Sedimentological Control on Mn, and Other Trace Elements, In Groundwater of the Bengal Delta


Department of Earth Sciences, University College London, Gower Street, London WC1E 6BT, United Kingdom

Department of Environment Management, Indian Institute of Social Welfare and Business Management, College Square, Kolkata 700073

School of Environmental Systems Engineering, The University of Western Australia, MO15, 35 Stirling Highway, Crawley, WA 6009, Australia

Department of Geology, RHUL, Egham, Surrey TW20 0EX, United Kingdom

School of Environmental Science, University of Liverpool, Brownlow Street, Liverpool L69 3GP

Department of Geology, Delhi University, Chattra Marg, Delhi 110007

Supporting Information

ABSTRACT: To reveal what controls the concentration and distribution of possibly hazardous (Mn, U, Se, Cd, Bi, Pb) and nonhazardous (Fe, V, Mo, PO₄) trace elements in groundwater of the Bengal delta, we mapped their concentrations in shallow groundwater (<60 mbgl) across 102 km² of West Bengal. Only Mn is a potential threat to health, with 55% of well water exceeding 0.3 mg/L, the current Indian limit for drinking water in the absence of an alternate source, and 75% exceeding the desirable limit of 0.1 mg/L. Concentrations of V are <3 μg/L. Concentrations of U, Se, Pb, Ni, Bi, and Cd, are below WHO guideline values.

The distributions of Fe, Mn, As, V, Mo, U, PO₄, and δ¹⁸O in groundwater reflect subsurface sedimentology and sources of water. Areas of less negative δ¹⁸O reveal recharge by sources of evaporated water. Concentrations of Fe, As, Mo, and PO₄ are high in palaeo-channel groundwaters and low in palaeo-interfluvial groundwaters. Concentrations of U, V, and Mn, are low in palaeo-channel groundwaters and high in palaeo-interfluvial groundwaters. Concentrations of Fe and Mn are highest (18 and 6 mg/L respectively) at dual reduction-fronts that form strip interfaces at depth around the edges of palaeo-interfluvial aquifers. The fronts form as focused recharge carries dissolved organic carbon into the aquifer margins, which comprise brown, iron-oxide bearing, sand. At the Mn-reduction front, concentrations of V and Mo reach peak concentrations of 3 μg/L. At the Fe-reduction front, concentrations of PO₄ and As reach concentrations 3 mg/L and 150 μg/L respectively. Many groundwaters contain >10 mg/L of Cl, showing that they are contaminated by Cl of anthropogenic origin and that organic matter from in situ sanitation may contribute to driving reduction.

INTRODUCTION

High concentrations of trace elements in potable water and irrigation water are problematic for reasons of aesthetics, practicality, or because of their impact on health, and agricultural sustainability. In the case of Mn, its ingestion may adversely affect human health, with the young and unborn being most at risk. To mitigate the hazard from ingestion of Mn, the Bureau of Indian Standards Acceptable Limit for drinking water (IS 10500, 1991) is 0.1 mg/L, with 0.3 mg/L being permissible in the absence of an alternate source. The World Health Organization’s guideline value (GV) for Mn in drinking water was set at 0.4 mg/L prior to mid-2011. That limit may have been too high. Surprisingly, the fourth edition of the World Health Organization’s Guidelines for Drinking Water Quality has no guideline value for Mn in drinking water because 0.4 mg/L of Mn is “well above concentrations of manganese normally found in drinking-water.” This is plainly not the case for groundwater consumed by many of the 240 million inhabitants of the Bengal delta (Ganges-Brahmaputra-Meghna River system of Bangladesh and West Bengal). In Bangladesh, 46% of shallow groundwaters (arbitrarily taken as <120 m deep) have >0.4 mg/L of Mn, and 5% have >2 mg/L (n = 3313; data from refs 11 and 12), with a maximum of 10 mg/L. For southern West Bengal, the figures are 47%, 11%, and 6 mg/L, respectively (527 wells <60 m deep; this work). Using the national standards of 0.1 mg/L for India and Bangladesh increases the percentage of non-compliant groundwater wells,
as does the use of the Indian limit of 0.3 mg/L Mn where no alternate source of water is available.

