Arsenic in groundwater: the deep Late Pleistocene aquifers of the western Bengal Basin.

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ABSTRACT: in groundwaters from 145 wells across central West Bengal, India, those from Pleistocene aquifers at depths > 70 m beneath palaeo-interfluves contain $< 10 \mu g/L$ As. Pleistocene aquifers beneath deep palaeo-channels typically host groundwaters containing 10 to 100 μ g/L As at depths between 120 and 180 m. The depth profiles of As and SO4, and the conservative tracers Cl/Br, δ^{18} O, and δ^2 H, show that the As in Pleistocene groundwater beneath deep palaeo-channels is relict and does not arise from migration downwards of As-polluted groundwater in overlying aquifers. We postulate that the As was liberated *in-situ* by reduction of minimal iron oxyhydroxides in the grey Pleistocene sands by organic matter infiltrating from river-beds during late Pleistocene or earliest Holocene times. Mitigation of the widespread As-pollution in shallow aquifers through exploitation of deep Pleistocene aquifers would improve if guided by an understanding of the distribution of buried palaeo-channels and palaeo-interfluves and the knowledge that As may be present naturally in groundwater at depths > 150 m beneath deep palaeo-channels.

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1. DEEP and SHALLOW ARSENIC

Across Bangladesh and West Bengal, water-wells tapping shallow aquifers, typically at depths less than 60 m, provide the domestic water supply for much of the combined populations of 250 million. At such depths, concentrations of arsenic (As) frequently exceed the World Health Organization's Guideline Value of 10 μ g/L for drinking water.¹⁻⁴ Such water is termed here As-polluted. As late as 2009, some 52 million people in Bangladesh⁵ and 26 million people in West Bengal⁶ consumed such groundwater, which adversely affects health and may prove fatal. $7-13$

The As-pollution (As $> 10 \mu g/L$) is largely confined to groundwater in aquifers of grey sand that were deposited onto a late Pleistocene landscape as sea-level rose after the last glacial maximum (LGM) at 18 ka; for convenience here, these aquifers are termed 'Holocene' despite the fact that their basal sands might be as old as 18 ka (Section S1of the Supporting Information, hereinafter SI). Groundwaters in Pleistocene aquifers underlying the late Pleistocene land-surface usually contains $\langle 10 \mu g/L \text{ As}^{3,4,14-20} \text{ and, as a consequence, wells in Pleistocene aquires}$ increasingly replace shallow wells in Holocene aquifers as a water source in order to avoid shallow As-pollution. The depth to the Pleistocene aquifer varies regionally within the basin and, although poorly known, is widely held to be no more than 150 m (Ref. 3 *et seq*). The default option is therefore to install a deep well, *i.e.* at a depth > 150 m, in order to ensure it is located in a Pleistocene aquifer hosting groundwater containing $< 10 \mu g/L$ As. In Bangladesh, deep wells have become the *de facto* preferred option for mitigation despite other options being favoured by government policy.^{13,21,22} In West Bengal, community wells 152 m deep (500 ft) were adopted in the late 1990's by the state government as a mitigation option.

Across the Bengal Basin, a small but significant number of deep wells (*i.e.* > 150 m depth) have been reported to contain more than 10 $\mu g/L$ of As^{3,4,22–26} (see also [www.wbphed.gov.in,](http://www.wbphed.gov.in/) accessed 28 08 2014). These occurrences raise concern that As is migrating to depth in response to deep abstraction of groundwater for irrigation and domestic supply.^{3,4,17,26–28}. In West Bengal the concern is acute, given the use there by government agencies since the 1960s of abstraction of deep groundwater for irrigation on an industrial scale (Ref. 29 and TOC Art). In the long-term, downward migration of As from the shallow aquifers may compromise the value of the deep aquifer as a source of low-As water. Here, using the spatial distribution of As, and the conservative tracers Cl/Br, $\delta^{18}O$, and δ^2H , we attempt to constrain the effect on deep groundwater in Pleistocene aquifers of downward migration of shallow As in Holocene aquifers and explain the relevance of our finding to As-mitigation.

