Do Ponds Cause Arsenic-Pollution of Groundwater in the Bengal Basin? An Answer from West Bengal

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We report time-series data collected over two years for $\delta^{18}O$, δ^2H, and Ca, Mg, K, and Cl, concentrations for 10 ponds in, and upflow of, an As-polluted region of southern West Bengal. We compare the compositions of As-polluted groundwaters from wells with the compositions of waters in ponds upflow, and within the range of influence, of the wells. Conservative tracers ($\delta^{18}O$, δ^2H, K), and other tracers (Ca, Mg) that are likely conservative in the waters, show that pondwater and groundwater are distinct and do not overlap in composition. These data show that water from ponds cannot be identified in As-polluted groundwater, so putative DOC in pondwater cannot be mixing into the As-polluted groundwater we have sampled. Separate estimates of the degree of recharge from ponds to groundwater, using calculations based on temporal variations in salt content and isotopic composition in ponds, and salt-balance, show that insignificant amounts of As-polluted groundwater are derived via pond recharge. It follows that pondwater in the study area does not contribute significant mass to arsenic-polluted groundwater and so does not provide organic matter to aquifers in amounts sufficient to drive reduction of iron oxyhydroxides and hence arsenic pollution.

Introduction

Serious pollution of groundwater in alluvial aquifers by dissolved arsenic occurs worldwide and is a cause for global concern. In the Bengal Basin, many millions of people have been exposed to water containing >10 μg/L As (the WHO guideline value) drawn from alluvial aquifers (*1–5*). In most cases of As-pollution of groundwater worldwide, the arsenic derives from microbial reduction of iron oxyhydroxides (FeOOH) which releases to groundwater the As sorbed to the dissolving host oxide (*6–8*, et seq.), although in a few localities other mechanisms might operate; e.g., in Argentina (*9*) and the southwest U.S. (*10, 11*). Reduction of iron oxyhydroxides is driven by microbial oxidation of carbon in organic matter (*12, 13*) and such microbial reduction is evident in aquifers of the Bengal Basin, both because they contain dissolved Fe(II), and because microbial activity has been observed in situ in the aquifer (*14*) and in laboratory culture using sediments from the aquifer (*15–17*).

Identifying the source(s) of the organic matter (OM) that drives FeOOH reduction in alluvial aquifers is an important goal because the availability of OM is one of the factors that governs the degree and duration of the pollution process. Mobilization of arsenic into groundwater will continue as long as arsenic-bearing FeOOH is available for reduction, and organic matter is available to drive reduction. If the source of OM is anthropogenic, e.g., from ponds, unsewered sanitation, or surface soils, concentrations of OM will never decline, so any decline in pollution will depend entirely on exhausting the sedimentary store of arsenic in FeOOH. If the source of OM is in subsurface sediments, concentrations of OM will decline over time, so driving downward the degree of pollution (but at what rate is unclear). It follows that any link that can be established, or broken, between arsenic pollution and any source of OM will be valuable to aquifer development and remediation.

Here we test the hypothesis that pond-derived OM drives subsurface redox reactions, and so arsenic pollution (*14, 18*). In doing so, we deliberately have not measured dissolved organic carbon (DOC) in pondwater or groundwater because DOC is not conservative in solution. For example, water leaking from ponds to underlying aquifers might either derive DOC from organic-rich bottom muds, or lose it through bacterial oxidation during passage through such muds. In addition, DOC may be sorbed to sediment particles during flow through the aquifer, or new DOC may be added by diffusion from aquitards, intercalated organic-rich lenses of sediment with the aquifer, or the aquifer itself. Finally, DOC may be present but not labile, so measurements of DOC concentration may mislead.

To overcome such difficulty, we trace the degree to which pondwater mixes with groundwater using conservative tracers. Our approach is based on the fact that a putative OM-rich water that derives from a pond, and evolves into As-polluted groundwater, must carry with it the conservative tracers present in the original pondwater. A groundwater from which pondwater tracers are absent will not contain a component of pondwater and so will not contain a component of pond-derived DOC. The conservative tracers of pondwater we use are those in the water molecule itself ($\delta^{18}O$, δ^2H), a conservative dissolved tracer (K), and two other tracers that are seemingly conservative in our waters (Ca and Mg). With these tracers, we examine whether As-polluted groundwater derives partly or wholly from ponds, and so test the role of pond-derived OM in driving reduction of FeOOH and arsenic pollution. We confirm our findings using mass-balances that provide estimates of leakage from ponds to underlying aquifers.

The Field Area. The study region comprises the three contiguous villages of Joypur, Ardivok and Moyna, 40 km NE of Kolkata (JAM hereinafter; Figure 1 and Supporting Information Figure S1). The area, and the distribution of arsenic within it, have been described elsewhere (*19*), so only a brief description is given here, and only of the arsenic-