Excess Mn in soil is also a problem worldwide, albeit mainly for acid soils.13,14 To mitigate the hazard to crops from Mn in irrigation waters, concentrations <0.2 mg/L are recommended.15 Across the Bengal delta, irrigation in the dry season, much of it using shallow groundwater, provides a third annual crop that is vital to rural livelihoods. In Bangladesh, 56% of shallow groundwaters contain >0.2 mg/L of Mn;11,12 for West Bengal, the figure is 62% (this report). The threat to agriculture from Mn in irrigation water is clear.

Given the potential hazards posed by Mn, and possibly other trace elements such as U,16–18 in groundwater, an improved understanding is needed of their source, transport, and fate. In Bangladesh and West Bengal, where As in groundwater is a major hazard to health of consumers,19,20 the distribution of As-pollution is influenced strongly by the subsurface distribution of palaeo-interfluvial and palaeo-channel aquifers.21,22 We show here that a similar control is exerted on the concentration and distribution of Fe, PO4, Mo, Mn, U, and V, in groundwater in the shallow aquifers of southern West Bengal. The concept we develop, of sedimentological control of groundwater composition, has applicability across the Bengal delta and in deltaic aquifers worldwide.

### GEOLOGICAL SETTING

#### The Bengal Basin.

The detailed sedimentology of the Bengal delta is documented elsewhere;1,12,23–26 so a synopsis only is given here. In the period 125 ka to 20 ka, falling sea level, coupled with weathering and erosion, created a coastal region of low-relief palaeo-interfluvices cut by major rivers and their lesser tributaries. A laterite,24 also described as a clay-rich, red, palaeosol (the Last Glacial Maximum Palaeosol, or LGMP, of ref 21), formed on the exposed palaeo-interfluvial surfaces: underlying palaeo-interfluvial sands were thoroughly flushed by oxic water, turning them oxidized and brown—the oxidized facies of ref 24. These brown sands comprise the Late Pleistocene palaeo-interfluvial shallow aquifers of today. As sea level rose after the Last Glacial Maximum at 20 ka, the incised valleys were infilled mainly by gray sands; these palaeo-channel sands constitute today’s shallow palaeo-channel aquifers. More recent alluvium capped the old topography with a variety of sediments. Where the capping was fine-grained, it formed an upper aquitard to the palaeo-channel aquifers that impeded the ingress of oxygen and allowed anoxic conditions to develop.

#### The Study Area.

The study area (Figure 1) occupies 1022 km of southern West Bengal, India, between 88° 41' and 88° 49' North, and 22° 29' and 22° 35' East. It has been reported on previously with respect to As-pollution.22 The region extends northeast from the town of Barasat. The mineralogy of sediments in the Bengal delta is described elsewhere.27,28 Across the region drilling and local knowledge attests to the presence of a clay aquiclude at depth-to-top of around 60 to 65 m. The clay is around 30 m thick, and separates sands below it, that form a deep aquifer, from sands above it, that form shallow aquifers.22 This work deals exclusively with the shallow aquifers.

Both palaeo-interfluvial and palaeo-channel aquifers21,25 occur upon the basal clay aquiclude. The palaeo-interfluvial aquifers comprise pre-LGM, brown, oxidized, sands capped by the impermeable LGMP,24,26,29 the depth to which in our area ranges from 16 to 24 mbgl. The LGMP is typically between 1.6 and 6 m in thickness, depending on location.22 In our area, it is commonly overlain by silts, peats, and clays. The LGMP prevents vertical recharge to palaeo-interfluvial aquifers, which are therefore recharged at their margins by lateral flow inward from surrounding palaeo-channels. This recharging groundwater is rich in dissolved Fe and As.21,22,29

