$  of As, corresponding to 14-63% of the As annually added via irrigation, were mobilized into floodwater over the course of one monsoon season.

### **Incomplete Arsenic-Removal by Iron-Amended BioSand Filters in Kandal Province, Cambodia**

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Naturally occurring arsenic in groundwater in Cambodia is common in the Mekong delta region. There are two principal strategies in dealing with this ubiquitous contamination, including the identification and utilization of nearby uncontaminated water sources, or water treatment that can remove both pathogens and arsenic. Here, we examine the long-term efficacy of an iron-oxide modified BioSand filter as a household water treatment option to remove arsenic and microbial pathogens from groundwater. The performance of modified BioSand filters filled with three natural arsenic-bearing groundwater

sources from Kandal province of varying compositions and spiked with lab-cultured E. Coli and MS2. These filters were used consistently under controlled conditions that mimic regular use. The effectiveness of arsenic and pathogen removal was not constant over time and was highly dependent on the influent composition. After an initial period of stabilization, each filter was relatively ineffective in treating arsenic contaminated groundwater and effluent arsenic concentrations were between 70 and 250  $\mu\text{g L}^{-1}$ , higher than accepted drinking water standards. The overall average arsenic removal stabilized at 40-70% respectively (depending on water source), with the extent of arsenic removal was not related to the influent arsenic concentration. The poor arsenic removal was due to the combination of high influent P ( $> 0.5 \text{ mg L}^{-1}$ ) and low Fe ( $< 5 \text{ mg L}^{-1}$ ) concentrations. E. Coli was removed under most conditions; however, the efficacy of microbial pathogen removal was strongly impacted by changing influent water to rainwater, a common local practice during, and subsequent to, the monsoon. The coliphage MS2 was not removed by filtration. These findings suggest that such amended filters should not be widely deployed in areas of widespread arsenic contamination until improvements are made to address the consistency and efficacy of treatment. In addition, the filter poses some potential health risk associated with the production of elevated nitrate levels in the effluent within the filter, possibly due to nitrification and high levels of ammonia in the groundwater.

#### **Sources, Seasonal Variation and Mobilization of Arsenic in Groundwater of Rautahat District, Central Nepal**

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This paper discusses the occurrence, distribution of arsenic contamination in relation to geological, hydrological and geochemical aspects of the Rautahat district. Arsenic was analyzed in surface water, groundwater and river sediments. Arsenic testing in water samples at field was done by field kit and digital arsenator. Some groundwater samples exceeded Nepal interim value and incase of surface water arsenic content is extremely low. River sediments contain appreciably high amount of arsenic. In majority of wells arsenic contamination is found little high in pre monsoon period than in post monsoon period. Mineralogical examination of sediment samples showed the absence of arsenic bearing sulphide minerals. The arsenic contaminated tube wells are more concentration in fine grained aquifer and near to river bank. Water There is no apparent relationship between fluctuation of groundwater level and arsenic occurrences. The arsenic concentrations in the groundwater are characterized by low concentration of sulphate and slightly positive correlation with iron, which can give some support to iron reduction as the process of arsenic mobilization. The available litho logs show that thick clay layer on the top, so the possibility of direct groundwater contamination by use of pesticides, fertilizers etc. are also limited.

#### **Chemical Characteristics of Dissolved Humic Substances From Arsenic-Rich Shallow Groundwater in Bangladesh**

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The dissolved organic material present in groundwater has been shown to play a significant role in mobilizing arsenic through several pathways in Bangladesh aquifers and other regions with As-rich sediments. Firstly, labile organic substrates may stimulate the growth of heterotrophic bacteria, resulting in anoxic conditions, which drives the use of alternate electron acceptors beyond oxygen, such as nitrate and ferric iron present in oxides in sediment. Another potentially important pathway is the electron shuttling by dissolved humic substances where the quinone moieties in the humic substances are reduced by microbial processes. These reduced humic molecules transfer electrons to ferric iron in iron oxides along the flow path. This redox cascade promotes the release of arsenic and potentially other toxic metals. Although all humic substances studied have shown some electron shuttling capability, there is a large variation among fulvic and humic acids of different origins. We have isolated preparative quantities of fulvic acid and transphilic acid from two well depths at a site in Bangladesh with high arsenic concentrations in the groundwater. At this site fulvic acid accounted for about 50 % of the total dissolved organic material. The fluorescence characteristics of these

samples, which were modeled using parallel factor analysis (PARAFAC) and compared to both terrestrial and microbial end-members, indicate that they are predominantly of terrestrial origin with a substantial content of quinone-like moieties. Characterization by <sup>13</sup>C-NMR provides a further indication of the aromaticity of these samples and their ability to form complexes with iron and act as electron shuttles.