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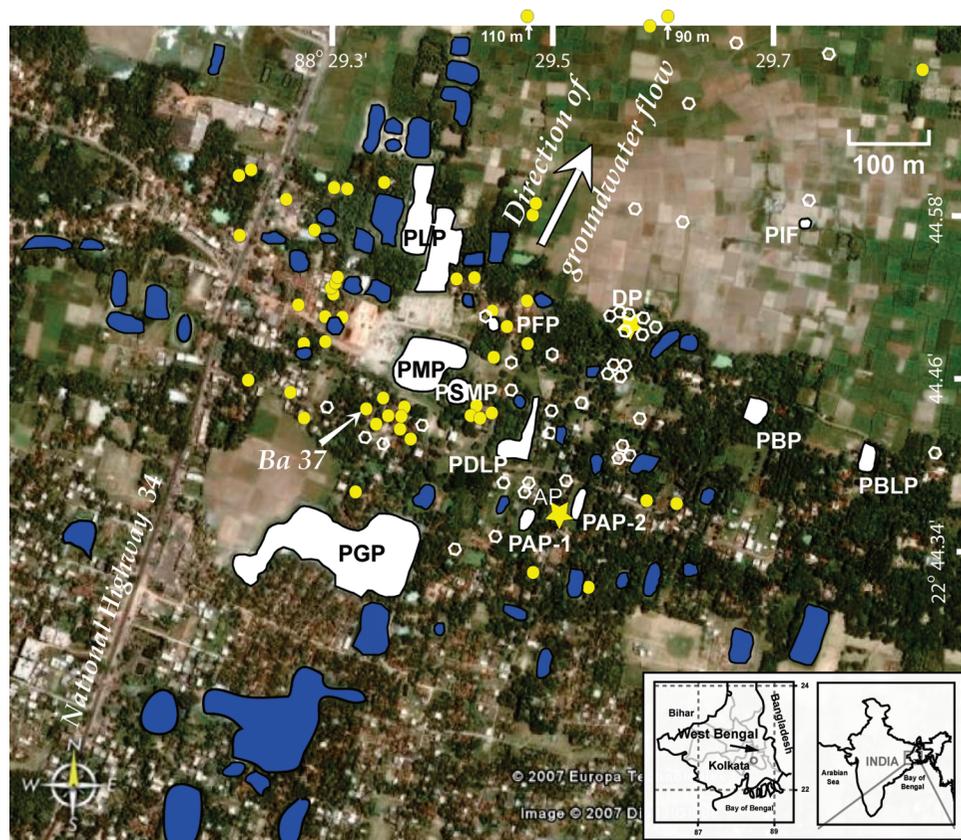[†] Indian Institute of Technology.
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FIGURE 1. Map of the JAM study area. For well numbers, see Figure S1 in the Supporting Information. Groundwater flow between depths of 20 and 45 m (the base of the shallow aquifer) is to the north northeast at a rate of 0.1 m per day, and vertically at similar, but site-dependent, magnitudes (*19, 20*). Filled stars are piezometer nests (*19*). Filled yellow circles denote wells with $>50\mu g/L$ As (*19*). Open white hexagons denote wells with $<50~\mu g/L$ As (*19*). Sampled ponds are shown as white; unsampled ponds are shown as blue. Pond labels (PLP etc.) are acronyms used for identification of ponds in the text. Base map from Google Earth; copyright 2006 Europa Technologies, 2006 DigitalGlobe, used with permission.

polluted part of the aquifer. The As-polluted aquifer in JAM is around 30 m in thickness and composed of gray sand of Holocene and Late Pleistocene age. It lies beneath an upper aquitard of dark gray, and sometimes peaty, silt that extends from the land surface to between 6 and 15 m below it. Beneath the base of the shallow As-polluted aquifer, at around 45 m depth, lies a clay aquiclude some 30 m in thickness. This lower aquiclude separates the shallow aquifer from an underlying deep aquifer of gray Pleistocene sand that is essentially arsenic-free. In the polluted regions of JAM, groundwater contains $>50~\mu g/L$ (Figure 1; ref *19*) over all, or locally the upper 90%, of the aquifer thickness and concentrations up to 1410 $\mu g/L$ have been recorded. Most wells tap the lower part of the aquifer at 30−45m depth (for depths of individual wells, see ref. *19* and Supporting Information Tables), because local knowledge tells that the base of the aquifer produces better quality water than do shallower levels.

Piezometry shows that horizontal groundwater flow in the shallow aquifer is to the north northeast at a rate of around 0.1 m per day, and at site-dependent rates of a similar magnitude vertically (*19, 20*). The flow direction is a response to natural hydraulic gradients and pumping of groundwater for irrigation from wells located in the fields between 150 m and 2 km to the northeast of the populated region in southern JAM. There is always a downward hydraulic gradient from the upper aquitard to the underlying aquifers (*19, 20*) an observation that eliminates the possibility of a deep source of recharge. There are no streams or rivers locally that could act as significant sources of recharge to the area's aquifers: the Hoogly River runs N−S some 15 km west of the area, which is too far for it to be an influence on JAM's hydrogeology. The Sunti River borders the area's eastern edge,

and the east−west trending Sunti Channel is some 1.5 km to the north. The Sunti River and Sunti Channel are infilled in stretches, ponded elsewhere, and do not flow, even in the monsoon season. Our study area is never flooded by river water. There are, therefore, no realistic alternative sources of local recharge to aquifers other than through surface soils, and via the numerous ponds in our area (Figure 1).

Ponds are designated by three- or four-letter acronyms that are based on abbreviations of local names. The 10 ponds studied in detail, and another, PIF, sampled less frequently, are shown in white on Figure 1; ponds not studied are shown in blue. Most wells are sited within 30 m of a pond, and some are closer (Figure 1); the majority of wells studied here are down-gradient of the largest ponds in JAM (PGP, PMP) and down-gradient of other large and small ponds further to the south southwest that we have not sampled (Figure 1). Sampled ponds vary in size from 300 m² (PFP) to 22 500 m² (PGP); they are used for aquaculture or washing; one, PLP, is also used for irrigation. Ponds are excavated to a typical depth of around 3.5 m within the upper aquitard, and pond construction and infilling occurs today in the field area. All sampled ponds existed in 2001, when our study commenced. The larger ponds have a history extending in time beyond local memory, with PGP and PMP documented on the Ordnance Survey map 79/B6 as present in 1965. In JAM, ponds are potential sources of recharge to groundwater because pondwater levels are always above the water table, as they are at Munshiganj (*18*) and Araihazar (K.M. Ahmed, personal communication) in Bangladesh. All ponds are recharged by rainfall only. During the dry season, pond-bases in JAM are perched 2−3 m above the water table.

period	$\delta^{18}O$ ‰	δ^2H ‰
June, 2004 and 2005	−3.78	−19.2
July, 2004 and 2005	−5.39	−36.3
August, 2004 and 2005	−5.17	−32.1
September, 2004 and 2005	−7.31	−47.5
October, 2004 and 2005	−11.8	−84.1
Total, June 2004 to October 2005	−6.20	−39.9
Intercepts on LMWL		
large ponds	−8.87	−61.0
all ponds	−9.24	−64.0
groundwaters, < 50μg/L As	−5.82	−37.0
Groundwater, Feb 04		
least ^{18}O enriched	−5.0	−35.0
most ^{18}O enriched	−2.1	−19.9
Pond means, Feb 04- Feb 06		
PGP	−1.4	−20.0
PLP	−0.6	−13.6
PMP	+0.1	−12.6

[a] Period means for rain data are computed from data of ref 21, with correction of 251 mm rainfall (not 51 mm) for late July, 2005.