The palaeo-channel aquifers comprise post-LGM gray sands some 20–50 m thick that infill palaeo-channels. In our area, these aquifers are capped by a silty aquitard between 5 and 12 m thick. The aquitard permits recharge but maintains semiconfined conditions in the palaeo-channel aquifers. The palaeo-channels are incised to different levels in different places. In our area, deep palaeo-channels cut through the full thickness of the late Pleistocene brown sands, but not through the underlying clay aquiclude (but may do so elsewhere). Shallow palaeo-channels cut to shallower levels, typically around 30 mbgl in our area, leaving a basal unit of brown Pleistocene sand underlying the post-LGM gray sands.

Groundwaters are anoxic, with a pH of 7 ± 0.5 and alkalinites typically of 400–600 mg/L.29 Palaeo-channel groundwaters have gone beyond the stage of complete Fe-oxhydroxide reduction, and so are rich in Fe, PO4, and As, but lack Mn. Palaeo-interfluvial groundwaters are typically poised at Mn-reduction, so they contain dissolved Mn, but little Fe, As, or PO4.

Across much of the western Bengal delta, the natural direction of groundwater flow is from north to south, except where locally perturbed by interaction with rivers. Since 1970, increasing pumping of shallow groundwater for irrigation has locally disturbed the natural flow, but the effect is poorly quantified. In Moyna (Figure 1), where the density of irrigation wells is high, pumping reverses the flow direction during some of the year, so that it is north northeastward.29 Eastward of Moyna, the density of irrigation wells is lower.

---

**Figure 1.** (a) Distribution of Mn in groundwaters of the study area. The base map is the 1 in. toposheet of West Bengal circa 1975. Arroved red square is study area at Moyna of refs 21 and 29. Distribution of palaeo-interfluvial aquifer (areas of yellow), and palaeo-channel aquifers (uncoloured areas) are updated from ref 22. Coordinates to WGS84. (b) wells used for the line of profile in Figure 2.
MATTERIAlS AND METHODS
We analyzed 527 groundwaters from domestic and irrigation wells that were collected in February 2009 and February 2010 for a previous study of As-pollution.22 Depths of wells (where known) were mostly between 20 and 60 m, with 13 less than 20 m deep. Wells tapping water from beneath the regional, basal aquiclude, are identifiable in the field (deep wells) and are not considered here. Samples acidified in the field to be 1% with respect to nitric acid were analyzed by ICP-AES for Mn, Fe, and PO₄ (527 samples). Analysis was by ICP-MS for trace elements (325 samples). Unacidified samples were analyzed for Cl by ion chromatography. Oxygen isotope data were obtained on 0.22 μm-filtered unacidified samples using a Picarro WS-CRDS laser instrument for which analytical precision is better than 0.08‰. The measured concentrations are in Supporting Information Table S1. Subsurface sedimentology is documented for 43 logged boreholes of ref 22, and by those authors’ mapping of palaeo-interfluvies and palaeo-channels.

MANGANESE IN GROUNDWATER
The distribution of Mn in groundwater across the study area is shown in Figure 1 (data in Supporting Information Table S1). In Figure 2, we profile concentrations of Mn, Fe, δ¹⁸O, and Cl, of Mn in groundwater are mostly <0.1 mg/L in the palaeo-channel aquifers. They are mostly 0.2 to 0.4 mg/L in groundwater from the interior of the palaeo-interfluvial aquifer. Concentrations of Mn in groundwater are highest (up to 6 mg/L) at the margins of the palaeo-interfluvial aquifer where it is being recharged through the interface at which gray palaeo-channel sands abut brown palaeo-interfluvial sands. This distribution of Mn in groundwater is explained below.

