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Rice Field Geochemistry and Hydrology: An Explanation for Why Groundwater Irrigated Fields in Bangladesh are Net Sinks of Arsenic from Groundwater

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Abstract

Irrigation of rice fields in Bangladesh with arsenic-contaminated groundwater transfers tens of cubic kilometers of water and thousands of tons of arsenic from aquifers to rice fields each year. Here we combine observations of infiltration patterns with measurements of porewater chemical composition from our field site in Munshiganj Bangladesh to characterize the mobility of arsenic in soils beneath rice fields. We find that very little arsenic delivered by irrigation returns to the aquifer, and that recharging water mobilizes little, if any, arsenic from rice field subsoils. Arsenic from irrigation water is deposited on surface soils and sequestered along flow paths that pass through bunds, the raised soil boundaries around fields. Additionally, timing of flow into bunds limits the transport of biologically available organic carbon from rice fields into the subsurface where it could stimulate reduction processes that mobilize arsenic from soils and sediments. Together, these results explain why groundwater irrigated rice fields act as net sinks of arsenic from groundwater.

Introduction

Dry-season, groundwater-irrigated rice cultivation has increased food security and economic opportunity in Bangladesh (1). However, groundwater used to irrigate many fields is severely contaminated with geogenic arsenic. This irrigation arsenic is detrimental to agriculture and human health because it can enter the rice field soil (2-8), impacting the yield (8, 9) and arsenic content of the crop (3, 7, 10-13), and it can cycle back with

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Supporting information Available: Sampling analysis methods, additional data, calculation details, and field site pictures. This information is available free of charge via the Internet at <http://pubs.acs.org>.

recharging water to the shallow aquifer, which serves as the primary drinking and irrigation water supply for the country.

With respect to groundwater arsenic contamination in Bangladesh, existing literature points to two possible roles for rice agriculture. It may result in a net loss of arsenic from groundwater if rice fields sequester a majority of arsenic pumped up from the aquifer in irrigation water. It is estimated that, nationwide, irrigation removes ~1400 tons of arsenic from the aquifer each year and deposits this arsenic onto rice fields (14), and previous work at our field site in Munshiganj showed that recharge originating from rice fields evolves into low arsenic groundwater (15). Or, rice agriculture could add arsenic to the shallow aquifer if recharge recycles irrigation arsenic back to the aquifer and mobilizes arsenic from soils and deeper sediments beneath fields. In Bangladesh, arsenic is released into groundwater by Fe(III) and/or As(V) reduction driven by microbial oxidation of organic carbon (16). Net primary productivity is high in tropical rice fields ($1050 \text{ g C m}^{-2} \text{ yr}^{-1}$) (17), and rice field soils and water can contain elevated levels of organic carbon (20 g/kg (18) and 20 mg/L (19), respectively). Thus, rice fields could provide recharge that fuels the geochemical transformations that release arsenic from soils and sediments. A recent column experiment with soil collected from beneath a Bangladeshi rice field demonstrated that dissolved organic carbon produced in rice field surface water, post harvesting, facilitated arsenic mobilization (20). The result suggests that if recharge draws rice-field generated organic carbon into the subsurface, it could gain arsenic from the subsoil as it travels to the aquifer.

Most irrigation return-flow from our studied rice field flows through bunds, raised soil boundaries around field perimeters (21). Bund flow dominates recharge because soils beneath bunds are more transmissive than soil in the planted portion of the field (22, 23). Bunds are not removed when the field is plowed; therefore cracks and void spaces beneath bunds are not sealed like they are in the plow pan that underlies the field's interior (21, 24).

Timing of recharge through bunds is particularly relevant for arsenic fate. Bund flow is greatest immediately after irrigation when larger cross-sectional areas of bunds are covered by water (21, 25). Arsenic concentrations in ponded surface water are also greatest immediately after irrigation, when bund flow occurs, and decrease with time due to the formation of As-bearing iron aggregates and arsenic sorption to soil minerals (26). Correspondence between peak bund flow and maximum arsenic concentrations suggests that a significant fraction of arsenic applied to fields in irrigation water may enter bunds, avoiding the rice crop and potentially re-entering the aquifer.

Here, we attempt to clarify the role that rice fields play in Bangladesh's arsenic contamination problem. We combine characterizations of flow dynamics in our studied rice field (21) with chemical measurements from soil, surface water, and soil porewater to track arsenic and other key solutes as water is deposited onto the field via irrigation, transported into bunds, and recharged back to the aquifer. By using relationships between total recharge and the perimeter-to-area ratios of rice fields (21), along with published data for another field in our study area (2, 26, 27), we also describe the movement of arsenic in a second, larger field.