Measurements of local and regional hydraulic gradients and hydraulic testing (19, 20) suggest that wells are in hydraulic continuity with ponds. The region is monsoonal and receives about 1.3 m of rain a year, mostly between June and October (21). The annual pan evaporation is around 1200 ± 10 mm/year ($n = 3$; the uncertainty measure, here and elsewhere in this paper, is ±1 standard deviation), as measured in 24-Parganas North and South by the West Bengal State Agricultural Meteorological Cell.

Analytical Methods and Results

Using a surveyor's staff and Abney level, water levels were measured monthly in ponds over one evaporative cycle. Measurements were relative to local benchmarks at each pond that were surveyed-in by laser-theodolite. Pondwaters were collected at 1−2 monthly intervals from February 2004 to February 2006. We sampled a distance of about 4 m from the edge of each pond using an integrating depth-sampler. Pondwaters were filtered through 0.45 μm acetate filters; groundwater samples were not filtered, but were crystal clear. Samples analyzed for cations were acidified in the field with Analar nitric acid to make them 1.5% acid; samples for anion analysis were not acidified. Anion samples were left without airspace and subsampled for isotopic analysis on return to the laboratory. Analysis for cations was done using a Perkin-Elmer ICP-AES. Analysis for anions was done using a Dionex ion chromatograph. Precision was better than 5% in both cases as judged by replicate analysis. Stable isotopic analysis was done by standard methods of gas-source mass spectrometry either at IIT Kharagpur, or at NIGL: an interlaboratory comparison of standards shows that data agree within analytical uncertainty of each laboratory (< ±0.1‰ for $\delta^{18}O$, 1.0 ‰ for δ^2H). All data used here are given in Tables 1 and 2, and Supporting Information Tables 1−3.

Ponds and As-Pollution. The distribution of arsenic pollution in groundwater of the Bengal Basin is not known; what is known is the distribution of arsenic pollution in water wells (22–24). Water wells are sited where there are people, and where there are people there are usually ponds, the traditional source of water for domestic use in the dry season. Because wells and ponds are usually closely juxtaposed, it is possible that OM in ponds might locally infiltrate the aquifer

and pollute nearby wells by driving local FeOOH reduction and As release (14, 18). Additionally, although ponds cover only a small area of the study region, the influence of recharge from ponds may be greater than this limited areal extent implies because ponds, at least in JAM, are dug into the silt aquitard overlying the shallow aquifer, thereby potentially reducing the hydraulic resistance to infiltrating water. However, as is well-known to villagers, and as we demonstrate, ponds quickly develop a low-permeability skin that inhibits leakage. Elsewhere in the Bengal Basin, ponds may be dug through the upper aquitard, or it may not be present, allowing the pond base to intersect the underlying aquifer. Assessing the role of ponds in driving pollution is therefore a matter of importance.

Isotopic Tracers of Pondwater. Rain collected in JAM during 2004−2006 defines a local meteoric water line (LMWL) for which $\delta^2H = (7.9 \pm 0.1)\delta^{18}O + (8.9 \pm 0.9)$ (21); Table 1) and shows that, as the monsoon progresses, the isotopic composition of rainfall becomes more negative in $\delta^{18}O$ and δ^2H. In response to the seasonal variation in the isotopic composition of rainfall, and to seasonal dilution and evaporation, pond waters show seasonal cycles of stable isotopic composition and salt content (Figure 2). The maximum chemical and isotopic enrichments in pondwater occur in earliest June, at the end of the dry season. A reduced major axis (RMA) regression model (25) fitted to the isotopic compositions of pondwater from the three largest ponds ($n = 46$) defines a local evaporation line (LEL, Figure 3) with $\delta^2H = 5.56\delta^{18}O − 11.88$, with parametric 95% confidence intervals (CIs) on the slope and intercept of {5.03, 6.08} and {−12.42, −9.75} respectively. An RMA fit, over a shorter interval (so proving more limited evaporation), to the arsenic-polluted groundwaters (>50μg/L As; Figure 1) defines a distinct LEL with $\delta^2H = 5.05\delta^{18}O − 7.61$ (Figure 3; $n = 56$) with 95% CIs of {4.49, 5.61} and {−9.62, −5.59}. For the small ponds, $\delta^2H = 6.06\delta^{18}O − 8.62$ ($n = 112$), with 95% CIs of {5.79, 6.34} and {−9.66, −7.59}. The reduced major axis model is used here in preference to the classic ordinary least-squares (OLS) fit as, unlike OLS, it assumes that errors of similar relative magnitude are present in both δ^2H and $\delta^{18}O$. Nonparametric bootstrap confidence regions (26) for the parameters of the fitted RMA models show (Figure 4) that the regression lines for groundwater and pondwater (from large or small ponds) are statistically distinct. Low-As groundwaters (<50 μg/L) from both shallow and deep aquifers plot on the LEL for As-polluted groundwaters (inset on Figure 3). The LEL for groundwater intercepts the LMWL at a point close to that of the volume-weighted mean of rain that fell during the period of monitoring (Table 1; 21). The LEL for pondwater intercepts the LMWL at a point between isotopic compositions for September and October rainfall (Figure 3).