### **An Ecological Approach to Understanding Arsenic in Nepal**

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To better understand the ecological cycling of arsenic in Nepal, this research analyzed arsenic concentrations from Himalayan rocks, identified arsenic tolerant microbes in groundwater and rivers, measured arsenic uptake and bioaccumulation of arsenic in jungle and wetland plants, and monitored monthly arsenic variations in tubewells.

Arsenic analyses from the Nepal Himalayas and Terai show that arsenic is ubiquitous throughout the mountains, rivers, and springs. The highest concentrations are found near two mining areas, the Central Mineral Belt located from Baglung to Palung and in the far eastern district of Illam. Soil and mineral samples in these areas are over 4000 ppm arsenic. Analyses of 104 cropping samples reveal that arsenic concentrations vary from 2 ppm to 85 ppm in the Lesser Himalayan rock formations. The highest values are found in a Carboniferous marine shale, the Benighat Formation. Soil and core samples were collected from two districts in the southern part of Nepal, Nawalparasi and Rautahat districts, sediments are clay, silt, and fine to coarse

sand. The arsenic concentrations did not exceed 48 ppm in soils or core sediments, the average arsenic concentrations are about 8 ppm. Several rivers in the central and north-central sessions of Nepal were analyzed for arsenic. River arsenic concentrations from Upper Mustang to Jhapa varied from 0 to 40 ppb. Hot springs in the Annapurna region are 76 ppb and cool springs are 40 ppb.

Groundwater arsenic concentrations in Nawalparasi District reveal high monthly arsenic variations, particularly in the high arsenic wells. Monthly and seasonal arsenic values may exceed 100 to 400 ppb in the tubewells in Nawalparasi in tubewells located near the Churia Hills and in the more clay and silt rich sediments. Aquifer heterogeneity is high, most likely due to the original depositional environment of braided streams on alluvial fans. High clay overbank deposits are barriers to strong lateral connectivity. A well in the Toribara Jungle and one in Madhav village, Rautahat both at 50 ft. depth, show that the wells act as isolated units in the dry season, but in the monsoon water depths in the wells indicate the wells (aquifer) are connected.

Indigenous plants and surrounding soils from the Toribari Jungle and Chandhi River Wetland in Rautahat district are analyzed to determine whole plant arsenic uptake. Soils surrounding the jungle plants ranged from 3.54 ppm to 8.02 ppm and wetland sediments contained 10.37 ppm. Plant arsenic concentrations range from 0.0078 ppm to 50.62 ppm. Results show that all jungle plants uptake arsenic and four wetland plants are arsenic bioaccumulators. To determine if plant uptake of soil arsenic altered soil arsenic concentrations sixty soil pits were installed in the jungle and non-jungle areas. In the jungle pits, arsenic concentrations were higher in the organic upper layer and decreased at the 30 inch depth. The reverse was observed in the

low vegetation pits, arsenic values were lower in the top of the pit and increased toward the bottom.

Microbial cultures from tubewell waters and rivers in both districts show a strong relationship between arsenic wells and arsenic tolerant microbes. Four microbial species colony growth continued to 1000 ppm (MIC). Microbial redox reactions may be the key to arsenic mobilization in Nepal.

### **Arsenic in Drinking Water Results in the Highest Known Toxic Substance Disease Risks**

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Arsenic in drinking water is now linked to many different adverse human health effects. Attention is often focused on skin effects which are unimportant and rarely occur without prolonged exposure to water concentrations of arsenic above 200 ug/L. The greatest initial mortality impact comes from acute myocardial infarction, followed by even larger numbers of deaths from cancer, in particular lung and bladder cancer. Early life exposure to arsenic results in marked increases in mortality in young adults from cancers of the lung, bladder and kidney, and also increased mortality from non-malignant disease of both the lung and kidney. Based on very clear data from Chile, exposure to water containing arsenic in the range of 500 and 1000 ug/L for about 10-15 years will eventually result in mortality of 5-10% of the population. These risk estimates are firmly based and supported by data from other countries, and are the highest

mortality risks ever reported for any environmental exposure. There is reason to believe the dose-response could be linear such that long term consumption of water containing 50-100 µg/L of arsenic might result in mortality on the order of 1 in 100 people. Using surface water has been proposed as one option to prevent exposure to arsenic-containing groundwater and is under debate because of the risk of microbial contamination. In contrast to mortality from arsenic, mortality risk estimates for consumption of surface water involve a large number of highly speculative assumptions with no firm data to support them. Persons consuming drinking water contaminated with arsenic should be urged to stop such exposure, with careful use of treated surface water being one option.