Methods

Field Site

Our field site is located in the Munshiganj district of Bangladesh, 30 km south of Dhaka and 7 km north of the Ganges River (Figure 1). Munshiganj is part of a cluster of nineteen districts (highlighted in grey in Figure 1) where, in 2007-2008, 70% of all rice produced was *Boro* rice (28-30). They produced approximately 37% of the country's 2007-2008 *Boro* crop, and enjoyed a higher than average yield (4.00 Mt ha^{-1} versus 3.79 Mt ha^{-1}) (28-30). Importantly, large areas of these districts are affected by elevated groundwater arsenic concentrations (Supporting Information, SI sec. 1).

At our site, *Boro* rice is usually planted in January and harvested in April or May. Groundwater with $\sim 400 \mu\text{g/L As}$ ($\sim 80\% \text{ As(III)}$) (26) is pumped from the aquifer and channeled through an irrigation canal into Field 1 at its southwestern corner and into Field 2 at its southeastern corner. In 2007, Field 1 (perimeter-to-area ratio of 0.1 m/m^2) received $134 \pm 5 \text{ cm}$ of water and $58 \pm 7\%$ flowed into bunds (21). Calculations utilizing perimeter-to-area relationships (21) suggest that seasonally, Field 2 (perimeter-to-area ratio of 0.07 m/m^2) receives $112 \pm 28 \text{ cm}$ of water and $37 \pm 10\%$ flows into bunds (SI sec. 2).

Field Campaigns

Water samples were collected from the surface and subsurface of Field 1 during the 2007 and 2008 irrigation seasons. See SI sec. 3 for a summary of samples successfully collected and analyzed during each campaign. In 2007, single-day sampling events were conducted in January, March and April. In 2008, multi-day sampling events that extended across an entire irrigation cycle were conducted in January and April. A bamboo structure was built for the 2008 season to access sampling locations without disturbing the rice field surface (see SI sec. 5 for pictures). Sampling procedures are described below; analysis details for water and soil samples are provided in SI sec. 6.

Water Samples

Soil porewater samples were collected with Prenart Super Quartz lysimeters, installed by pushing the lysimeter tip into the bottom of an augered hole and backfilling with $\sim 30 \text{ cm}$ of natural material followed by $\sim 15 \text{ cm}$ of locally obtained bentonite followed by natural material to the surface. Lysimeters were left to equilibrate for eight months before sampling.

A vacuum system was developed to extract water from the low-permeability soil. Samples were collected in foil bags with inner polypropylene lining (SKC Flex Foil bags). Laboratory tests indicated that oxygen permeated the bags at a rate of $0.03 \text{ mg}\cdot\text{L}^{-1}\cdot\text{hr}^{-1}$ (SI sec. 7). Bags were purged three times with argon immediately before they were attached to the lysimeter tubing and placed in a vacuum chamber. A $\sim 0.8 \text{ bar}$ vacuum was applied to suck water from the soil, through the lysimeters, into the bags. Chambers were covered with black plastic bags to deter photochemical oxidation (31), and all lysimeters were purged for a minimum of 12 hours before sampling.

After >100 ml of water were collected (~12 hours), a flow-through probe system containing pH, ORP, conductivity, temperature, and dissolved oxygen electrodes (Microelectrodes Inc.) was attached to the nozzle of the foil bag. All probes were calibrated on site prior to use. Water was slowly drawn from the bag through the probes directly into a plastic syringe, thereby avoiding atmospheric exposure. Both unfiltered and filtered (0.2 μm polyethersulfone membrane) subsamples from the syringe were collected, and left unacidified for alkalinity titrations, or acidified down to pH 1 with nitric acid for metal and cation measurements, and sulfuric acid for organic carbon measurements. The sulfuric acid did not oxidize organic carbon (SI sec. 8). Samples were kept in an ice-filled cooler during sampling and transport back to MIT.

Surface water samples were collected directly above soil porewater samples using plastic syringes and similarly processed.

Soil Samples

Soil cores were collected from bunds of Field 1 (January and May 2006) and Field 2 (May 2007) in two ~60 cm sections down to a depth of ~1.2 m using an AMS Multi-Stage Soil Core Sampler lined with plastic tubes. The corer was hammered into the ground and manually pulled out. Ends of retrieved, soil-filled tubes were capped with plastic caps for shipment back to MIT.

In Field 2, surface samples were collected May 2007 off bunds where they intersected the field surface by scraping the top 2 cm of soil into plastic collection bags. Three samples were collected at each location.

Results and Discussion

A. Porewater Chemistry and Arsenic Mobilization

Our data indicate that porewater concentrations in soils beneath rice fields are consistent with recharge pathways. To demonstrate this similarity, we summarize the infiltration patterns described in detail by Neumann et al. (21). Most irrigation water applied to fields rapidly enters and flows through bunds, while the remainder infiltrates through the plow pan (Figure 2a). Water that infiltrates through the plow pan either enters isolated macro-pores within the subsoil or penetrates only ~40 cm into the soil matrix (21). Thus, away from bunds, most porewater below 40 cm is residual water that did not originate from recent irrigation. It entered the subsoil during previous irrigation seasons and/or previous transitions between irrigation and monsoon seasons. Consequentially, this water beneath the central part of the field was exposed to oxygen when the field dried out at the end of previous irrigation seasons. We estimate it takes ~12 years for residual water to travel from the field surface to the aquifer (SI sec. 9).