The separation of the LELs for groundwater and pondwater, and the fact that the data do not show a continuum between the mean isotopic compositions of the large ponds and that for average groundwater, show that mixing between groundwater and pondwater is insignificant. The isotopic composition of pondwaters scatter more than do those of groundwaters: we attribute this increased scatter to be the result of slow mixing in ponds after rain, a problem that may have introduced a slight bias in pondwater isotope composition toward the LMWL when sampling took place soon after rain: samples that are displaced from the pond LEL apparently toward the groundwater LEL are, in reality, displaced toward the LMWL. Three groundwater samples that are the most displaced toward the pond-LEL (arrowed in Figure 3 inset) all contain <50μg/L of As; this confirms that where the spread of groundwater data implies that minor mixing of pondwater into groundwater might have occurred, it has not led to arsenic pollution. Mixing of groundwater into ponds is not

TABLE 2. Chemical Composition of Weekly-Bulked Rain Waters Collected at JAM[a]

Barasat	from	to	Cl mg/L	$\delta^{18}O(\%)$	$\delta^2H\ (\%)$	rain, mm
June, 2004	11/06/04	17/06/04	2.21	−6.78	−43.7	135
July, 2004	02/07/04	09/07/04	2.21	−3.37	−18.4	53
August, 2004	15/08/04	21/08/04	1.77	−9.32	−67.2	25
	28/08/04	04/09/04	0.41	−6.12	−34.3	140
Sept., 2004	05/09/04	11/09/04	1.32	−2.38	−8.3	72
	19/09/04	25/09/04	0.21	−12.69	−90.1	23
	26/09/04	02/10/04	0.83	−6.72	−42.0	35
July, 2005	08/07/05	15/07/05	9.03	−5.43	−37.5	112
	23/07/05	30/07/05	0.62	−7.99	−56.1	52
	08/08/05	13/08/05	0.52	−7.17	−49.4	32
	21/08/05	27/08/05	0.65	−2.17	−11.4	251
Sept., 2005	04/09/05	10/09/05	1.34	−9.42	−63.6	28
	25/09/05	01/10/05	1.37	−6.47	−40.2	31
October, 2005	02/10/05	08/10/05	1.30	−10.10	−71.9	45
	09/10/05	15/10/05	0.59	−8.15	−57.8	44

[a] The samples are some, but not all, of those reported in ref *21*, and are reported with the correction of 251 mm rainfall, not 51 mm, for late July, 2005.

possible as levels of water in ponds are always above the water table.

The isotopic separation between pondwater and groundwater that we document in JAM is similar to, but larger than, that seen between surface water and groundwater from Araihazar, in Bangladesh (ref *27*; their Figure 3, redrawn here as Figure 5). Nonparametric Bootstrap confidence regions (*26*) for the RMA regression models fitted to the data from Araihazar (Figure 6) again show that the surface waters and groundwater are different. This is so despite the fact that the surface water is undifferentiated and may include rivers and ephemeral flow that bias the data. The similarity of offsets between surface water and groundwater trends in Araihazar and JAM (Figures 3 and 5) suggests that such isotopic separation could be widespread across the Bengal Basin. Such an offset has also been reported for groundwaters elsewhere in West Bengal (*28*); the offset is slight but discernible when those isotopic compositions are plotted against the LMWL of ref *21*, rather than ref *28*.

The isotopic data presented here indicate that As-polluted groundwater in JAM does not contain detectable amounts of pondwater. It follows that ponds cannot be the dominant source of organic matter that drives FeOOH reduction and arsenic pollution in the area. This reasoning is not compromised by differences in age between pondwater and groundwater. The residence time of water (but not solutes) in ponds is estimated to be around 5 years, given annual fluctuations of around 1.0−1.5 m in pond level and water depths in ponds of around 3.5 m. Tritium dating shows that the age of As-polluted groundwater ranges from 2 to >50 years. Despite the differences in age, a comparison of isotopic composition between groundwater and pondwater is valid because the large ponds upflow of most of the arsenic-polluted wells are old. In addition, compositions of pondwater and groundwater reflect processes that are generic, and not site specific. In a region where rainfall, temperature, and topography are uniform for many tens of kilometres around JAM, processes of recharge and pond evaporation should be similar in all regions that might supply local groundwater.

Chemical Tracers of Pondwater. The concentrations of K in ponds range from 6 to 51 mg/L (Figure 7), whereas a pond remote from habitation and used only for irrigation (pond PIF; Figure 1) contains only 3.7 mg/L of K. The elevated concentrations of K are exceptionally high compared to those in most natural waters (ref *29*, p 105) and are particularly high considering the low TDS of the waters, see Supporting Information Table S1. The Na/K (mg/L ratios) in pondwater range from 0.55 to 6.6 and most are less than 4; most natural waters have values above 10. The K enrichment in pondwater

derives from K in wood ash that is used to scour pots at the pondside, thereby contributing its K directly to pondwater. Wood-ash from a cooking fire in the study area contained 4.5% of water-soluble K.

The K concentration in groundwater (Table 3 of ref *19* and Supporting Information Table S2) is around 20 times less than that found in pondwaters in JAM (Supporting Information Table S1) and groundwater and pondwater plot in distinct fields on element cross-plots (Figure 7). Were mixing to have occurred between these waters, the Cl and K concentrations (Figure 7a) would spread between the end-members of the groups, rather than clustering distinctly into two populations. Piezometer profiles at three sites in JAM (ref (*19*), especially their Figures 3, 4, 5, and 15) show concentrations of K generally <3.2 mg/L, with many values <2 mg/L, at all levels in the shallow aquifer. The one groundwater plotting with pondwater in Figure 7a (Well Ba 37 of ref *19*) occurs within a dense cluster of As-polluted wells (Figure 1) and its aberrant composition is likely to be the result of contamination by leakage of K-rich water down the annulus of a (presumably poorly constructed) borehole, following pot-washing at the well-head using K-rich charcoal.