2. FIELD AREA

The field area comprises 235 km^2 of the western Bengal Basin between latitudes 22.9° and 23.1 $^{\circ}$ and longitudes 88.5 $^{\circ}$ E to 88.7 $^{\circ}$ E (Fig. 1a) in West Bengal. Previous work in this same study area³⁰, based largely on drilling, defined the extent and depth of palaeo-interfluves and palaeochannels and showed how they controlled the distribution of As-pollution of groundwater at depths $<$ 70 mbgl. In this paper, we deal with the distribution of As-pollution in late Pleistocene aquifers $>$ 70 m deep, all of which are composed of grey (not brown) sand, and all of which underlie either palaeo-channels or palaeo-interfluves. For details of the distribution of palaeo-channels and palaeointerfluves, see Ref. 30, references therein, and Section S2 of the Supporting Information (SI) where an East-West cross-section through the area, Fig. S1, is given along the profile line A–A on Fig. 1a.

The study area comprises a buried late-Pleistocene landscape of palaeo-interfluves and palaeo-channels that is overlain with mostly grey sands deposited since the termination of the last glacial maximum (LGM) at 18 ka. The top of the palaeo-interfluves is typically between 35 and 38 metres below ground level (mbgl), based on drilling of 73 boreholes³⁰. The depth to the bases of the palaeo-channels is \leq 70 mbgl, a figure based both on the depth to the base of the oxidised brown sands underlying the palaeo-interfluves^{20,30} and considerations of land elevation and sea-level lowering up to the time of the LGM (see Section 1 of the SI for an extended discussion of these points). We acknowledge that neither OSL nor 14 C dates are available from the study area to validate the depth to the LGM surface.

Palaeo-interfluves in the Bengal Basin are, by definition, capped with a palaeosol, termed here the last-glacial maximum palaeosol, or LGMP.³¹ The presence of the LGMP defines the extent of two palaeo-interfluves that cross the study area from north to south (Fig. 1a). The LGMP forms an effectively impermeable barrier to downward flow of water³¹ so palaeo-interfluvial aquifers are recharged at palaeo-interfluvial margins by focussed flow of groundwater from adjacent palaeochannels³¹⁻³³ (see also Fig. S2). The LGMP is underlain by Pleistocene sand, the uppermost 30 m of which is brown through oxidation during LGM times^{3,20,30} Deeper grey sands were not oxidised during LGM times. Groundwater from the grey sands only was sampled here.

Palaeo-channels in the Bengal Basin have a range of forms simplified here for clarity into two main types. The main river-channels of LGM times now infilled with grey, mostly Holocene, sands are termed here deep palaeo-channel aquifers; their groundwaters are widely polluted by As. These aquifers are at depths between 35 and 70 mbgl and termed deep to distinguish them from shallow palaeo-channel aquifers which are at depths between 0 and 35 mbgl. The latter were formed by reworking during river avulsion of the uppermost 35 m of sediment since 6 ka, which has left a near-continuous blanket of post-6 ka shallow paleo-channel sands covering both palaeo-interfluves and deep palaeo-channels across most of the study area and much of the southern and central Bengal Basin. 19,20,30

3. SAMPLING and ANALYSIS

During the period February 2011 to February 2014, we sampled 145 wells > 70 m depth tapping groundwater in Pleistocene aquifers of grey sand sited beneath both deep palaeo-channels and beneath palaeo-interfluves (Fig. 1; Table S1 and Figs S1, S2, of the SI): the locations of wells are referenced to the WGS 84 co-ordinate system. Many were private hand-pumped wells. Most others were hand-pumped community wells fitted with Mark II piston-pumps, installed by the government of West Bengal between 1986 and 2013 in order to mitigate As-pollution, and at a intended depth of 152 m (500 ft) depth with screen lengths of 11 m (36 ft). For 24 deep wells, the pump was removed and depth measured including the 8 wells, all Mark IIs, which had elevated Cl/Br in their waters. These 8 wells were sampled through a plastic pipe, ⅝- inch in diameter and 150 foot long, that was inserted down the well after removal of the pump assembly. We also sampled two well-nests installed in 2011 in Dasdia at sites MP and SP (Fig. 1a). Site SP is in a palaeo-channel $\lt 10$ m from the edge of a palaeo-interfluvial margin. Site MP is 120 m into the palaeo-interfluve west of SP and so near a palaeo-channel margin. We analyzed groundwaters for As, Cl, Br, SO₄, δ^{18} O and δ^2 H by methods given in Section S3 of the SI.