Porewater that entered during the current irrigation season, whether sampled beneath bunds or directly beneath the plow pan, has consistent chemical characteristics that distinguish it from residual water. Recently infiltrated water contains higher concentrations of As, Mn, Fe and dissolved organic carbon than residual water (Figure 2c-f). The deepest sample from location C, however, represents a possible exception. Based on large volumes of water

collected by this lysimeter (SI sec. 10), we hypothesize that this location received water infiltrating through a macro-pore during the ongoing irrigation season.

While recently infiltrated water contains slightly more DOC than residual porewater, its DOC concentrations are unexpectedly low; they are equal to or lower than that measured in irrigation water applied to the field (7.7 mg/L (26)) and much lower than DOC concentrations measured in ponded surface water a few days after irrigation (13 mg/L, Figure 2c). Low DOC concentrations within bunds are related to bund-flow dynamics. Bund flow peaks immediately after irrigation (Figure 3e and 3f) when DOC concentration in ponded water is low, matching that measured in irrigation water; bund flow decreases with time after irrigation as the ponded water gains DOC (Figures 2 and 3). Thus, a majority of DOC flowing into bunds is likely older, more recalcitrant DOC pumped up with irrigation water, rather than young DOC generated within the field.

These measurements were made within 25 meters of the irrigation inlet. Data from Roberts et al. (26) show that immediately after irrigation, at distances greater than 50 m from the inlet, DOC concentrations in surface water increase at a rate of ~ 0.2 mg/L per meter, presumably due to mobilization of carbon off the rice field surface. These data suggest that in larger fields, at the far corner opposite the irrigation inlet, a greater proportion of rice-field generated organic carbon may enter bunds. This phenomenon is likely unimportant for Field 1 with a center-transect length of only 59 m.

Porewater ~ 10 cm beneath the plow pan (Figure 2c) also contains low DOC concentrations relative to ponded surface water. This porewater slowly infiltrated through the organic-rich muck layer sitting above the plow pan, and low concentrations suggest that DOC is attenuated by sorption onto soil (32) and/or quickly oxidized by air that may imbibe soil beneath the plow pan (Figure 2a and (21)).

Although DOC in recently infiltrated porewater is less than that in overlying surface water, our data suggest that recharge from the rice field carries some, ~ 4 mg/L (Figure 2c), biologically available organic carbon (BDOC) into the subsurface. Mineralization of this BDOC accounts for decreasing DOC (Figure 2c) and increasing dissolved inorganic carbon concentrations (SI sec. 11) within bunds, as well as As, Fe and Mn concentration differences between recently infiltrated porewater and residual porewater deeper beneath the rice field (Figure 2). However, water sampled from the deepest bund lysimeter in April 2008 lacked BDOC (15), indicating that BDOC is mineralized within the top ~ 1.7 m of the field. This mineralization process does not mobilize arsenic from the subsoil. Dissolved arsenic concentrations in recently infiltrated porewater within bunds and directly beneath the plow pan are an order of magnitude lower than that in irrigation water, and have no clear trend with depth (Figure 2d and (15)). Lack of arsenic mobilization is likely due to a large K_d value (~ 1000 L/kg for bunds from data in Figure 2 and 5: $(10 \text{ mg/kg})/(10e-3 \text{ mg/L})$) that is sustained over time by the field de-saturating between irrigation events and oxidizing down to a depth of at least 2 m after rice is harvested (21).

B. The Fate of Arsenic from Irrigation Water

The previous section demonstrated that rice field recharge does not mobilize arsenic off soils beneath fields, largely because BDOC is not transported into the subsurface with recharging water. In this section, we track the fate of arsenic applied to fields in irrigation water. Knowledge of both components is required to understand the role that rice fields play within the contamination problem.

B.1. Arsenic in Ponded Rice Field Water: Irrigation of Wet and Dry Fields—The first step in tracking arsenic is to determine the loss of arsenic from ponded surface water after irrigation. When irrigation water was added to Field 1 while it was dry (multi-day sampling campaign, April 2008), arsenic concentrations decreased with increasing distance from the irrigation inlet (Figure 4a), matching the pattern previously observed under similar conditions in Field 2 (26). However, when irrigation water was added to Field 1 while it was still flooded (multi-day sampling campaign, January 2008), the spatial concentration trend did not clearly develop. A few hours after the January irrigation event, only $9\pm 3\%$ of irrigation arsenic was lost from the water column at five sampling points within a 25 m distance from the irrigation inlet. This calculation accounts for the dilution of ~ 4 cm of irrigation water with ~ 2 cm of existing, low arsenic water (Figure 3a). In contrast, during the April irrigation event, at the same five points, $19\pm 3\%$ of arsenic was lost from the water column (SI sec. 13).