### **Contamination of Arsenic and Other Trace Elements in Groundwater: A Case Study in Cambodia and Lao PDR**

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In Cambodia, concentrations of arsenic and other trace elements in groundwater were examined at six villages (PT, POT, CHL, TT, DS and PPK) in the Kandal Province. Arsenic in the groundwater ranged from not detectable (ND) (the DS village) to 1,543 µg/L (the PT village) with average and median concentrations of 408 and 333 µg/L, respectively. About 83% of these samples contained arsenic

concentrations exceeding WHO drinking water guideline of 10 µg/L. Arsenic (III) was found to be a dominant species in all groundwater samples, constituting mostly at least 60% of the total arsenic, with its concentrations varying from ND µg/L (the DS village) to 1,334 µg/L (the PT village). In addition, about 50%, 63%, 43% and 100% of groundwater samples had higher concentrations of barium, manganese, lead and selenium than WHO drinking water guideline, respectively. Finally, it is clearly found the linear relationship between arsenic level in human hair and in groundwater.

In Lao PDR, twenty one groundwater samples were collected in Champasak (11 samples) and Attapu (10 samples) provinces for determination the concentrations of both arsenic and trace elements. Arsenic concentration ranged from ND to 278 µg/L, with its average and median values of 36 and 8 µg/L, respectively. About 48% of these samples exceeded 10 µg As/L set by WHO. Arsenic (III) was clearly found as a dominant species in the Champasak province. Concerning the trace elements, about 24% and 10% of groundwater samples had higher concentrations of manganese and barium, respectively, exceeding the WHO drinking water guideline. Finally, 22% of hair samples had the total arsenic at the concentrations □ 1.00 µg/g indicating of toxicity.

### **Environmental Tracer Applications in Floodplain Aquifers with Elevated Arsenic Concentrations**

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An understanding of the groundwater flow and transport regime, e.g. determination of

flowlines, recharge and discharge areas and rates is required to (a) constrain sources and processes that contribute to As mobilization, as well as to (b) evaluate the sustainability of currently low [As] aquifers. Floodplain aquifers are characterized by low relief, very high geological and geochemical heterogeneity, and in some cases (e.g. in Bangladesh) by heavy pumping and irrigation, which complicates the application of classical hydrogeological methods. Environmental tracers (e.g.  $^3\text{H}/^3\text{He}$ ,  $\text{SF}_6$ , noble gases,  $^{18}\text{O}$ ,  $^2\text{H}$ ,  $^{14}\text{C}$ ,  $^{13}\text{C}$ ;) serving as dyes or radioactive clocks can fill this gap and provide constraints on sources, fluxes, flowlines and can ultimately serve as calibration targets of groundwater flow and transport models. Case studies conducted by several research groups illustrate the strengths and weaknesses of this approach. The effects of flooding, gas stripping, subsurface production, mixing, and geochemical processes on the applicability of these tracers in geologically young floodplain aquifers will be discussed.

### **Similarity of Behavior of Arsenic and Antimony in River-Sediment Systems**

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Migration of Sb and As released from Ichinokawa Sb mine (ore mineral:stibnite) in Ehime, Japan in a river-sediment system was investigated. The system consists of two rivers; one is Ichinokawa River flowing close to the Sb mine, which is incurrent into a largerriver, Kamo Riever. The increase of Sb and As concentrations from up to down stream in Ichinokawa River were similarly observed, suggesting that the sources of the two elements into the river are similar without significant fractionation of the two elements from the mine area. After the confluence of the two rivers, the concentration of Sb decreased to downstream, the trend of which was identical to that of As. EXAFS analyses and sequential extraction of the sediments showed that As and Sb were present as the species sorbed on Fe hydroxides in the sediments, suggesting that the decrease of the two elements from the river water is caused by the scavenging on Fe hydroxides. All the results showed that the two elements behave similarly at least under oxic condition. Similar studies on the comparison of Sb and As behavior in river-sediment-groundwater system in Ganges Delta Plain is in progress in our laboratory.