4. RESULTS and DISCUSSION

Spatial Distribution of As. In our study area, groundwaters from beneath palaeointerfluvial interiors contain ≤ 8 ug/L of As but shows a range of concentrations, with the highest clustering around depths of 50 m and 150 mbgl (Figs. 2, S3). In contrast, only 8 groundwaters from beneath deep palaeo-channels contain $\langle 10 \mu g/L \rangle$ As (Fig. 1b; Table S1); the rest contain concentrations from 10 and 100 μ g/L As, with most high concentrations clustering around depths of 30 mbgl and 130 mbgl (Figs. 2, S3).

Establishing the reality of the maximum As concentration at 130 m is compromised by the lack of wells in the depth range 65 to 90 mbgl. Nevertheless, the As profiles in our well-nests at SP and MP accord with this deep maximum, and the minimum around 90 m depth (Section S4 of the SI). Furthermore, concentrations of As in groundwaters across Bangladesh^{3,4,34} and West Bengal^{35,36} are highest between 20 and 40 mbgl and decline with depth thereafter to depths around 90 m. These similar concentration profiles exists despite deep pumping for irrigation being common in West Bengal since the 1960s but uncommon in Bangladesh. The profiles suggests that drawdown of As may be less than commonly presumed and that the low concentrations of As around 65 – 90 mbgl are real.

The depth profiles show that As concentrations reach $150 \mu g/L$ in some groundwaters from beneath palaeo-interfluvial margins (Figs. 2, S3). This is not unexpected, given that aquifers beneath palaeo-interfluves are partly recharged from As-polluted palaeo-channels, but the fact that As-pollution of groundwater is not found everywhere under palaeo-interfluvial margins (Fig. 1b) shows that regional flow into the palaeo-interfluves may be enhanced by local pumping *e.g.* where a high-yield irrigation well is sited inside a palaeo-interfluve and close to its margin.

Groundwaters in Pleistocene aquifers beneath palaeo-interfluves are essentially free of As, whilst those in Pleistocene aquifers beneath deep palaeo-channels are mostly As-polluted. This deep As may have three origins. Firstly, it may have been drawn down from As-polluted *shallow* palaeochannel aquifers by deep pumping, although the minimum at \approx 90mbgl in the depth profiles of As and SO⁴ (Figs. 2, S3) make this unlikely. Secondly, it may have been drawn down from overlying As-polluted *deep* palaeo-channel aquifers by deep pumping. Thirdly, it may have been generated *insitu* at or close to its present location and depth. We examine these three possibilities below.

Cl/Br and SO4. A plot of Cl concentrations versus Cl/Br mass ratios for groundwaters allows discrimination of sources of Cl. The plot can distinguish waste-water contributions to groundwater from those made by brackish connate-water of marine origin.³⁷⁻³⁹ Using Cl/Br, shallow palaeo-channel aquifers in the study area⁴⁰, and elsewhere in West Bengal³³, have been shown to be pervasively contaminated by Cl from waste-water. They are also pervasively polluted by As.³⁰ Mixing with brackish connate water elevates concentrations of Cl above 10 mg/L in a few deep groundwaters, but these are identifiable because they plot on the brackish mixing line (Fig. 3).

From the above, it is clear that shallow groundwater and its As-pollution could not invade deep Pleistocene aquifers of the study area without being revealed by the presence of more mobile contaminant Cl and an elevated Cl/Br. Yet none of our groundwaters from Pleistocene aquifers beneath palaeo-interfluvial interiors have elevated Cl/Br (Fig. 3) and so none contain shallow groundwater or its As-pollution. This observation is consistent with the conclusions of the previous section.

Around 72 % of groundwaters from beneath deep palaeo-channels have Cl/Br ratios that plot on or below the mixing line between recharge and brackish connate water (Fig. 3), suggesting that they are uncontaminated by Cl or As in shallow groundwater. These 72% of groundwaters nevertheless contain typically 10 to 100 μ g/L As with outliers up to 326 μ g/L (Table S1). Some 28% of groundwaters from beneath deep palaeo-channels have elevated Cl/Br. A Cl-mixing model (Section 6 of the SI) assigns a contribution to these groundwaters from As in shallow groundwater of \leq 16 µg/L As and mostly very much less. Thus, little of the As, and that in only 28% of our deep groundwaters, is likely to be derived from shallow groundwater.