Thus, the immediate loss of arsenic from the water column (Figure 4a and (26)) appears to depend on irrigation water interacting with the soil surface as it moves across the field. Solid phase arsenic data from Field 2 follow the same pattern as dissolved concentrations; they are elevated near the irrigation inlet and decrease with increasing distance from the inlet (2). Field 2 is generally irrigated when dry (26), and thus the combined data sets (2, 26) demonstrate that under this irrigation condition, the surface soil efficiently removes arsenic from the water column. Exposure to soil sorption sites and contact between As-bearing iron particles and soil are likely lower when irrigation water mixes with existing water in the field rather than flowing through soil pore space. After irrigation water has spread across the field, the subsequent, slower loss of arsenic from the water column appears independent of initial soil conditions; 80 to 90% of arsenic was lost from the water column within three days of irrigation for both sampling events (Figures 3g–h and SI sec. 13).

The different rates of arsenic loss immediately following irrigation in wet or dry fields imply that farmers' irrigation practices influence arsenic fate. When irrigation water is added to flooded fields, less arsenic immediately enters surface soils, and thus, more arsenic is available to flow into bunds where it does not impact the rice crop but has the potential to recycle back into the aquifer.

B.2. Arsenic Fluxes into Bunds and Surface Soil—Arsenic that remains in the ponded surface water immediately after irrigation is transported into bunds. The cumulative flux of arsenic entering bunds is the time integration of the volumetric water flux from ponded surface water and the concentration of arsenic in this water. Hourly fluxes of water into Field 1 bunds for the January and April 2008 sampling events are presented in Figures

3e–f, and were calculated from water level data (Figures 3a–b), meteorological data, and estimates of other water inputs and outputs (SI sec. 15). Except during the January rainstorm, estimated bund water fluxes increased and decreased with field water level (Figures 3a–b, e–f), supporting the understanding of bund flow developed by Neumann et al. (21). Lack of bund flow during the rainstorm is due to the groundwater level topping the plow pan (Figure 3c); the downward hydraulic gradient driving flow was erased by a regionally rising water table.

Hourly arsenic fluxes into bunds (Figures 3i–j) were determined by combining estimated bund water fluxes (Figures 3e–f) with surface water arsenic concentrations (Figures 3g–h). Arsenic concentrations in surface water were assumed uniform for the January event and spatially trending for the April event. An hourly concentration function was constructed from daily measurements by assuming an exponential decay between data points, and, for the April event, by assuming that the spatial trend in the five sampling locations in Field 1 (Figure 4a) extended across the entire field and matched trends measured across other fields in the study area that were irrigated when dry (SI sec. 16). Figures 3i–j illustrate that bunds received a pulse of arsenic with each irrigation event. Proportionately less arsenic entered bunds during the April sampling event than during the January event ($32\pm 3\%$ versus $49\pm 11\%$ of irrigation input) due to more arsenic sequestration by surface soils when water was added to a dry field.

Assuming that the percentages of arsenic entering bunds during the January and April sampling events are representative of irrigation events under flooded and dry conditions, respectively, and considering that for Field 1, between January and April, $28\pm 7\%$ and $72\pm 9\%$ of irrigation water was applied to a wet and dry field, respectively, we calculate that Field 1 lost $37\pm 7\%$ of its seasonal irrigation arsenic into bunds (SI sec. 17).

Most arsenic that enters bunds does so immediately after irrigation when both water fluxes and arsenic concentrations are high. Combining the total bund water flux, a function of the perimeter-to-area ratio (21), with the spatially averaged arsenic concentration measured in surface water immediately after irrigation estimates that Field 1 lost 185 ± 38 mg/m² or $33\pm 7\%$ of its irrigation arsenic into bunds (SI sec. 18). This number is not significantly different than that calculated above using percentages from the two sampling campaigns, and implies that arsenic bund fluxes for any field can be determined from initial arsenic concentrations and perimeter-to-area ratios. The method predicts that Field 2 loses 85 ± 34 mg kg⁻¹ year⁻¹ or $19\pm 8\%$ of irrigation arsenic into bunds (SI sec. 18), assuming, as suggested in the studies of Roberts et al. (26), that Field 2 is always irrigated when dry. In agreement with this number, a multi-year soil study of Field 2 (27) estimated that $0 - 95$ mg kg⁻¹ year⁻¹ (best guess: 40 mg kg⁻¹ year⁻¹) of irrigation arsenic was lost from the top 40 cm of soil to percolating water. Our data suggest this arsenic loss is due to bund flow.