Manganese at Palaeo-Interfluvial Margins. The palaeo-interfluvial aquifer is capped by the impermeable LGMP, so it can be recharged only by lateral inflow at depth from the flanking palaeo-channels (Figure 2). This subsurface flow into the palaeo-interfluvial aquifers creates dual Fe- and Mn-reduction fronts that appear to be ubiquitous around the margin of the palaeo-interfluvial aquifers (Figures 1,2). In the field, the Mn-reduction front is revealed by intense black stain on well-completions from precipitation of manganese oxide, and the Fe-reduction front is revealed by intense red stain from the precipitation of iron oxide.22 The fronts generate extreme concentrations of Mn and Fe in groundwater, with the Mn-front occurring downflow of the Fe-reduction front (Figure 2). These reduction fronts have parallels in water-supply schemes involving both river-bank infiltration,30–32 where they are driven by DOC in river water, and aquifer recharge and recovery,33 where they are driven by DOC in injected wastewater.

The reduction fronts are developed more strongly at the northern margin of the palaeo-interfluvial aquifer than at the southern margin (Figure 2). At the northern margin, concentrations of Fe reach 18 mg/L and those of Mn reach 6 mg/L. At the southern margin, concentrations reach 3.5 mg/L for Fe and 1.5 mg/L for Mn. This asymmetry results from the combining of radially inward flow, induced by pumping from the palaeo-interfluvial aquifer, with the regional, natural, flow of groundwater to the south. At the northern margin of the palaeo-interfluvial aquifer, these flows (and so DOC supply) reinforce each other. At the southern margin of the palaeo-interfluvial they oppose each other, making flow sluggish.

The distribution of δ¹⁸O values in groundwater along the line of traverse (Figure 2) supports this explanation. They are least negative beneath the conurbations (Bira, Kharki) that straddle the palaeo-interfluvial margins. Southward along the traverse from both localities, but most noticeably from Bira, the groundwater becomes isotopically more negative (Figure 2). The isotopic enrichments of δ¹⁸O result from focused recharge of partly evaporated water. One source is irrigation return-water derived locally, and from southward flow of infiltrated return-water above the palaeo-interfluvial, which rolls over the LGMP margin to recharge the palaeo-interfluvial aquifer. Another is domestic wastewater evaporated during the dry season in the conurbations of Bira and Kharki. Such water includes that in urine, which is also isotopically enriched in δ¹⁸O by around 10‰ compared to ingested water.34

The asymmetry of the profile of δ¹⁸O is consistent with groundwater flow being predominantly to the south, with recharge to the palaeo-interfluvial aquifer being derived predominantly from the north. The tailing of δ¹⁸O to less enriched values southward from Kharki, and the weak redox fronts in its vicinity, suggests that, at least locally, irrigation pumping has only marginally impaired the natural southerly flow of groundwater at the southern margin of the palaeo-interfluvial. The effect on flow may be seasonal and related to pumping times (and their lags), as it is in Moyna in the west of...
our field-area. Elsewhere, the impact of irrigation pumping might be more severe.

**The Redox Driver.** In sediments, microbial metabolism of organic carbon drives reduction of both Mn-oxides and Fe-oxyhydroxides. Because our Mn-reduction fronts are downstream of the Fe-reduction fronts (Figure 2), Mn-reduction may be driven by dissolved Fe(II). Nevertheless, both fronts ultimately result from metabolism of DOC. Possible sources of DOC include: natural solid organic matter in aquifers; waste organic-matter in in situ sanitation; degrading hydrocarbons; that may be derived from diesel fuel. To these may be added DOC in rivers entering aquifers via river-bank infiltration and cow dung, which is used to thicken drilling fluid when drilling in areas where caving occurs. We discuss these sources in turn below.

River-bank infiltration is too small-scale and localized in our area to be an influence on the reduction we document (Figure 1). Nor, on mass balance grounds, can spilt fuel drive it. Cow dung adds organic carbon directly into the aquifer, but at present its effect cannot be quantified. Any dissolved organic carbon infiltrating from ponds does not noticeably drive reduction of either Fe- or Mn-oxyhydroxides.