### **Hydrological and sedimentary controls leading to arsenic contamination of groundwater in the Hanoi area, Vietnam: The impact of iron-arsenic ratios, peat, river bank deposits, and excessive groundwater abstraction**

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Groundwater contamination by arsenic in the Red River Delta (Vietnam) poses a serious health threat to millions of people consuming this water without treatment. In the larger Hanoi area, elevated arsenic levels are present in both, the Holocene and Pleistocene aquifers. Family-based tubewells predominantly tap the Holocene aquifer for daily water needs, while the public drinking water supply of Hanoi city extracts >600,000 m<sup>3</sup> of groundwater per day from the Pleistocene aquifer. Detailed groundwater and sediment investigation were conducted in three villages located in different settings, i.e., high arsenic at the river bank, low arsenic at the river bank, and medium arsenic in an area of buried peat and excessive groundwater abstraction. In-depth chemical analysis of water from Holocene and Pleistocene tubewells, surface water, sediment cores (>30 m), sites of nested wells, as well as sequential leaching of sediment samples were conducted. Seasonal fluctuations in water chemistry were studied over a time span of 14 months.

Sediment-bound arsenic (1.3–22 µg/g) is in a natural range of alluvial sediments, it correlates with iron ( $r^2 > 0.8$ ), and its variation is largely related to grain size (or surface area). Fractions of 23–84% (av. 56%) arsenic were extracted with 1 M phosphate from all sediments, indicating that arsenic can readily be mobilized at each of the three locations. Vertical migration of DOC-enriched groundwater from the young clayey sediments to the aquifer at the river bank, or from the Holocene to the Pleistocene aquifer in the peat area, were found to promote iron-reducing conditions leading to arsenic contamination in the aquifers.

Low groundwater arsenic levels (<10 µg/L) generally exhibit manganese reducing conditions with manganese levels reaching up to 8.7 mg/L. Elevated arsenic levels are caused by reductive dissolution of sediment-bound arsenic under iron- and sulphate reducing conditions. They averaged 121 µg/L at the river bank and 60 µg/L in the peat area. The lower levels of arsenic contamination in the peat area are likely controlled by the high abundance of iron present in both, the aqueous and sediment phases. With median molar Fe/As ratios of 350 in water and 8'700 in the sediments of the peat area, it is likely that reduced iron forms new mineral phases that resorb previously mobilized arsenic to the sediment. Despite similar redox conditions, resorption of arsenic is much less significant at the river bank (Fe/As(aq) = 68, (s) = 4'700), and hence, arsenic levels can reach considerably higher concentrations.

Drawdown of Holocene water to the Pleistocene aquifer caused by the pumping for the public drinking water supply of Hanoi did not show an observable increase of arsenic during the 14 month study. However, DOC, ammonium, and iron are leaching down from the Holocene aquifer, thereby enhancing the reducing conditions in the Pleistocene. Seasonal fluctuations (11–66%) of redox sensitive species in 70 m deep Pleistocene wells were concurrent with water table fluctuations. This indicates shifted mixing ratios of deep groundwater with iron-reduced groundwater that is seeping down from the Holocene aquifer.

### **The Impact of Groundwater Chemistry on the Performance of the Kanchan Arsenic Filter in Cambodia**

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The Kanchan Arsenic Filter (KAF) was developed by the Massachusetts Institute of Technology (MIT) and a Nepali NGO, Environment and Public Health Organization (ENPHO) based on extensive laboratory and field studies in rural villages of Nepal with up to 10,000 households having received KAFs since 2002 from ENPHO and other small non-profits, large agencies (UNICEF, UN-Habitat) and the Nepali government. The KAF is currently being tested in Cambodia to determine the applicability of this technology for use in high-arsenic areas of Cambodia. A total of 40 KAFs have been tested at 31 different tubewells in Cambodia as part of this evaluation. Key results to date have shown that groundwater chemistry of the specific tubewell that is being treated is the most important issue relative to predicting arsenic removal performance. This is consistent with the field of drinking water treatment in general, that the chemistry of the source water is typically considered a very important parameter for achieving effective treatment. Some of the groundwater chemistry parameters that have been evaluated in Cambodia for their importance relative to impact on KAF treatment performance include: pH, total hardness levels, phosphates, iron, raw water arsenic levels, and total dissolved solids.

The work in Cambodia consists of two phases. Phase 1 includes field research carried out over a 30 week period during 2008. During Phase 1, a total of 10 KAFs were installed in 5 different configurations, 2 filters for each configuration. The configurations were: the original configuration applied in Nepal

(5 kg of nails placed in the diffuser basin of an otherwise traditional biosand filter); pre-rusted nails configuration; submerged nails configuration; manual aeration configuration and mechanical aeration configuration.