B.3. Porewater Arsenic within Bunds—Immediately following an irrigation event, surface-water arsenic pulses into bunds. However, porewater samples collected from multiple depths beneath bunds of Field 1 during both the January and April 2008 sampling events showed no corresponding change in arsenic concentration (Figures 3k–l); concentrations remained steady over both irrigation cycles. Only the shallowest lysimeter at

location F, the location closest to the irrigation inlet, showed a slight increase in arsenic (55 to 62 $\mu\text{g/L}$) after the April irrigation event (Figure 3l).

Based on spatial patterns of surface water arsenic concentrations (Figure 4a), more arsenic enters bunds closer to the irrigation inlet. Between January and April, porewater concentrations in the shallow (30 cm) lysimeter located closest to the irrigation inlet increased by $\sim 40 \mu\text{g/L}$ while the shallow lysimeter located furthest from the inlet increased by an insignificant amount (Figure 4b). However, concentrations in all deeper lysimeters (100 cm), regardless of their proximity to the irrigation inlet, either did not increase or increased by only $\sim 2 \mu\text{g/L}$ (Figure 4c). These data demonstrate that on a seasonal time scale, bund arsenic fluxes impact shallow porewater concentrations, but have a negligible impact on deeper porewater concentrations. In fact, the arsenic concentration trend in the deeper lysimeters was opposite to the loading; concentrations decreased towards the irrigation inlet (Figure 4c). Over two field seasons, porewater samples collected beneath bunds at depths of 1 m or more had arsenic concentrations below 25 $\mu\text{g/L}$, an order of magnitude less than that in irrigation water (Figures 2e, 3k–l, 4b–c and (15)).

Lack of a strong response by porewater concentrations to the spatial and temporal nature of arsenic entering bunds is not explained by a slow travel time for irrigation water; we estimate that bund water from a single irrigation event reaches, at a minimum, the two shallowest lysimeters (SI sec. 19). Thus, consistent concentrations suggest that most arsenic entering bunds is sorbed by bund soil or transported to depth via preferential flow, bypassing lysimeters. However, based on the volume of collected water and a chloride concentration response to irrigation (SI sec. 10), we believe the deepest bund lysimeter (168 cm) at location A is installed within a macropore (similar to the deepest lysimeter at location C). Concentrations within this bund lysimeter ($12 \pm 2 \mu\text{g/L}$) suggest that even within preferential flow channels, most arsenic is sorbed by soil.

B.4. Solid Phase Retention of Arsenic—Field 1, the smaller field with a larger perimeter-to-area ratio, receives more irrigation water, and thus more arsenic, per area than Field 2 (553 ± 24 versus $437 \pm 110 \text{ mg/m}^2$). However, it also loses proportionately more arsenic into bunds (185 ± 40 versus $85 \pm 34 \text{ mg/m}^2$ for Field 1 and 2, respectively). These two effects largely counteract such that surface soils of both fields retain similar amounts of arsenic, 368 ± 47 and $352 \pm 115 \text{ mg/m}^2$ for Field 1 and 2, respectively. In agreement, Dittmar et al. (27) estimated that the top 10 cm of Field 2 gains $330 \pm 30 \text{ mg/m}^2$ As during the irrigation season. Perimeter-to-area calculations predict that in our study area, surface soils of all fields retain between 300 and 500 mg/m^2 of arsenic during the irrigation season, with larger fields (smaller perimeter-to-area ratios) retaining smaller amounts (SI sec. 20).

Solid-phase arsenic concentrations measured in bund soils are elevated, reaching almost 60 mg/kg . Cores taken through bunds illustrate that arsenic is retained within the top 30 cm (Figure 5). This retention pattern agrees with both low concentrations of arsenic measured in shallow bund porewater ($\sim 5 \text{ cm}$ depth, Figure 3 and (15)) and rice field flow patterns (Figure 2a). Initially, water flowing into bunds is focused into a small volume of soil, resulting in high solid phase concentrations. Beneath bunds, water spreads out laterally through a larger area resulting in lower solid phase concentrations.

C. Net transfer of Arsenic from Groundwater to Rice Fields

The shallow aquifer is recharged by water flowing through bunds and isolated macro-pores in subsoil beneath the planted portion of fields (21). Arsenic concentrations are low within the sampled macro-pore beneath the planted portion of Field 1 (location C, Figure 2e), and thus this recharge pathway appears to return a minimal amount of irrigation arsenic back to the aquifer ($<1 \text{ mg/m}^2$, SI sec. 21). Water within bunds flows through both the soil matrix and bund macro-pores. Dissolved concentrations are low along both bund pathways. Assuming that bund water recharging the aquifer contains $12 \pm 2 \text{ } \mu\text{g/L}$ As, the concentration in the presumed bund macro-pore, we estimate that bund recharge in Field 1 and Field 2 recycles 9 ± 2 and $4 \pm 1 \text{ mg/m}^2$ As, respectively, back to the aquifer (SI sec. 21). These amounts equate to only $\sim 2\%$ of arsenic applied in irrigation water.