By elimination, DOC at the reduction front is supplied in three sources of recharge to the palaeo-interfluvial aquifers. First, groundwater flowing laterally from palaeo-channels (Figure 2) carries DOC derived from aquifer diffusion, or from organic-rich sediments intercalated within the palaeo-channel sands. Second, groundwater flowing laterally above the impermeable LGMP reaches the nearest palaeo-interfluvial margin, where it rolls over the edge to contribute focused recharge. This water likely contains DOC derived from the peat and peaty sediment that is abundant in units that overly the palaeosol. Peat sensu stricto, and peaty sediment, is also abundant elsewhere in the Bengal delta. Finally, some DOC may derive from sewage and sewerage water. We draw this inference from the fact that Cl concentrations in many of our groundwaters exceed the natural maximum of 10 mg/L (Figure 3), particularly in palaeo-channels. The Cl is not derived from saline connate water which, in our area, is found only in groundwaters deeper than those we have sampled. It follows that the high Cl represents anthropogenic contamination.

**Manganese in Palaeo-Interfluvial Interiors.** In the interiors of the palaeo-interfluvial aquifers, the groundwaters contain mostly 0.2–0.4 mg/L of Mn (Figure 1; Supporting Information Table S1). Concentrations are higher around Moyna, at the western end of the palaeo-interfluvial aquifer where it thins and pinches out. At this tapered western tip, the concept of margin and interior become indivisible, and where it thins and pinches out. At this tapered western tip, the Moyna, at the western end of the palaeo-interfluvial aquifer

Information Table S1). Concentrations are higher around aquifers via river-bank infiltration and cow dung, which is used to thicken drilling fluid when drilling in areas where caving occurs. We discuss these sources in turn below.

River-bank infiltration is too small-scale and localized in our area to be an influence on the reduction we document (Figure 1). Nor, on mass balance grounds, can spilt fuel drive it. Cow dung adds organic carbon directly into the aquifer, but at present its effect cannot be quantified. Any dissolved organic carbon infiltrating from ponds does not noticeably drive reduction of either Fe- or Mn-oxyhydroxides.

By elimination, DOC at the reduction front is supplied in three sources of recharge to the palaeo-interfluvial aquifers. First, groundwater flowing laterally from palaeo-channels (Figure 2) carries DOC derived from aquifer diffusion, or from organic-rich sediments intercalated within the palaeo-channel sands. Second, groundwater flowing laterally above the impermeable LGMP reaches the nearest palaeo-interfluvial margin, where it rolls over the edge to contribute focused recharge. This water likely contains DOC derived from the peat and peaty sediment that is abundant in units that overly the palaeosol. Peat sensu stricto, and peaty sediment, is also abundant elsewhere in the Bengal delta. Finally, some DOC may derive from sewage and sewerage water. We draw this inference from the fact that Cl concentrations in many of our groundwaters exceed the natural maximum of 10 mg/L (Figure 3), particularly in palaeo-channels. The Cl is not derived from saline connate water which, in our area, is found only in groundwaters deeper than those we have sampled. It follows that the high Cl represents anthropogenic contamination.

**Manganese in Palaeo-Interfluvial Interiors.** In the interiors of the palaeo-interfluvial aquifers, the groundwaters contain mostly 0.2–0.4 mg/L of Mn (Figure 1; Supporting Information Table S1). Concentrations are higher around Moyna, at the western end of the palaeo-interfluvial aquifer where it thins and pinches out. At this tapered western tip, the concept of margin and interior become indivisible, and concentrations of Mn are higher than in palaeo-interfluvial interiors further east, which are remote from reduction fronts.