Furthermore, groundwaters show an inverse relation between Cl/Br and As (Fig. S4). They do so because waste-water has elevated Cl/Br and contains many mg/L of Cl, NO₃, and SO₄⁴⁰. The NO³ suppresses reductive dissolution of iron oxyhydroxides and As-release. The SO⁴ sequesters As from solution into neoformed pyrite.^{14,41} Our analysis may therefore overestimate the contribution to deep As that could be made by shallow groundwater.

Some deep groundwaters with $\langle 12 \text{ mg/L Cl} \rangle$ plot below the brackish-water mixing-line (Fig. 3). They do so for one or more of three reasons: they have received additional Br from organic decay; $33,40,42$ they have suffered evaporative concentration during recharge; the end-member, chosen to represent the freshest shallow groundwater, is inappropriate for deep groundwaters. Addition of organic Br can displace Cl/Br downwards from positions above the mixing line or from positions on the mixing line. If the former, the Cl mixing-model shows that they contain no more than 4% of waste-water, with amounts up to 9% for the two highest Cl concentrations. These additions would carry $< 6 \mu g/L$ of As (Section 6 of the SI) and so contribute little to As-pollution.

Further constraint on downward movement of groundwater can be obtained from a consideration of the depth profile of SO_4 . Below 70 mbgl, most concentrations of SO_4 are below our detection of 0.01 mg/L. Where SO_4 is found below 70 mbgl, Cl/Br shows that it was contributed by mixing with brackish water. Although $SO₄$ is not a conservative tracer, its steep downward decline in concentrations is unlikely to reflect only sulphate-reduction given the high concentrations of SO_4 in the shallow aquifers (Fig. 2) and the persistence of SO_4 in brackish-water pockets at depth. Below 70m depth, the lack of SO₄ derived from shallow groundwaters probably also reflects the maximum depth to which they are drawn by pumping, a view consistent with a piston-flow calculation that suggests irrigation pumping has drawn shallow groundwater regionally to depths of \leq 70 mbgl (Section S5 of the SI). ^{43,44}

Our data confirm the findings of spatial analysis that As-polluted groundwater in Pleistocene aquifers beneath deep palaeo-channels has not been drawn down from *shallow* palaeo-channel aquifers by deep pumping. The As may have been drawn down from overlying As-polluted *deep* palaeo-channel aquifers by deep pumping; or been generated in the Pleistocene grey-sand aquifers close to or at the levels at which it is now found. We examine these two possibilities below.

Stable Isotopes. Downward migration of As-polluted groundwater in deep palaeochannel aquifers to pollute underlying Pleistocene aquifers cannot have happened in historic times because the Cl/Br tracer shows that groundwaters in the Pleistocene aquifers are largely unaffected by contaminant Cl. Such downward movement of groundwater might have happened in pre-historic times before Cl contamination of groundwater became widespread. In this latter case, the groundwaters in deep palaeo-channels and those in the underlying Pleistocene aquifers should have

similar isotopic compositions. Conversely, if the As-bearing groundwater in the deep Pleistocene aquifers is *in-situ*, it should have a different isotopic composition to groundwater in overlying deep palaeo-channels: each type of groundwater would have been recharged at different times under different climatic regimes.

The δ^{18} O and δ^2 H of groundwaters from Holocene deep palaeo-channel aquifers plot along an extended evaporation line that trends to the right of the local meteoric water line (LMWL) of Ref 45 and intersects it at the value for local volume-weighted rainfall (Fig. 4a). Groundwaters from Pleistocene aquifers beneath the deep palaeo-channels cluster tightly around two local evaporation lines (LELs) labelled A and B in Fig. 4a, with slopes different to the LEL for deep palaeo-channel groundwaters. The LELs A and B intercept the LMWL at isotopic compositions more positive than that for annual, volume-weighted, rainfall, which is the intercept on the LMWL of the LEL for deep palaeo-channel groundwater. Deep palaeo-channel groundwaters also have a much wider range of composition than do deeper groundwaters in the Pleistocene aquifers. The majority of groundwaters from beneath palaeo-interfluvial interiors also cluster tightly around LELs A and B, the tightness of fit being particularly close for groundwaters from depths > 150 mbgl.