Water level data ((21) and SI sec. 12) demonstrate that towards the end of the irrigation season, fields are irrigated less frequently, which could potentially cause surface soils to dry and the plow pan to crack. Although arsenic concentrations in all porewater samples collected from Field 1 in April and May are low ($<20 \text{ } \mu\text{g/L}$), data from Field 2 (34) suggest that towards the end of the season, high-arsenic water may enter the subsurface through a broken plow pan. If all arsenic applied with irrigation during this period recycles back to the aquifer, an unlikely occurrence, the postulated process could increase the amount of arsenic recharging the aquifer by 40 mg/m^2 (SI sec. 21). Thus, at most, we estimate $\sim 10\%$ of arsenic applied to rice fields with irrigation water may return to the aquifer.

Our data indicate that rice fields remove arsenic from the shallow aquifer. Only a small amount of irrigation arsenic recycles back to the aquifer, and most rice-field generated organic carbon, which can promote reductive dissolution and arsenic mobilization within the subsurface (20), is retained within the field surface (Figure 2). BDOC that does manage to enter bunds is oxidized before it reaches a depth of 1.7 m (15), and it does not mobilize arsenic from soils beneath rice fields (Figure 3, 4 and (15)), explaining why rice field recharge evolves into low-arsenic groundwater (15). We believe these results are likely representative of other puddled Bangladeshi rice fields surrounded by raised bunds and irrigated with arsenic-contaminated groundwater.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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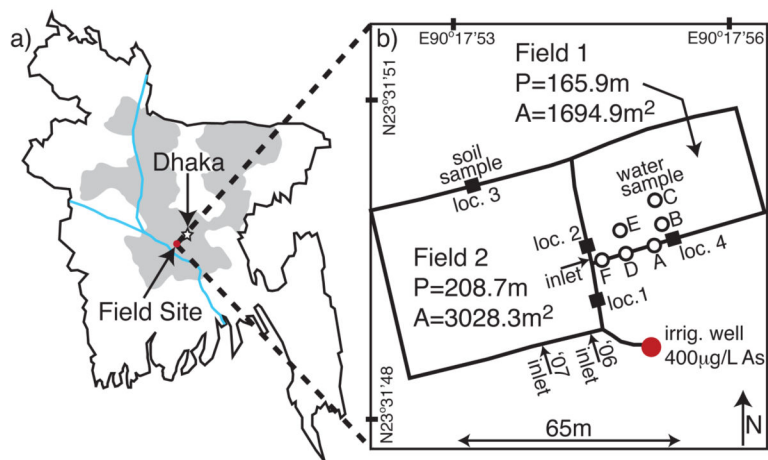


Figure 1. Site overview

- a) The grey shading highlights the cluster of nineteen districts where 70% of all 2007-2008 produced rice was *Boro* rice.
- b) Circles mark surface and porewater sample locations. Squares mark soil sample locations. Neumann et al. (21) worked in Field 1, while Roberts et al. (26, 34) and Dittmar et al. (2, 27) worked in Field 2.

