

Arsenic Release and Transport in Sediments of the Mekong Delta

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Abstract—The spatial distribution of arsenic (As) within ground waters of South and Southeast Asia is often erratic, and the sources of As are generally difficult to ascertain. Previous work has illustrated that Himalayan-derived, near-surface (0 to 12 m) sediments contribute a substantial quantity of As to the subsurface, and that this release is driven by the reduction of As(V) and As-bearing Fe (hydr)oxides. However, the complexities of groundwater flow will ultimately dictate the distribution of As within the aquifer, and these patterns will be influenced by natural physical heterogeneity in the subsurface and anthropogenic activities. Here, we provide a brief synopsis of the natural As cycle in sediments of the Mekong Delta, and present a biogeochemical and hydrologic description of As release to the subsurface environment of an As-afflicted aquifer in Kandal Province, Cambodia. The reactive transport model MIN3P is used to simulate 2-D geochemical profiles of the near surface and aquifer environment. Near-surface As release (0–12 m) contributes enough As to the aquifer to account for observed field values, and the spatial distribution of As within the aquifer is strongly impacted by near-surface changes (excavation), resulting in erratic spatial distributions of As.

Keywords: arsenic, Asia, groundwater, reactive-transport, Mekong Delta

INTRODUCTION

The world's largest mass poisoning is transpiring in South (S) and Southeast (SE) Asia, with over 100 million people exposed to hazardous levels of arsenic (As) (Ravenscroft *et al.*, 2009). The dominant pathway of exposure is through consumption of contaminated groundwater. Tainted food—mainly derived from rice grown in paddies irrigated with high-As groundwater—also contributes (Khan *et al.*, 2009). The areal extent of groundwater contamination is enormous, and aqueous concentrations of As within the aquifers of the vast sedimentary basins of S and SE Asia often range from 100–1000 $\mu\text{g/L}$ or more, far greater than the World Health Organization's suggested limit of 10 $\mu\text{g/L}$ (Harvey *et al.*, 2006; Polizzotto *et al.*, 2008). To date, thousands of individuals in these regions have died or are severely ill as a result of chronic As toxicosis. Symptoms of chronic exposure range from mild (e.g., keratosis, skin lesions) to severe (e.g., serious

cancers (Mandal and Suzuki, 2002)).

For many years, the source of As within these aquifer systems was unclear, but is now generally attributed to the reductive dissolution of As-bearing iron (hydr)oxides—a process which liberates As from these strong sorbents to the aqueous phase (Cullen and Reimer, 1989; Smith *et al.*, 1998; Smedley and Kinniburgh, 2002). But while in recent years the biogeochemical conditions under which As release have been better constrained, few studies have examined coupled biogeochemical-hydrologic processes and their effect on the release and transport of As. Here, we discuss the dominant processes governing the cycling of As in sediments of the upper Mekong Delta. Further, we use reactive transport modeling to illustrate the tight coupling of hydrologic and geochemical processes that lead to As release and transport from reducing sedimentary environments.

A synopsis of the arsenic cycle in S and SE Asia

The modern (Holocene) natural cycle of As in S and SE Asia begins in the Himalaya, where the weathering of As-bearing earth materials contributes massive sediment loads to the major river systems, particularly during the monsoon season (Goodbred and Kuehl, 2000). Sediments represent the major carrier of As to the massive sedimentary basins; negligible concentrations of As exist in the aqueous phase (river water). The major As-bearing solids within the sediment load are iron (hydr)oxides (Kocar *et al.*, 2008; Fendorf *et al.*, 2010, and references therein). While these solids may be found within many As contaminated sedimentary basins (e.g., in Bangladesh), the As-bearing sediment solid(s) initially deposited within the upper Mekong delta are primarily comprised of As-bearing iron (hydr)oxides with a range of thermodynamic properties, including ferrihydrite-like solids and more stable phases such as goethite (Kocar and Fendorf, 2009). Solid phase concentrations of As in these sediments are variable, but are generally low, ranging from 5–30 ppm (BGS and DPHE, 2001; Kocar *et al.*, 2008; Postma *et al.*, 2010). The weathering, deposition and burial of these solids represent the first process by which As enters aquifers of afflicted regions.