The isotopic differences between groundwaters in the Holocene deep palaeo-channels and those in the Pleistocene aquifers beneath them (and at depths > 70 mbgl beneath the palaeointerfluves) shows that the groundwater in the deep Pleistocene aquifers cannot be derived from deep palaeo-channel groundwater. It follows that the As-polluted groundwater in Pleistocene aquifers beneath deep palaeo-channels has obtained its As in or near its present locality and depth. We postulate that it has been generated *in-situ* by microbial reduction of sedimentary iron oxyhydroxides and discuss the potential driver for that reaction in a later section, whilst digressing slightly here to examine the special case of wells at palaeo-interfluvial margins.

Palaeo-interfluvial Margins. Direct recharge downward into palaeo-interfluvial aquifers to replace abstracted groundwater is prevented by the LGMP, so recharge is focused at their margins and occurs from adjacent aquifers, and by upflow from deeper levels (Fig. S2; Refs 31–33). It is therefore at palaeo-interfluvial margins that the penetration to depth of As and Cl from shallow levels should be greatest. Below, we examine the evidence for such penetration in our field area.

Concentrations of As in groundwater from Pleistocene aquifers are lower beneath the palaeo-interfluvial margins than in groundwaters from beneath deep palaeo-channels. Also, the marginal sites show their highest concentrations at slightly shallower depth than are seen at deep palaeo-channel locations (Figs. 2, S3).

Of 22 groundwaters from beneath palaeo-interfluvial margins, only 7 have Cl/Br much above the brackish-water mixing-line (Fig. 3). Of these 3 contain $\lt 3 \mu g/L$ As, the others contain 36

to 135 g/L As. The Cl mixing model between shallow As-polluted groundwater and uncontaminated recharge (Section S6 of the SI) shows that shallow groundwaters contributes ≤ 10 μ g/L to groundwater under palaeo-interfluvial margins, which is \leq 12% of the As in these wells, and mostly much less. These figures show that few of the As-affected groundwaters in Pleistocene aquifers beneath palaeo-interfluvial margins derive significant As from shallow groundwaters.

The profiles and concentrations of As are consistent with the movement into Pleistocene aquifers at palaeo-interfluvial margins of groundwaters mostly from Pleistocene aquifers *beneath* deep palaeo-channels, with localized contributions from palaeo-channel groundwaters. The widespread presence of the LGMP prevents downward recharge of palaeo-interfluves, thereby focusing flow into them through palaeo-channels.³¹⁻³³ Alluvial channel deposits are known for their heterogeneity and discontinuous fine-grained units (*e.g.* abandoned-channel fill³³) restrict vertical flow more than they restrict horizontal flow. Deep rotary drilling in the Bengal Basin²⁶ tends to confirm this general rule as has our shallower drilling (Fig. S7).

The Redox Driver. We have shown that As is present in groundwater in deep Pleistocene aquifers of the study area, and that it did not migrate to those aquifers from overlying levels. It must therefore be in-situ. How did it arise? We postulate that is arises from reductive dissolution of sedimentary iron oxyhydroxides, a mechanism widely accepted as the cause of natural As-pollution of anoxic groundwaters worldwide. $46-51$ We further postulate that the driver of reduction was dissolved organic matter in Late Pleistocene or earliest Holocene river-water that infiltrated downward through river beds. When induced by pumping to infiltrate river banks, organic matter in river water drives reduction in aquifers⁵²⁻⁵⁴ and natural infiltration of organic matter would have a similar effect. The opportunity for such infiltration would have been greatest between 50 ka and 18 ka as sea-level declined⁵⁵, the coastline retreated southwards from the study area, and the climate became gradually drier.⁵⁶⁻⁵⁸ The declining sea-level would have left river beds at increasing elevations, a maximum of 125 m above sea level being reached at the LGM at 18 ka.

5. IMPLICATION for MITIGATION

Modelling the migration to depth of As in groundwater of the Bengal Basin^{26,27,59,60} predicts a variety of outcomes from deep pumping. Those outcomes will be modified as local knowledge at large scale refines the assumptions that underpin such models. In the mostly rural settings we have studied, the deep As is relict and unconnected to pumping. Our findings are based on a smallish region of central West Bengal. Nevertheless, palaeo-channels and palaeo-interfluves are found across much of the Bengal Basin^{3,4,19,20,30-33} so our findings will likely apply widely. Further surveys of groundwater arsenic, coupled to analysis of Cl/Br and stable isotopes, ideally with

tritium/ 14 C analysis as well, are needed to show just how widespread across the Bengal Basin our findings will be applicable.