Reduction of Mn in palaeo-interfluvial interiors probably has not been driven by residual sedimentary organic matter in the aquifer. These aquifers were thoroughly flushed and oxidized during the period 125 ka to 20 ka. Such flushing would have destroyed any organic matter present. The Mn in palaeo-interfluvial interiors may have resulted from migration inward of Mn from marginal reduction fronts. Such migration would necessarily have been historical, because migration of more mobile anthropogenic Cl into the palaeo-interfluves is limited (Figures 2 and 3) and because the asymmetric traverse profile of δ¹⁸O bears no relation to that of Mn, which is flat (Figure 2). Most likely, the Mn in palaeo-interfluvial groundwater results from reduction of MnO₂ driven by recalcitrant DOC that escaped reaction at palaeo-interfluvial margins and was carried into the aquifer over historical time by natural flow. Being recalcitrant, it has been metabolized slowly and so has not driven much reduction.

**OTHER TRACE ELEMENTS: AS, U, MO, PO₄, V**

**Trace Elements at Palaeo-Interfluvial Margins.** When reduction fronts move through aquifers, elements released from aquifer materials can resorb downflow, only to be released again, at higher concentrations, as the moving redox front sweeps through these downflow regions: the aquifer is, in essence, zone-refined. Species that are conservative in solution, such as Cl, lead the plume and travel at the same rate as the groundwater. Migration distances of other species depend on their propensity to sorb, or form insoluble products such as carbonates.

Profiles of trace elements along our line of traverse (Figure 4) show that V, Mo, PO₄ and As have also been generated at either the Mn- or the Fe-reduction fronts. As with Mn and Fe, the fronts have developed to different degrees at the northern and southern margins of the palaeo-interfluve. At the northern edge, the front for V leads the Mn front; at the southern margin it is hardly resolved from background. The Mo front coincides with the Mn front, but Mo concentrations are higher in the northern front. As Mo sorbs strongly to Fe-oxides, resorption downflow to Mn-oxides is indicated. The As and PO₄ fronts appear coincident with the Fe-reduction front at the northern margin, but are not discernible at the southern margin. Denser sampling would better resolve detail in these fronts.

**Trace Elements in Aquifer Interiors.** Concentrations of Mo, As, and PO₄ are high in the Fe-rich palaeo-channel waters (Figure 4), from supply by the reductive dissolution of some sedimentary iron oxyhydroxides. In palaeo-interfluvial groundwaters, the concentrations of As, PO₄, or Mo are low because
the waters are insufficiently reducing for Fe-reduction to liberate them to solution. Any entering the palaeo-interfluvial sediments in recharge are sorbed by, or reacts with, palaeo-interfluvial marginal sands downflow of the reduction fronts. The sink for Fe may be reduction of Mn-oxides,\textsuperscript{44}−\textsuperscript{46} or formation of magnetite or green rust.\textsuperscript{56,57} Magnetite in sediments from Ariahazar, Bangladesh, is detrital.\textsuperscript{58} Analysis by SEM and EDAX microprobe of magnetic separates from many of our cores also reveals only detrital magnetite. If magnetite is forming at palaeo-interfluvial margins, it is too minor a component to be seen easily and further research is needed to identify this sink.

Palaeo-interfluvial groundwater contains 5−15 μg/L U and 1−2 μg/L V (Figures 4 and 5). Palaeo-channel groundwaters contain none. Uranium solubility is sensitive to redox;\textsuperscript{17,59} under reducing conditions it is immobilized as insoluble U(IV). Our data show it to be soluble under conditions of Mn-reduction. Others have shown U to be soluble under even more reducing conditions.\textsuperscript{59} As is the case elsewhere,\textsuperscript{60} the U in our Mn-reducing, palaeo-interfluvial, groundwater may be stabilized through the formation of a Ca−U−CO₃ complex in these water, which contain much Ca (∼ 100 mg/L) and bicarbonate (400−600 mg/L).