After deposition and burial, As-bearing sediments are subjected to biogeochemical processes that may conspire to release As. If sediments are deposited in the presence of sufficient organic carbon to drive reducing conditions, two reductive processes will transpire which contribute to As release from the solid to aqueous phase (Kocar *et al.*, 2008). The first process is the reduction of As(V) to As(III). Arsenic, which during transport and deposition exists on or within iron (hydr)oxides as the less mobile species As(V), may be reduced during the onset of anaerobiosis, often before the reduction of iron (hydr)oxides (Kocar and Fendorf, 2009). The reduced form, As(III), possesses a lower affinity toward iron (hydr)oxides—and other aquifer materials such as clays—and are thus mobilized under flow conditions. The second process which facilitates an increase in mobility is the reductive dissolution of As-bearing iron (hydr)oxides. Iron(III) within iron (hydr)oxides, also reduced under anaerobic conditions, is reduced to Fe(II), which either mediates the transformation of iron (hydr)oxides to more

thermodynamically stable phases, re-precipitates as Fe(II)-bearing minerals, or enters the aqueous phase without re-precipitating. With few exceptions (e.g., the formation of magnetite), all of these processes are thought to ultimately result in the release of As from the solid to the aqueous phase (Kocar *et al.*, 2006; Tufano and Fendorf, 2008). While it is known that these processes liberate As, the nature of the depositional environment as well as the hydrologic cycle will also impart equally important controls on the fate of As.

Arsenic-bearing sediments are deposited in the floodplains of S and SE Asia primarily in the wet season, when swollen rivers overtop or break surrounding levees (Polizzotto *et al.*, 2008). They then settle in a variety of biogeochemical environments, such as ephemeral water bodies where redox conditions are oxidizing for the majority of the year, and permanently saturated locations, where reducing conditions predominate over long time scales (decades to centuries). An important distinction can be made between these environments, which represent end-members of redox state; within permanent water bodies (e.g., ponds), organic matter continuously accumulates as aquatic vegetation dies and decays. Sediments that are deposited in these environments are therefore subjected to reducing conditions, fueled by the presence of abundant electron donor(s) (Kocar *et al.*, 2008). Conversely, residual organic material that is subjected to predominately oxidizing conditions will be rapidly (aerobically) degraded; thus sediments that are deposited in ephemeral wetlands, where conditions are (on average) dominantly oxic, will possess appreciably less organic matter. Geographical locations with the highest propensity for As release in sediments therefore exist within zones where carbon/sediment co-deposition occurs. Such areas include topographical lows such as wetlands and abandoned river channels (oxbows) (Kocar *et al.*, 2008).

While the biogeochemical release of As from sediments initiates contamination of soil and aquifer systems, the hydrologic system will act as a conduit mediating the extensive transfer of As from zones of release to the aquifer. Thus, the tight coupling of biogeochemical processes with the hydrologic system will dictate the fate and distribution of As within subsurface environments.

REACTIVE TRANSPORT OF ARSENIC IN AN As AFFLICTED AQUIFER, UPPER MEKONG DELTA

To demonstrate how the subsurface distribution of As is influenced by the coupling of coupled biogeochemical-hydrologic processes, we perform a simulation of As release and transport within the sediments of an extensively studied field site in the upper Mekong Delta, Cambodia, where active As release occurs within the upper 12 m of sediment. A thorough description of our field area is described in Polizzotto *et al.* (2008), Kocar *et al.* (2008) and Benner *et al.* (2008). Briefly, our field area is in the Kandal province of Cambodia and comprises approximately 50 km² between the Mekong and Bassac Rivers within the upper Mekong River delta. Below surficial clays, the aquifer consists primary of water-producing fine grey sand typically extending >50 m in depth and overlain by a 3 to 20 m thick red and grey clay unit. A network of >80 installed