The distinct difference in K concentrations, and Na/K ratios, between As-polluted groundwaters and pondwaters show that the latter have little influence on the former. This conclusion is confirmed by a comparison of Mg and Ca concentrations in each (Figure 7b,c). Infiltrating pondwater would need to dissolve substantial amounts of aquifer calcite (around 225 mg/L) for its Mg and Ca concentrations to reach those found in groundwater, which are three times higher (Figure 7b and c; Supporting Information Tables; ref *19*). Mass-balance calculations show that the acidity required to do so far exceeds the acid-generating capacity of infiltrating pondwater, which is limited by its low concentration of dissolved oxygen (around 10 mg/L) available to convert DOC into CO_2, and so carbonic acid for dissolution of calcite. Once anoxic, further metabolization of OM would involve reduction of NO_3, MnO_2, FeOOH, and SO_4, processes that produce alkalinity and so suppress carbonate dissolution or lead to calcite precipitation. Indeed, the concentrations of Ca and Mg in the groundwaters are minima as both may have been reduced by precipitation of calcite from the groundwaters, with which they are oversaturated (see p 1264 of ref *19*). The acidity required for carbonate dissolution could be produced in an anoxic environment by fermentation of sedimentary OM to give methane and CO_2, the latter generating acidity via carbonic acid production, but we have found no methane in our groundwater, so we discount this process. It follows that our As-polluted groundwaters could not have attained
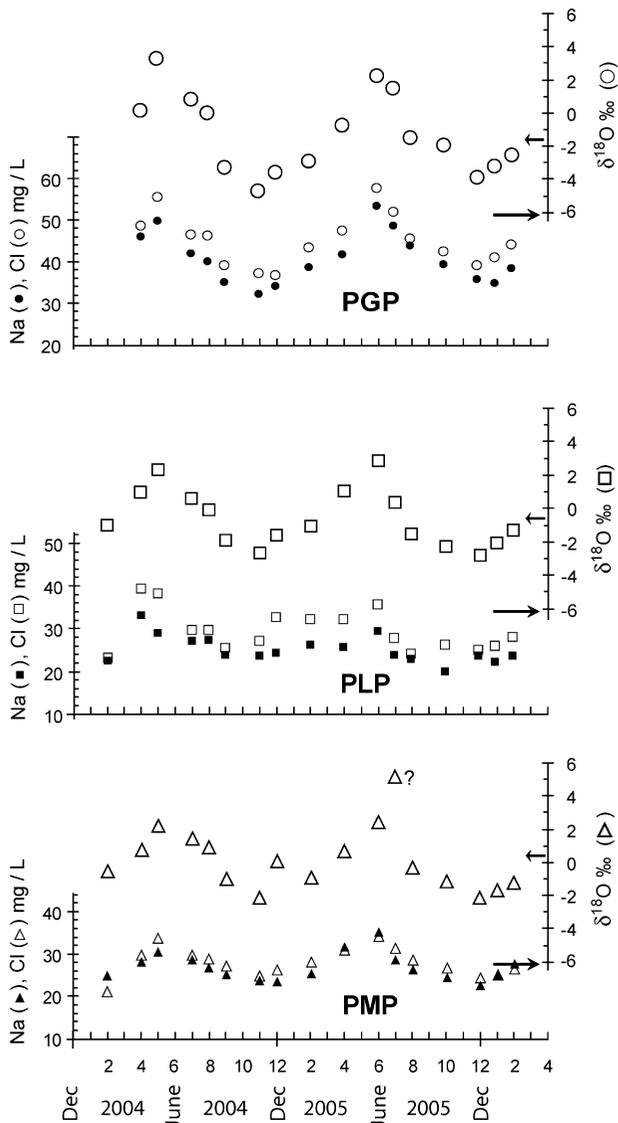
FIGURE 2. Seasonal changes in $\delta^{18}O$, Na, and Cl in ponds PGP, PLP, and PMP, the three largest ponds in JAM (see Figure 1 for locations) during 2004–2005. Large, right-facing, arrows on $\delta^{18}O$ axes show volume-weighted mean for the 2004 and 2005 monsoon rainfall ($-6.2‰$); small, left-facing, arrows show pond-means for the study period. Data are provided in the Supporting Information Tables.

their observed concentrations of Mg and Ca by evolution from infiltrating pondwater. The acidity (quantity of dissolved CO_2) needed to generate the Ca and Mg content in the groundwater is available during infiltration of rainwater and floodwater through soils because of the high pCO_2 in the soil zone, the CO_2 arising from microbial oxidation of soil-OM under oxic conditions of advective and diffusive resupply of O_2 from the atmosphere.

Annual Salt Mass-Balance. The arguments above suggest that As-polluted groundwater at the study site, sampled here from depths of 30–40 m, is not derived from ponds, yet ponds must leak to groundwater. If they did not, their solute concentration would have risen to the point where ponds would be unusable for aquaculture, which has not happened: the monitored ponds contain ≤45 mg/L of Cl, irrespective of their size or age (Supporting Information Table 1, Figure 1) and are at, or near to, long-term steady state (Figure 2), although solute concentrations fluctuated through the study period in response to evaporation and dilution. Mass balance can therefore be used to constrain the degree to which ponds recharge groundwater.
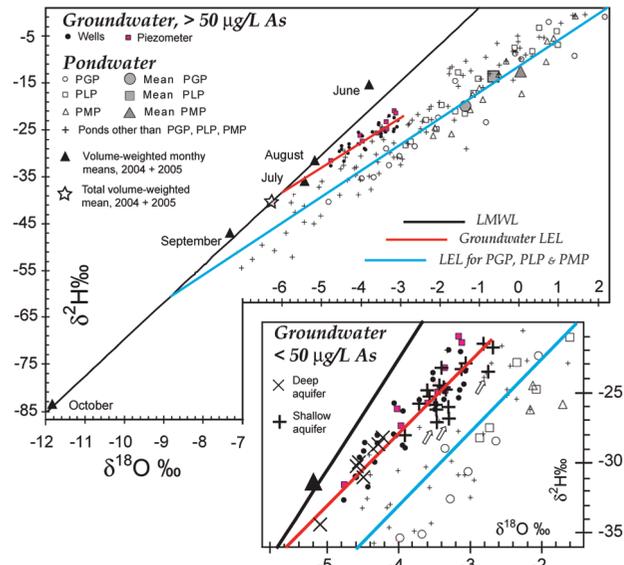