Phase 2 which is currently ongoing, consists of testing KAFs at 30 different tubewells in Cambodia under varying groundwater chemistry conditions. The results from the KAF testing and the importance of each of the individual groundwater chemistry parameters will be discussed in detail during the conference presentation. Specific levels of these parameters that are likely to impact performance will be identified and discussed. These specific levels will be compared against levels of these parameters generally found in groundwater in other high arsenic areas of Cambodia from other published studies.

### **Sustainability of Groundwater Pumping From Low-arsenic Aquifers in Southern Asia: Proposal for a Case-Study in Vietnam South of Hanoi**

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Emphasis on the elevated level of arsenic in groundwater tapped by millions of shallow tubewells across southern Asia over the past two decades tends to obscure that anoxic aquifers that are low in As are also widespread and often within reach of drilling in the affected regions. There are two key issues for assessing the vulnerability of such low-As aquifers: (1) whether dissolved or particulate organic carbon (DOC or POC) drives aquifers towards microbial dissolution of Fe oxyhydroxides and (2) to what extent adsorption and precipitation of As attenuate the impact of high-As groundwater drawn into low-As aquifers. The village of Van Phuc, 15 km south of Hanoi, presents an opportunity to address both issues because large groundwater withdrawals by the city of Hanoi have laterally drawn groundwater elevated in As from Holocene grey sands through orange Pleistocene sands for several decades.

In order to assess the vulnerability of the low-As aquifer in Van Phuc, we have proposed to apply an unprecedented combination of analytical methods to the transition from grey to orange sands:  $^{14}\text{C}$ -analysis of phospholipid fatty acids (PLFAs) constituting the membranes of living cells, probing of the redox state and bonding environment of As and Fe in aquifer sands by X-ray absorption spectroscopy,  $^3\text{H}$ - $^3\text{He}$  dating of groundwater, and optically-stimulated luminescence (OSL) dating of quartz grains. The proposed measurements will

provide a basis for testing several working hypotheses. H1: Reductive dissolution of Fe oxyhydroxides associated with the release of As to groundwater is driven primarily by the microbial degradation of POC deposited at the same time as the aquifer sands. H2: DOC advected by groundwater flow does not result in significant reductive dissolution of Fe oxyhydroxides and therefore does not trigger conversion of orange sands to grey or the release of As. H3: Mixing of high-sulfate ( $\text{SO}_4$ ) groundwater with high-As groundwater results in precipitation of As-sulfides fueled by the oxidation of POC in the aquifer deposit. The proposed research will also help to determine whether the As content of groundwater tapped by the municipal water supply of the city of Hanoi, and similarly situated groundwater pumping stations throughout southern Asia, could be lowered at the source by favoring entrainment of river water, herewith reducing the need for treatment.

### **Targeting Low-Arsenic Aquifers by Processing and Re-Distributing Field-Kit Data**

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Close to 5 million tubewells distributed across 45,000 villages of Bangladesh were systematically tested for As with a field-kit between 2001 and 2004. The data have been compiled by the government and used primarily to install ~800 ft deep wells in the subset of 7500 villages where >80% of existing tubewells contain >50 ug/L As. The data show that initial exposure of the population in these particularly affected villages averaged 250 ug/L As and contrasts with an average exposure of <10 ug/L in the subset of 10,500 villages with <20% of existing tubewells containing >50 ug/L. Well-switching in response to field-kit testing and the installation of deep wells has significantly reduced exposure throughout the country.

The available data, processed by aggregating at the village level and taking into account depth information provided by households, could be disseminated much more widely to guide the large number of households that continue to install tubewells. The processed data are particularly valuable in the 27,000 villages with 20-80% of tubewells, for 13,000 of which the depth of a transition to groundwater that is systematically low in As can be estimated with a probability of success >0.8. The depth of these transitions can vary widely between neighboring villages and should therefore not be averaged over large areas. Monitoring of 50 community wells installed in Araihasar according to this approach has shown that, by and large, these deeper aquifers have been dependable sources low-As drinking water for up to 7 years.

Safe depth estimates may soon be used more widely as the government is expected to approve their dissemination by Grameenphone, the largest mobile phone service provider in Bangladesh with over 20 million subscribers. Grameenphone will provide this service at a nominal cost through a popular call-in health line as

well as text messaging. The probability of success calculated by processing field-kit data at the village level could also help calculate the premium needed to sustain a money-back guarantee program that would reimburse households that installed a new tubewell at the prescribed depth but failed to reach low-As groundwater. Systematic processing and re-distribution of test data via mobile phones should be considered in neighboring countries that are affected by arsenic in groundwater.