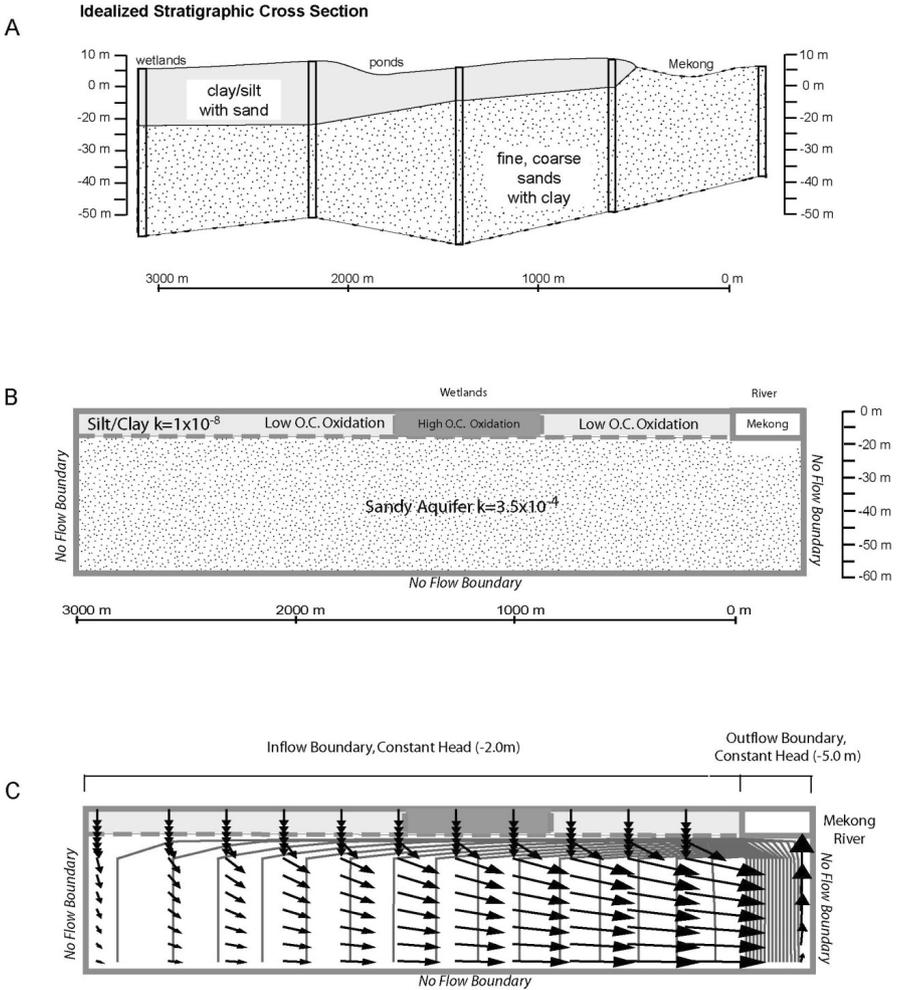


Fig. 1. (A) Drilling logs and sediment cores were used to construct the field area cross section. (B) 2-D idealized model domain consist of a 12 m clay aquitard overlying 48 m of sand, with a surficial (center) zone of high organic carbon degradation (representing a zone where high As release rates occur). (C) Darcy flux vectors illustrate the net annual groundwater flow in our “base case” scenario.

wells and 10 surface water monitoring sites are distributed throughout the field area. Arsenic release was observed within oxbow (pond) channels (Figs. 1A and 2A), with subsequent transport occurring through the underlying aquifer toward the Mekong River.