FIGURE 3. Cross-plot of $\delta^{18}O/\delta^2H$. Main figure: ponds, and groundwaters containing >50 $\mu g/L$ of As. Inset, including groundwater with $<50\mu g/L$ As from both deep and shallow aquifers. For clarity, only the largest ponds are individually identified and the pond regression line is for data from the three largest ponds. The isotopically heaviest groundwater is -2.1% for $\delta^{18}O$ and -19.9% for δ^2H. Inhomogeneity of ponds, caused by slow mixing after rainfall, introduces some scatter in pond water data, with some samples thereby shifted towards the LMWL and so closer to the groundwater LEL. Samples of groundwater do not fall along a putative mixing line between the mean pond compositions and mean volume-weighted rainfall, as would happen were mixing to have occurred between pond water and groundwater. Data are provided in the Supporting Information Tables. For clarity, values of $\delta^{18}O > +2$ ‰ are not plotted, but are given in the Supporting Information tables. For reasons explained in the text, the linear models relating δ^2H to $\delta^{18}O$ for ponds and groundwater are fitted by reduced major-axis regression (25), except for LMWL, which is the least-squares regression of ref 21: LMWL (black line), $\delta^2H = 7.88(\delta^{18}O) - 8.93$. Groundwater $>50\mu g/L$ (red line; $n = 56$), $\delta^2H = 5.05(\delta^{18}O) - 7.61$. PGP, PLP, PMP (blue line; $n = 46$), $\delta^2H = 5.56(\delta^{18}O) - 11.88$ (three largest ponds). All ponds (not shown; $n = 158$), $\delta^2H = 5.85(\delta^{18}O) - 9.92$. For intercepts on LMWL, and volume-weighted averages for monsoon rain, see Table 1; see text for parametric 95% confidence intervals on the fitted RMA regression parameters.

Given the steady state of solutes in ponds, the annual solute flux into ponds (taking Cl as the index) must equal the annual flux out. Outflow of solute is by leakage to the underlying aquifer only, as ponds are never overtopped. Thus, the mass balance for solutes, exemplified by chloride, is

$$F_I = F_L \text{ hence } C_I x\, V_I = C_L x\, V_L; \text{ so, } V_L/V_I = C_I/C_L \quad (1)$$

where F is flux, C is concentration, V is volume, and suffixes I and L indicate input and loss by leakage, respectively. We apply this mass balance to only the three largest ponds, as these are volumetrically the most important; two are known to date to before 1965, and these two are upflow of many As-polluted wells (the third is used as a check on uniformity of the result). Mean annual Cl concentrations for PGP, PLP, and PMP, the largest ponds, are 45.1, 29.5, and 28.0 mg/L respectively (Supporting Information Table S1). Concentrations of Cl in rainfall (C_I) are between 0.5 and 1.5 mg/L, from analysis of weekly bulked samples collected in JAM (samples of ref 21 that were analyzed here; Table 2). The Cl concentrations in ponds exceed those in rainfall by factors of between 30 and 90 for PGP, and between 20 and 60 for PMP and PLP.
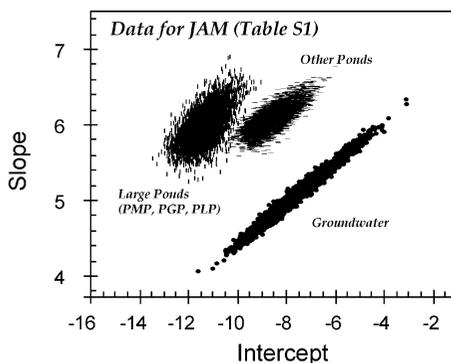
FIGURE 4. Cross-plot of intercept and slope values forming nonparametric bootstrap confidence regions (see text for explanation and ref *26* for method) for the estimated parameters of the RMA regression models fitted to δ^2H and $\delta^{18}O$ for the groundwaters and surface waters (large and small ponds) in JAM. The complete separation between the three clouds of points shows that surfacewaters and groundwaters are distinct statistically. The regression fits for the two types of pondwater are more similar to each other than are either to groundwaters. The confidence regions calculated separately for groundwaters, small ponds, and the three largest ponds, were each obtained as follows: (1) A random sample of size *n* was taken, *with replacement*, from the *n* pairs of points ($\delta^{18}O$, δ^2H) forming the original data set, thereby making a new (synthetic) data set, also of size *n*. Because the pairing of $\delta^{18}O$ and δ^2H is maintained, the new data set has a correlation structure similar to that of the original data. (2) An RMA regression model was fitted to the synthetic data set and its slope and intercept values were noted. The sampling (1) and fitting (2) process was repeated 5000 times. This gave 5000 estimates of the RMA slope and intercept for each of the *original* data sets. The plotted estimates yielded the ellipsoidal confidence regions for the parameters of the fitted regression models for each sample type that are plotted here.

These figures suggest that between 3 and 1% by volume of annual Cl replenishment to PGP is lost per year to leakage, and that between 5 and 2% of annual chloride replenishment in PMP and PLP is lost as leakage.

Some uncertainty attends these estimates because the volume of surface runoff, and its concentration of Cl, that replenishes ponds is known poorly. Additionally, Cl may derive from the washing of cooking utensils. While such uncertainties may have an impact on our estimates of recharge, we suspect that the impact is small. First, the effect on contributions of cooking salt will diminish as pond size increases and we deal only with the largest ponds. Second, the concentration of Cl in runoff to ponds will be similar to that in rain because soluble matter in dry deposition laid down in the dry season will be washed through to the aquifer by the first rains that fall on dry ground, rather than into ponds by surface runoff later in the season as aquifers fill. Third, although some runoff occurs from made ground, such hard surfaces store little Cl. Finally, the pond catchments are small (Figure 1); the ratio of direct rainfall entering ponds to runoff supply increases as pond size increases, so runoff would be volumetrically minor in the large ponds on which we focus most attention. If we underestimate Cl input by as much as a factor of 2, it is still apparent that leakage from ponds is low, a conclusion that is confirmed by our other estimators of leakage (see below).