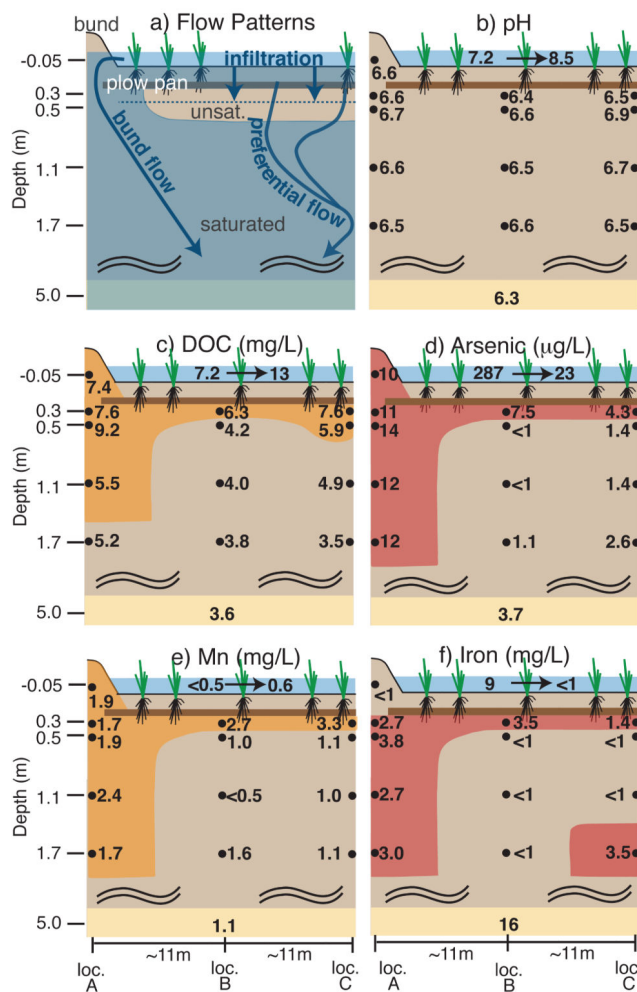


Figure 2. Chemical data along transect extending from location A to C

Black dots mark lysimeter locations and numbers show the average of concentrations measured for all sampling events (see SI sec. 3 for data tables). The aquifer concentration, located at 5-m depth, represents the average of samples collected January 2008 from 4.8-m- and 5.3-m-deep wells installed in Field 1.

a) Flow patterns in Field 1 determined by Neumann et al. (21).

b–f) Chemical data. In panels (d–f), red and orange shading highlights that recently infiltrated porewaters have higher concentrations than residual water, with red shading signifying a larger difference than orange shading. Iron concentrations suggest that the deepest lysimeter at location C was installed in a macro-pore. In panel (c), orange shading suggests recently infiltrated water contains BDOC. Incubations demonstrated that the deepest bund lysimeter lacks BDOC (15).

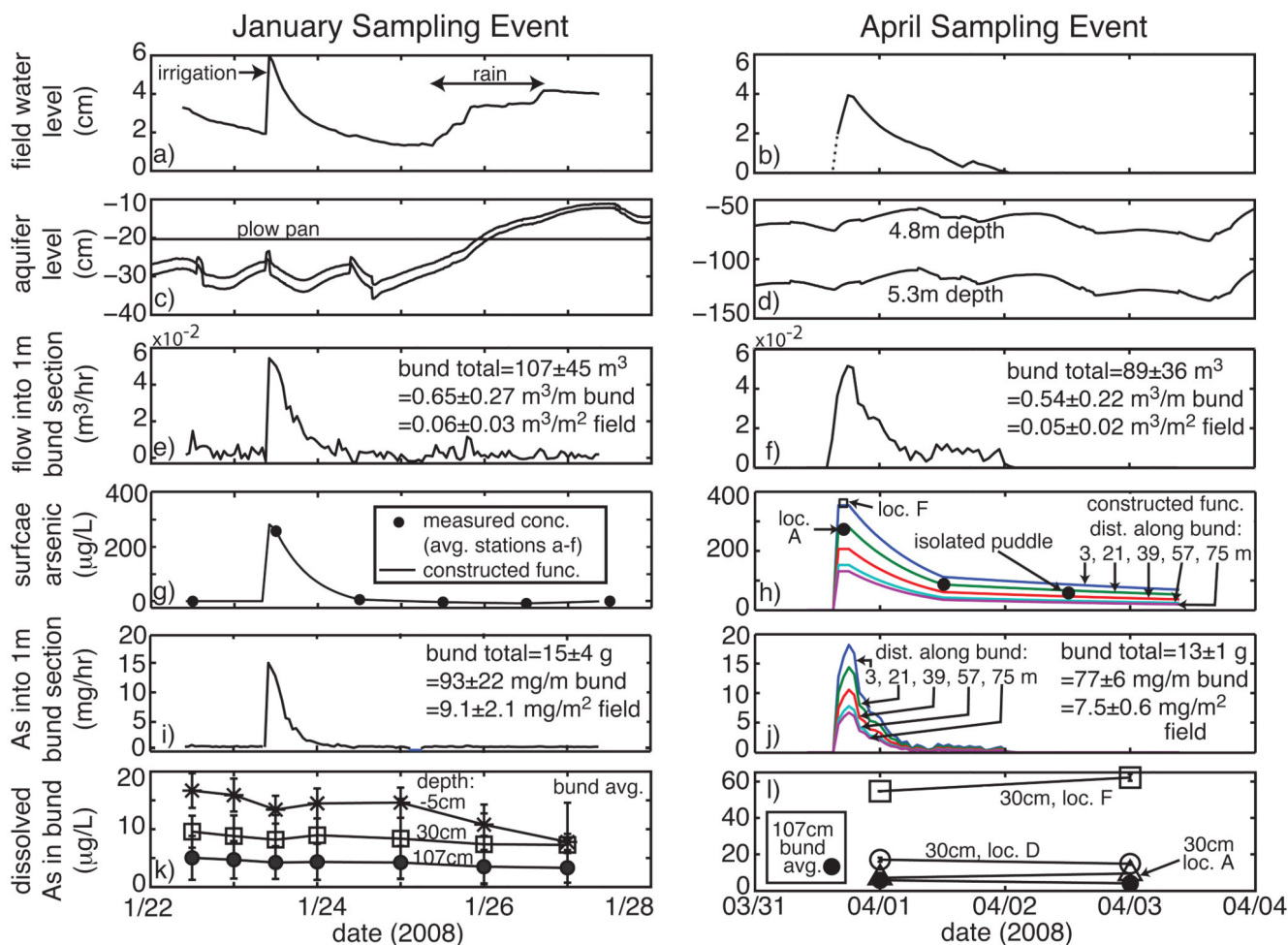


Figure 3. Surface water, bund flux and bund porewater for Field 1 versus time for the January and April 2008 sampling campaigns

(a,b) Ponded surface water depth.