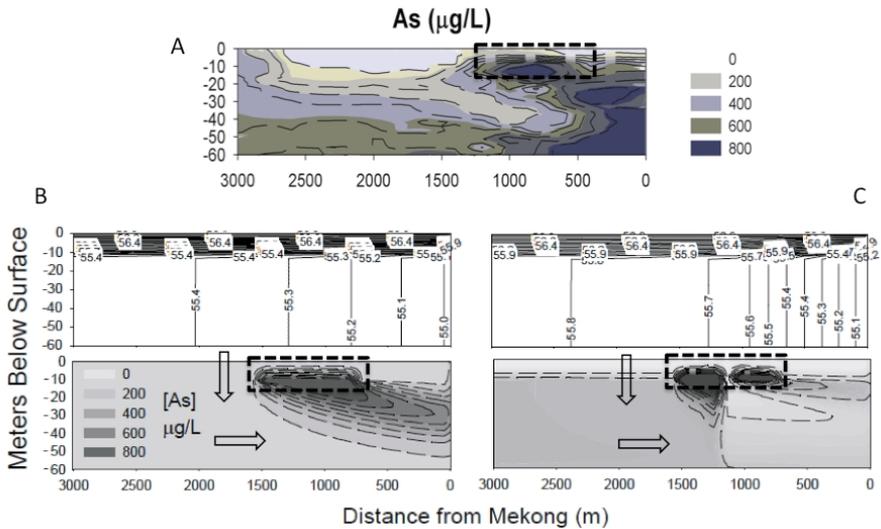


Fig. 2. (A) Field aqueous As concentrations within a transect of wells extending from the Mekong River. (B) Base case scenario, where As emanates from the simulated wetland and is carried toward the Mekong River (right side of the graphs) with coincident hydraulic head isobars, demonstrating that most head drop occurs within the clay aquitard. (C) “Clay window” scenario, where a high K (6.0×10^{-7}) cell was added to the center of the wetland. Higher groundwater flux to the aquifer dilutes As and disrupts flow patterns, and results in a different distribution of hydraulic head; less head drop occurs in the clay aquitard and more occurs in the aquifer between the clay window and the Mekong River (thereby resulting in a zone of higher groundwater flow between the high K window and Mekong River relative to the base case scenario). Black dashed boxes signify where active zones of As release are occurring, and arrows represent direction of groundwater infiltration and subsurface flow.

Hydrology and sedimentary profile

A cross-sectional profile of the site stratigraphy (Fig. 1A) was constructed by interpretation of well log data (visual and texturally based documentation of well cuttings during well installation) and sediment core data. Throughout our field area, a silt-clay aquitard overlying the sand aquifer was observed at all drill locations; the upper silt/clay unit ranges in thickness from 5 to 22 m, is typically orange colored at the surface, and is green to grey at its base. Below the upper clay/silt unit, a distinct transition to sand-rich sediments is observed. The aquifer sand unit extends from an average depth of 15 m to the maximum depth of drilling (60 m), and this unit is characteristically fine to course grained and is grey in color. Depth to bedrock is constrained to 60 m. For modeling purposes, the stratigraphy of our site is idealized as a 12 m clay cap overlying a 48 m grey sandy aquifer (Fig. 1B).

Two-dimensional aquifer system simulations

Our idealized sediment profile, consisting of 12 m of clay with 48 m of underlying sandy aquifer (Fig. 1), was used to construct a coupled hydrological-biogeochemical 2-D simulation of our field area, using calibrated biogeochemical reactions (Kocar, 2008) and known hydrologic parameters (Kocar *et al.*, 2008). A grid of 35 horizontal and 36 vertical cells were used, with the upper 12 m in the vertical direction discretized in 1 m intervals, and the lower (aquifer) portion of the profile discretized in 4 m intervals. Two constant head boundaries were assigned to simulate previously determined hydrologic conditions (Fig. 1). The zone of outflow (the Mekong River) was assigned a constant head of 5.0 mbg, and the zone of inflow (the interior wetlands) was assigned a constant head of 3.0 mbg to achieve groundwater residence times simulated by Benner *et al.* (2008). All biogeochemical processes are driven by the oxidation of organic matter, and occur within the first 12 m (overlying aquitard) of the profile, where active release of As is known to occur. Thus, the primary variable controlling the extent of As release is organic matter oxidation, which is calibrated to observed spatial patterns of dissolved organic carbon (DOC). The simulation time was 4000 years, enough time for the aquifer to be flushed several times. In another simulation, we insert a window of high hydraulic conductivity into the overlying surficial clays. This window is placed within the surficial zone of As release to demonstrate the influence of subsurface heterogeneity on As release and transport. For more simulation details, please see the previous report by Kocar (2008).