Seasonal Evaporative Mass Balance in Salt. Because leakage from ponds is small, it can be estimated from the seasonal (evaporative) change in chloride concentration (Figure 2) and seasonal change in pond level. The maximum seasonal change in salt concentrations for PGP, PLP, and PMP, are, respectively, 57, 41, 38%. Using a standard model of evaporation that relates volume and solute concentration
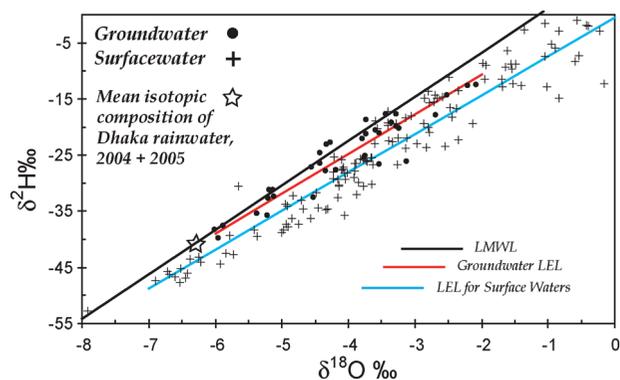

FIGURE 5. Cross-plot of stable isotopic data for Araihazar, Bangladesh (data from ref *27*). The local meteoric water line (LMWL) for Dhaka is shown in black. The red line is the RMA regression line for groundwater and defines its local evaporation line (LEL). The blue line is the RMA regression fit for surface waters and defines the LEL for surfacewaters. The fits have similar slopes but are offset, as in JAM. The surface water LEL intercepts the LMWL at isotopic compositions lighter than that for mean Dhaka precipitation. The groundwater LEL intercepts the LMWL at the isotopic composition of mean Dhaka precipitation. Groundwaters in Araihazar are nearer the LMWL than in JAM, possibly because of the lesser confinement of the aquifers at Araihazar compared to JAM. Regression parameters for groundwater (red line; $n = 56$) are: $\delta^2H = 7.10(\delta^{18}O) + 3.63$; 95% CIs on slope and confidence interval are {6.24, 8.00} and {0.01, 7.25}, respectively. Regression parameters for surface water (blue line; $n = 45$) are: $\delta^2H = 6.87(\delta^{18}O) - 0.59$; 95% CIs are {6.61, 7.14} and {−1.57, 0.39}.
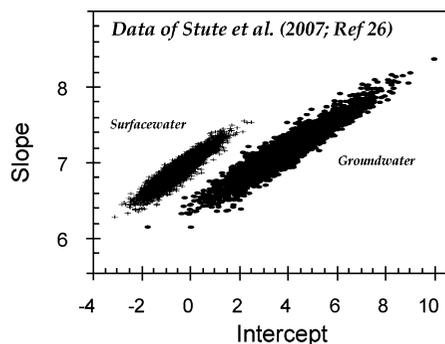
FIGURE 6. Cross-plot of intercept and slope values forming nonparametric bootstrap confidence regions for the estimated parameters of the RMA regression models fitted to δ^2H and $\delta^{18}O$ for the groundwaters and surface waters in Araihazar, Bangladesh (data from ref *27*, where surface waters are undifferentiated). The groups are statistically distinct. See legend to Figure 4 for method of calculation.

(i.e., concentrations double for a 50% loss of water by evaporation, and equivalent scaling), these changes in concentration equate to changes in volume of 36, 29, and 27%, respectively, and so into changes in pond level of 1.26, 1.01, and 0.95 m for PGP, PLP, and PMP (given an average depth of 3.5 m). Monthly monitoring of the water levels in the three largest ponds showed decreases in level of 1.14 m (PGP), 1.26 m (PLP), and 1.00 m (PMP) in the dry season. Given an average pond depth of 3.5 m, the differences between the calculated and measured changes in level translate into leakage losses of 0, 20, and 5%, respectively. The larger difference for PLP reflects an enhanced change in level arising from the use of this pond, alone of all our ponds, for irrigation pumping. Such a calculation is approximate, but shows that leakage from ponds is low.

Seasonal Evaporative Mass Balance in $\delta^{18}O$. Where leakage is small compared to evaporation, leakage may be constrained using a Rayleigh distillation calculation (*30*) applied to the
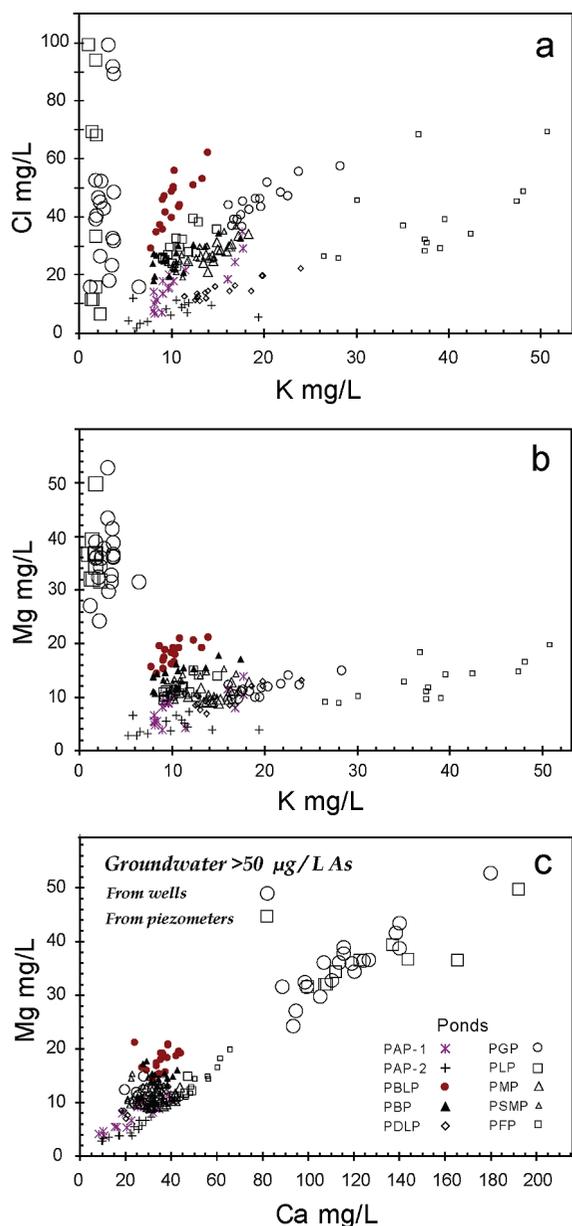
FIGURE 7. Cross-plots of K, Cl, Ca, Mg in pondwaters and groundwaters. 7a, K and Cl. 7b, K and Mg. 7c, Ca and Mg. In all cases, there is a clear separation between groundwaters and pondwaters, with no spread between the groups, thus showing that mixing has not occurred. The separation in Mg and Ca between the sample groups cannot be bridged by calcite dissolution in the aquifer because the temperature-dependent solubility of free molecular oxygen is too low for pondwater to contain dissolved oxygen in amount sufficient to generate the required acidity (as carbonic acid) via oxic degradation of OM: see the text for a fuller explanation. Groundwater data from ref *19* and are also provided in the Supporting Information Tables.