(c,d) Shallow aquifer head, referenced to the rice field surface.

(e,f) Flow of surface water into bunds per unit length of bund.

(g,h) Measured and constructed arsenic concentrations for field surface water.

(i,j) Arsenic flux into bunds per unit length of bund.

(k,l) Unfiltered arsenic concentrations in bund porewater. The -5 cm-deep concentration in (k) is from location A (error bar represents analytical uncertainty) while the 30 cm- and 110 cm-deep concentrations represent the average from locations F, D and A (error bars represent one standard deviation). In (l), the 110 cm-deep concentrations represent the average from locations F, D and A.

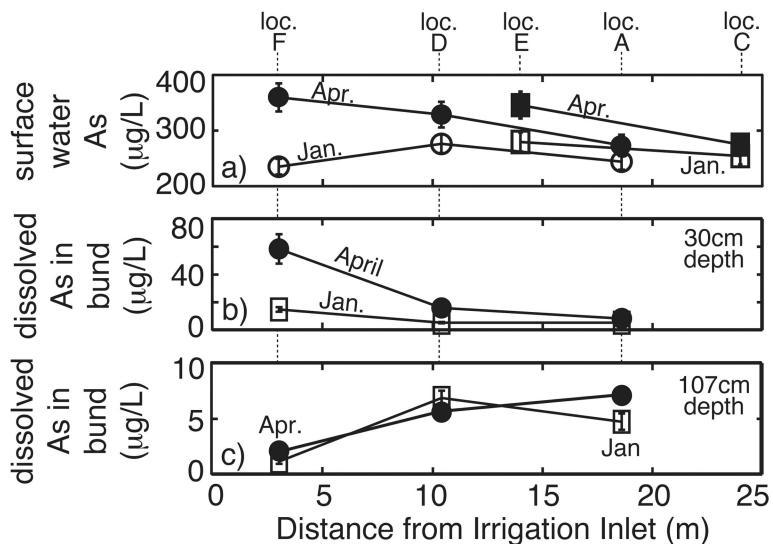


Figure 4. Surface water, bund flux and bund porewater for Field 1 versus distance from the irrigation inlet for the January and April 2008 sampling campaigns

All error bars represent analytical uncertainty.

- (a) Unfiltered arsenic concentrations in surface water immediately after (January) and during (April) an irrigation event. Squares mark locations directly adjacent to bunds. Circles mark locations that fall along the field's center transect.
- (b, c) Unfiltered arsenic concentrations in bund porewater at 30 cm and 100 cm depths, respectively.

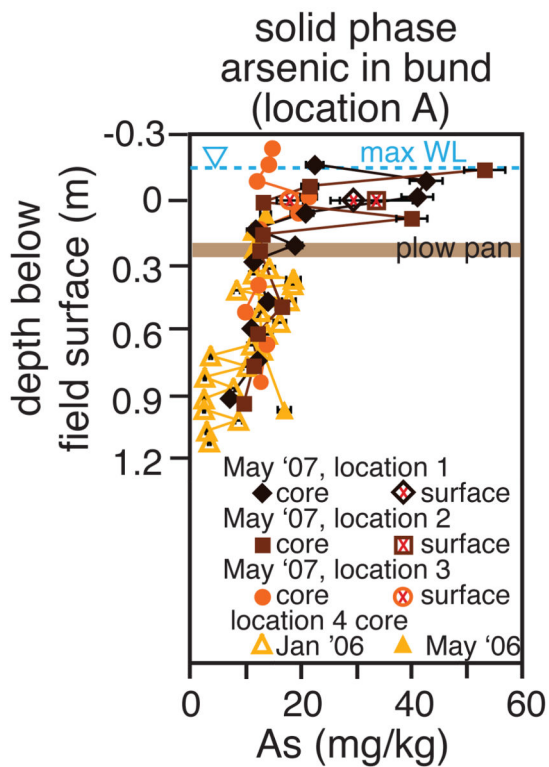


Figure 5. Solid-phase arsenic in bunds

Solid phase arsenic concentrations measured in cores and surface samples collected from bunds (Figure 1). Locations for the maximum height of ponded water and the plow pan are marked for reference.