**IMPLICATIONS FOR HEALTH AND AGRICULTURE**

**Drinking Water.** Concentrations of Mn between 0.2 and 0.4 mg/L occur widely across southern West Bengal. Concentrations of Mn >2 mg/L occur in our area only at the margins of palaeo-interfluvial aquifers. High concentrations of Mn in groundwater elsewhere in the Bengal delta\textsuperscript{11,12} may also result from reduction at the interface of pre-LGM brown sand and post-LGM gray sand. The limited width of the strip interfaces we document restricts their impact on water quality and explains why it is uncommon to find a well that taps groundwater containing >2 mg/L of Mn. Migration of extreme concentrations of Mn into palaeo-

---

Figure 4. Concentrations of U, V, Mn, As, PO₄, Mo, and Cl, along the line of profile shown on Figure 1. Highest concentrations of Mn, Fe, Mo, and V, occur at Fe- and Mn-reduction fronts at the northern margin of the palaeo-interfluvial aquifer. Highest concentrations of As, and PO₄, occur in palaeo-channel groundwaters. Dotted guide lines arbitrarily drawn through the samples with the highest concentrations of Mn.

Figure 5. (a) Distribution of U in groundwaters of the study area. (b) Distribution of V in groundwaters of the study area. The base map and aquifer distribution for both are as in Figure 1.
interfluvial interiors has yet to occur, and is limited by sorption of Mn to, or its reaction with, marginal sediments of the palaeo-interfluvial aquifer. Concentrations of Mn in groundwater from palaeo-interfluvial interiors will therefore remain low for decades-to-centuries, as in the case of As. When retardation factors for Mn migration are known, this conclusion can be refined. Data of others show that Mn is widely distributed in groundwater of the Bengal delta at concentrations that may be hazardous in the light of modern epidemiological study. Nevertheless, in 2011, soon after these studies appear in print, WHO abandoned its Guideline Value for Mn in Drinking Water. Its stated reason for doing is that 0.4 mg/L of Mn is “well above concentrations of manganese normally found in drinking-water”. This statement is plainly wrong. This report, and further studies of Mn in groundwater, should provide the evidence needed to reverse that decision, if only as a precautionary measure to protect human health while epidemiological studies advance to the point of being definitive on this risk.

Concentrations of U in the groundwater of our area do not exceed the WHO GV of 30 μg/L (and rarely exceed the previous GV of 15 μg/L). Concentrations >5 μg/L are found confined to palaeo-interfluvial groundwaters. Concentrations of V are typically 1–2 μg/L in palaeo-interfluvial groundwater, and nil in palaeo-channel groundwater. Concentrations of Sb, Se, Cd, Pb, and Bi, (Supporting Information Table S1) are mostly undetectable (<1 ppb) by ICP-MS under the conditions used for analysis, or occur at concentrations (Supporting Information Table S1) that are less than the health-related guideline values of WHO (4th edition).

**Irrigation Water.** Manganese in irrigation water may be “toxic to a number of crops at a few-tenths to a few mg/L, but usually only in acid soils” (see also ref 14). In our study area, around half the irrigation wells tap the shallow palaeo-interfluvial aquifer. Its groundwaters typically contain 0.2–0.4 mg/L of Mn, so its long-term use for irrigation might adversely affect Mn-intolerant crops. The risk is greatest in acidic soils, some soils in the Bengal delta are acidic in the dry season, with acidity increasing with the length of time under cultivation. The reducing conditions of paddy soils when flooded may also mobilize Mn by reduction of Mn-oxides in the soil.

The risk to dry-season rice, the main irrigated crop, posed by Mn is lessened, during the period of growth in waterlogged soils, by the Fe- and Mn-plaque that rice forms around its roots by aeration. The plaque protects roots by sorbing and precipitating many trace elements, thereby reducing the potential toxicity of Mn and other trace elements to rice. As palaeo-interfluvial groundwater typically contains 0.2–0.4 mg/L Mn, except at its narrow margins, the potential for harm may be small, except at those margins. Paddy-field soils away from roots are reduced in the wet season, but are oxidized in the ripening period, during which fields are allowed to dry for harvesting. The oxidation generates acidity through ferrolysis. Whether a problem of Mn toxicity may be present in the dryland, ripening, phase of rice production in the dry-season crop is, therefore, a possibility, but one that is beyond the scope of this paper to address.