RESULTS AND DISCUSSION

Our simulations (Fig. 2) illustrate that biogeochemical processes occurring within near-surface sediments (0–12 m) of oxbow channel(s) contaminate large sections of the underlying and surrounding aquifer with hazardous concentrations of As (>500 $\mu\text{g/L}$). Near-surface release is initiated under As/Fe reducing conditions, which is stimulated in the oxbow channels (shown conceptually in Fig. 1B) by ample organic carbon inputs and permanently saturated conditions. Groundwater flow extends from the oxbow and the surrounding floodplain environment to the Mekong River (Fig. 1C), imparting a “plume-like” spatial distribution of As within a transect of our field site (Fig. 2A and Kocar *et al.*, 2008). Our simulation, which utilizes extensively field-calibrated biogeochemical and hydrologic parameters, accurately describes this distribution (Figs. 2A and 2B, respectively). Moreover, we show that subsurface alteration such as excavation (resulting in zones of higher hydraulic conductivity) will alter hydraulic flowpaths, and thus natural or anthropogenic physical impacts on the sediment profile will alter the subsurface spatial distribution of As (Fig. 2C). Altered (higher) hydraulic conductivity within surficial clays creates a large zone of greater flow velocity through the clay window and the underlying sandy aquifer extending toward the Mekong River, relative to surficial clay and aquifer sediments upstream of the clay window. Thus, within the high K window, continuously released As is diluted by faster groundwater flow (a larger water volume), which is reflected in

a more dilute “plume” emanating beneath the window (Fig. 2C). However, As concentrations remain locally high beneath the simulated wetland, both on the leading and trailing edge of the high As plume, where flow is relatively diminished but does not cease. On the trailing edge (closer to the Mekong River), As follows flowlines above the dilute plume, and is thereby elevated in concentration just below the clay layer. However, upstream of the dilute plume, the hydraulic gradient between the surface and the underlying aquifer is lower than the base case, resulting in lower porewater velocities and more accumulation of As in solution along the vertical flowpath, thus resulting in higher As concentrations within the underlying aquifer.

The results of these simulations are clear; only small differences in subsurface heterogeneity, including natural textural variations or anthropogenic perturbations (e.g., excavation) are required to completely alter the subsurface flow regime and, in parallel, the subsurface spatial distribution of As. Such alterations in flow should be considered prior to major alterations in the landscape or groundwater extraction. Further, the simulations stress the importance of the relationship between biogeochemical processes and hydrology. Future land use alterations in the Mekong Delta will disrupt groundwater flow and hence the sources of As will become even more obscured, shifting the spatial patterns of As concentration in groundwaters. Thus, wells containing low As ($<10 \mu\text{g/L}$), may become contaminated after hydraulic flow perturbation; it is therefore important that safe wells be periodically re-tested for As, especially after the onset of intensive irrigation pumping and large-scale excavation projects.