seasonal change in $\delta^{18}O$ in the larger ponds (Figure 2). Adopting an isotopic fractionation in $\delta^{18}O$ on evaporation of −13‰ (*30, 31*), this model yields evaporation losses of 36, 31, and 26%, respectively. Given the average pond depth of 3.5 m, these losses translate into changes in pond level of 1.26 m (PGP), 1.08 m (PLP), and 0.92 m (PMP). The difference between the predicted and measured changes equate to loss by leakage of 0, 14, and 8% of volume per year. As with the previous balance calculations, the larger figure for PLP may be explained by the use of this pond for irrigation.

Abstraction Balance. Finally, we can constrain leakage from ponds by using abstraction information from ref *19*.

The annual groundwater abstraction in the study area, mainly for irrigation of the fields to the north northeast of JAM, is about 400 000 m³ from aquifers that are fully recharged each year. The measured area of ponds monitored in JAM is 47 000 m² (scaled from Figure 1) and the average depth is 3.5 m, so a 5% annual loss by leakage yields around 8125 m³. This is 2% of annual abstraction and recharge. The amount is so small that large changes in the calculation's inputs do little to alter it: increasing pond leakage by a factor of 2 (an upper limit, the largest ponds are included in our areal estimate) to account for ponds not monitored in our study, and increasing leakage to 10%, yields a figure of 8% of recharge. This not only remains a small part of the total, but is a part that we have not been able to identify in arsenic-polluted groundwater either chemically or isotopically. Such small losses by leakage are unlikely to carry into the underlying aquifer enough OM to cause the widespread FeOOH reduction and As pollution that has been documented in JAM (*19*).

Wider Considerations. Using stable isotopic data ($\delta^{18}O$, δ^2H), and major element data (especially concentrations of K), we have shown that pondwater does not drive As-pollution in our field area. Such a finding is not unexpected: ponds are built to hold water. To facilitate sealing, villagers often puddle the base of new ponds, and seepage losses reduce over time owing to the accumulation of a layer of fine-grained, organic-rich, bottom sediment. Where the groundwater level falls below the base of ponds, as they do in the study area in the dry season, compaction reduces the permeability of the bed, a phenomenon known to affect river-bank filtration-schemes (*32*).

The proposal that surface sources of OM drive subsurface redox reactions in the Bengal Basin (*14, 18*), including FeOOH reduction and As-pollution, is contrary to the observation (*14, 18*) that concentrations of both DOC and arsenic in groundwater increase with depth to around 35 m at Munshiganj, Bangladesh. The hypothesis is not supported by measurements showing that pondwater is rich in labile DOC, nor by a demonstration that, were it so, infiltrating DOC would pass the barrier posed by microbial metabolism in the bottom muds of ponds. With respect to other surface sources of OM, that irrigation return-water carries into aquifers DOC from a soil source to drive arsenic pollution at Munshiganj, in Bangladesh, has been refuted (*33*). At Araihazar, in Bangladesh, surface sources of OM cannot drive subsurface reduction because arsenic concentrations increase as the age (and depth) of groundwater increases (*27*).

Wider considerations also confirm that pondwaters are unlikely to be a major driver of As-pollution in the Bengal Basin. For example, ponds and irrigation are found in all parts of Bangladesh and West Bengal, but arsenic pollution is found only in areas underlain by Holocene alluvium; in particular, arsenic pollution is almost unknown in aquifers beneath the Barind and Madhupur Tracts (ref *22*), and many since). In modern clastic sediments, both on the world's continental margins and on lake bottoms, reduction is driven by organic matter contained within the water-saturated sediment, so it seems unnecessary to invoke an exogenous redox driver simply because a body of water-saturated sediment now stands above sea level. In aquifers worldwide, subsurface redox is driven by sedimentary pyrite, or by DOC derived from the aquifers themselves or from confining or interbedded strata. Except in the case of organic pollution (e.g., hydrocarbon spills or landfill leachate), it is rarely driven by allochthonous dissolved OM introduced from external sources by flow-through. In rare cases, organic-rich surface waters may debouch into fracture-flow aquifers, as happens in the Floridan aquifer in Georgia (*34*), but even there, where blackwater rivers are captured by sinkholes, the subsurface effect is of limited extent (Figure 4 of ref *34*). The limited role of surface-derived OM in driving subsurface redox in granular

aquifers is further attested to by the fact that many aquifers that are oxic at depth are overlain by soils that contain OM, yet the groundwaters remain oxic because the aquifer sediments themselves are organic-poor e.g. the Sherwood Sandstone aquifer of the UK, in which in situ sedimentary OM is all but absent and groundwater retains dissolved oxygen for up to 5000 years (35). Such examples emphasize the overwhelming role of in situ sedimentary OM, in contrast to allochthonous OM, in driving redox in sediments, including sediments in alluvial aquifers. In summary, both detailed studies, and wider considerations, show that surface sources of OM, including ponds, play no significant part in driving As-pollution in the Bengal Basin.

Acknowledgments

Supporting Information Available

Table S1 (time-series data on pondwaters), Table S2 (groundwater compositions), Table S3 (piezometer waters), and Figure S1. This material is available free of charge via the Internet at http://pubs.acs.org.

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