**Well Color.** The color of stain on well completions, pumps, and domestic utensils, can be used to screen wells for the presence or absence of As-pollution and to locate palaeo-interfluvial aquifers. Those authors noted that the margins of palaeo-interfluvial aquifers were exceptionally easy to locate using the color differences between palaeo-channel wells, which yield Fe-rich water that stains red, and palaeo-interfluvial wells, which yield Mn-rich water that stains black. The reason for that ease is now clear. It is because the margins of palaeo-interfluvial aquifers are the locus of focused Fe- and Mn-reduction fronts, so wells at the palaeo-interfluvial margins tap water that is especially rich in either Mn or Fe. The juxtaposition of the reduction fronts heightens the contrast between the two colors of stain developed from each type of water. Marginal wells tapping the Mn-front stain more strongly black than do wells in the palaeo-interfluvial interiors where Mn concentrations are lower. Marginal wells tapping the Fe-front stain more strongly red that do most of those in palaeo-channel settings. The intensity of stain can, therefore, provide confirmation that a well is located at the Mn-reduction front or Fe-reduction front, which, today, means at the palaeo-interfluvial margin.

**WIDER IMPLICATIONS**

The palaeo-interfluvial and palaeo-channel aquifers of the Bengal Basin that we have studied were created as a result of eustatic changes in sea-level since 125 ka. The changes created similar coastal landforms around the world, so the sediment architecture seen in the Bengal delta may be found in other modern deltas (for some examples, see ref 21). That architecture will affect groundwater composition as it does in the Bengal delta. In other deltas, extreme concentrations of Mn (>2 mg/L) and Fe (>15 mg/L) in groundwater mark the presence of strip-interfaces at the margins of buried palaeo-interfluvial. If so, palaeo-interfluvial margins will be identifiable using the criteria of well-color that has proven successful in the Bengal delta. Despite the operation of regional variations governed by geological and climatic setting, the context of palaeo-channels and palaeo-interfluvial may provide a unifying concept to assist development of deltaic aquifers and explain the distribution of Fe, Mn, Mo, V, PO₄, U, and other dissolved constituents and pollutants, in deltaic aquifers worldwide.

**ASSOCIATED CONTENT**

**Supporting Information**
Table S1 shows concentrations of dissolved species in well water and well depth and includes GPS coordinates to WGS84 datum. This material is available free of charge via the Internet at http://pubs.acs.org.

**AUTHOR INFORMATION**

*Phone 0044 (0)20 7679 2376; e-mail: j.mcarthur@ucl.ac.uk.

**ACKNOWLEDGMENTS**

This work was funded by the Department of Earth Science at UCL, by the University of Western Australia (B.N.) and by NERC grant NE/G/016879/1 (J.M.McA. and P.K.S.), and the University of Liverpool. We thank J.D. Ball, of the Lifer Laboratory at Liverpool University, for the isotopic analysis, Elliot Harper for separating and identifying magnetite from sediments cored in West Bengal, and Jim Davy for driving the EDAX-SEM.

**REFERENCES**

(1) Kondakis, X. G.; Makris, N.; Leotsinidis, M.; Prino, M.; Papapetropoulos, T. Possible health effects of high manganese...


(12) DPHE. Arsenic Contamination of Groundwater in Bangladesh, BGS Technical Report WC/00/19 (4 vols); Department of Public Health Engineering, British Geological Survey and Mott MacDonald: Dhaka, 2001


(15) Ayers, R. S.; Westcot, D. W. Drinking-water by arsenic in Bangladesh: A public health emergency.


(52) Datta, S.; Neal, A. W.; Mohajerin, T. J.; Ocheltree, T.; Rosenheim, B. E.; White, C. D.; Johannesson, K. H. Perennial ponds are not an important source of water or dissolved organic matter to groundwaters with high arsenic concentrations in West Bengal, India. J. Geophys Res. 2011, 38, L20404.