### **Equilibrium and Kinetics of As Sorption to Bangladesh Gray and Orange Sediments Determined by Batch Experiments**

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Unlike the shallower grey Holocene aquifers of Bangladesh, deeper Pleistocene aquifers typically consist of orange colored sands and are low in groundwater As and easily mobilizable sediment As. It is not clear, however, to what extent this attractive source of drinking water is protected by adsorption should some shallow groundwater elevated in As be introduced by leakage. To address this issue, batch experiments were conducted by adding As(III) or As(V) to a mixture of sediment and groundwater in the field immediately upon sample collection in Araihasar, Bangladesh. Care was taken to maintain anoxic conditions by conducting

experiments in a nitrogen filled glove box. Four sediment samples were obtained at depths of 130, 150, 180 and 190 ft. The first two intervals were gray fine sands and the second two fine orange fine sands. The gray sediments were mixed with groundwater pumped from 130 ft with 220 ug/L As, whereas the orange sediments were mixed with groundwater pumped from 190 ft with < 2 ug/L As.

The kinetics experiments started with ~ 4000 ug/L As(III) in the solute in a mixture of ~ 50 g of wet sediment and 130 mL of groundwater sealed in a serum bottle. For the gray sediment sample from 130 ft, the solute As concentration dropped to ~ 2200 ug/L in 7 hrs and remained so to the end at 400 hrs. For the orange sediment sample from 190 ft, the solute As concentration dropped to ~ 2200 ug/L in 5 hrs and continued to decline exponentially to reach a final concentration of 230 ug/L at 400 hrs, i.e 95% of As(III) was adsorbed in 16 days. Sorption of As(III) to both gray and orange sediment is fast, with half time of hours.

The equilibrium experiments started with a series of As(III) or As(V) concentration ranging from 0 to 33,000 ug/L in a mixture of ~ 7 g of wet sediment and ~ 10 mL of groundwater also sealed in serum bottles for 6 days. For As(III) isotherms, all four sediment samples follow Langmuir sorption isotherms, but with distinctly different sorption capacities. The gray sediment has a sorption capacity of 6-8 mg/kg whereas the orange sediment has a sorption capacity of 35-40 mg/kg. For As(V) isotherms, two sediment samples from 130 ft and 190 ft used show nearly identical isotherms as for As(III). Whereas this is not surprising for the sediment from 130 ft because As(V) added to the supernatant was found to be entirely reduced As(III), there was no evidence of reduction of As(V) to As(III) in experiment with sediment from 190 ft.

Sorption equilibrium and kinetic results from batch experiments conducted using Bangladesh Pleistocene aquifer sediment support the potential of using this aquifer as a sustainable drinking water source.

### **Iron Plaque on Rice Root Surface and Arsenic Dynamics in Paddy Soils: Microbial-Mediated Processes**

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Rice is the staple food for nearly half of the population globally, and arsenic (As) elevation in rice has recently been reported to add cancer risks to populations in many regions (Zhu et al., 2008; Meharg et al., 2009). Arsenic enters paddy soils from anthropogenic (mining activities) and geogenic (As in groundwater used for irrigation) sources. It is therefore an urgent need to mitigate the accumulation of As in rice grains, particularly in Southeast Asia. Rhizosphere processes, among many others are crucial in determining the mobility and bioavailability of As in soil-rice systems. Several studies have now pointed to the role of iron plaque on rice root surface in modulating the dynamics of As in soil-rice systems (Liu et al., 2004; Liu et al., 2006). It is well known that microbes are heavily involved in the oxidation and reduction of iron, but their role in iron plaque formation/dissolution, and thus As bioavailability is not clear. In the past five years or so, our group has been investigating whether nitrate-dependent iron oxidizing bacteria and iron reducing bacteria are involved in As sequestration and release in paddy soils, and rhizosphere soils in particular. Since nitrate might be involved in iron dynamics in paddy soils (Chen, et al., 2008), we also examined the community structure of ammonia oxidizing microbes. Molecular tools, such as qRT-PCR were employed to study the microbial ecology. This review

aims to present a synthesis of the status of current knowledge, and discuss future needs in better understanding how microbes in paddy soils and rice rhizosphere are involved in determining As bioavailability, and possible ways of mitigating As accumulation in rice grains.