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REFERENCES

- Benner, S. G., M. L. Polizzotto, B. D. Kocar, S. Ganguly, K. Phan, K. Ouch, M. Sampson and S. Fendorf (2008): Groundwater flow in an arsenic-contaminated aquifer, Mekong Delta, Cambodia. *Appl. Geochem.*, **23**, 3072–3087.
- BGS and DPHE (2001): Arsenic Contamination of Groundwater in Bangladesh, ed. by D. G. Kinniburgh and P. L. Smedley, British Geological Survey, Keyworth.
- Cullen, W. R. and K. J. Reimer (1989): Arsenic speciation in the environment. *Chem. Rev.*, **89**, 713–764.
- Fendorf, S., H. A. Michael and A. van Geen (2010): Spatial and temporal variations of groundwater arsenic in South and Southeast Asia. *Science*, **328**(5982), 1123–1127.
- Goodbred, S. L. and S. A. Kuehl (2000): Enormous Ganges-Brahmaputra sediment discharge during strengthened early Holocene monsoon. *Geology*, **28**, 1083–1086.
- Harvey, C. F., K. N. Ashfaq, W. Yu, A. B. M. Badruzzaman, M. A. Ali, P. M. Oates, H. A. Michael, R. B. Neumann, R. Beckie, S. Islam and M. F. Ahmed (2006): Groundwater dynamics and arsenic contamination in Bangladesh. *Chem. Geol.*, **228**, 112–136.
- Khan, M. A., M. R. Islam, G. M. Panaullah, J. M. Duxbury, M. Jahiruddin and R. H. Loeppert (2009): Fate of irrigation-water arsenic in rice soils of Bangladesh. *Plant Soil*, **322**, 263–277.

- Kocar, B. D. (2008): Soil-Sediment Processes Responsible for the World's Largest Mass Poisoning through Release of Arsenic to Asian Groundwaters. Ph.D. Thesis, Stanford University.
- Kocar, B. D. and S. Fendorf (2009): Thermodynamic constraints on reductive reactions influencing the biogeochemistry of arsenic in soils and sediments. *Environ. Sci. Technol.*, **43**, 4871–4877.
- Kocar, B. D., M. J. Herbel, K. J. Tufano and S. Fendorf (2006): Contrasting effects of dissimilatory iron(III) and arsenic(V) reduction on arsenic retention and transport. *Environ. Sci. Technol.*, **40**, 6715–6721.
- Kocar, B. D., M. Polizzotto, S. Benner, S. Ying, M. Ung, K. Ouch, S. Samreth, B. Suy, K. Phan, M. Sampson and S. Fendorf (2008): Integrated biogeochemical and hydrologic processes driving arsenic release from shallow sediments to groundwaters of the Mekong Delta. *Appl. Geochem.*, **23**, 3059–3071.
- Mandal, B. K. and K. T. Suzuki (2002): Arsenic round the world: a review. *Talanta*, **58**, 201–235.
- Polizzotto, M. L., B. D. Kocar, S. G. Benner, M. Sampson and S. Fendorf (2008): Near-surface wetland sediments as a source of arsenic release to ground water in Asia. *Nature*, **454**, 505–508.
- Postma, D., S. Jessen, T. M. H. Nguyen, T. D. Mai, C. B. Koch, H. V. Pham, Q. N. Pham and F. Larsen (2010): Mobilization of arsenic and iron from Red River floodplain sediments, Vietnam. *Geochim. Cosmochim. Acta*, **74**, 3367–3381.
- Ravenscroft, P., K. Richards and H. Brammer (2009): *Arsenic Pollution: A Global Synthesis*. Wiley-Blackwell, New York.
- Smedley, P. L. and D. G. Kinniburgh (2002): A review of the source, behaviour and distribution of arsenic in natural waters. *Appl. Geochem.*, **17**, 517–568.
- Smith, E., R. Naidu and A. M. Alston (1998): Arsenic in the soil environment: A review. p 149–195. In *Advances in Agronomy*, Vol 64, ed. by D. L. Sparks, Academic Press, San Diego.
- Tufano, K. J. and S. Fendorf (2008): Confounding impacts of iron reduction on arsenic retention. *Environ. Sci. Technol.*, **42**, 4777–4783.

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