Arsenic pollution in deep groundwater in West Bengal has been reported before 24.25 but those authors report a linear decrease in As concentrations with depth, a trend not seen in our work, so care is needed when comparing those studies' results to ours. The different trends with depth may reflect the different well-types sampled. The studies of Refs. 24 and 25 appear to have sampled deep high-yield municipal wells with screens between 10 and 30 m long. The mixed-redox state of many of their groundwaters, which contained reduced and oxidised species (e.g. dissolved O_2 and dissolved Fe) may reflect mixed waters sampled by such long screens. High-yield wells may draw down shallow groundwater locally, as those authors state, but perhaps only to the top of the screen. For this study, we sampled mostly village, hand-pumped, wells of low yield with screen lengths typically ≤ 11 m because we sought to quantify the regional effect of drawdown by irrigation pumping, rather than the localized and specific effect of any particular high-yield well. Given our findings, it is unwise to use as groundwater tracers either Cl without Br, or $\delta^{18}O$ without δ^2H , especially when interpreting depth profiles.

To avoid As-pollution fully, community wells may need to be place remote from major pumping centres. In order to avoid natural deep As, they may also need to be deeper than the 500 ft (152 m) depth specified by the Government of West Bengal as the presumed depth to As-free water. Mitigation through the installation of deep wells would be best accomplished in the light of a detailed knowledge of the subsurface distribution of palaeo-channels and palaeo-interfluves because sedimentological setting is one of the main controls on the risk of As-pollution of the Pleistocene, aquifers.

If screened beneath a palaeo-interfluve and > 50 m from its margin, wells of low-yield that tap Pleistocene aquifers are likely to remain safe for decades. The exception will occur where a low-yield well lies between a high-capacity well and a palaeo-interfluvial margin. Greatest protection will accrue to low-yield wells tapping brown sand beneath palaeo-interfluves at around depths of $50 - 70$ mbgl because such sands sorb $As^{27,32,61}$ that may migrate laterally from adjacent aquifers.

Wells that tap Pleistocene aquifers beneath palaeo-channels at depths between 120 and 180 mbgl are liable to encounter natural As-pollution. Local knowledge of that deep arsenic will typically be lacking, so appreciating that regulation operates remotely from local knowledge, wells deeper than 200 m may be prudent for low-yield wells beneath deep palaeo-channels in order to provide reasonable assurance that low-As groundwater can be obtained. The top of the screen should be as far as is practicable below the base of any overlying palaeo-channel in order to minimize the hazard from drawdown of As-polluted groundwater in deep palaeo-channels over the long term. Annual well-testing should be sufficient to identify encroaching As and could be conducted using field kits which, in competent hands, are sufficiently accurate for such a purpose. We reiterate the view⁶² that the benefits of abstracting groundwater *via* wells that tap the Late Pleistocene aquifer outweigh the risk from migration of As, provided those benefits are not subject to elite capture as described in Ref. 63.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the via the Internet at [http://pubs.acs.org.](http://pubs.acs.org/)

Detailed sedimentology, methods, draw-down calculations, well-nest profiles, supporting tables, and supporting figures (PDF)

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Notes

The authors declare no competing financial interest.

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List of Figures

Fig. 1. *a*) Study area, location of sampled wells, all $>$ 70 m deep, and aquifer types. Areas shaded yellow are subsurface palaeo-interfluves with tops 35 – 38 mbgl; deep palaeo-channels exist under unshaded areas (modified from Ref. 30). Cross-section along line A-B is shown in Fig. S1 (Supporting Information), with the solid part of the line schematized in Fig. S2. b). Spatial distribution of As in groundwaters, all of which are from depths > 70 m.

Fig. 2. Depth profiles of As and SO₄ in groundwater. Note scale changes on concentration axes. Data for depths < 70 m are from Ghosal et al. (2015). Concentrations of As beneath deep palaeochannels form a broad maxima between 120 and 180 mbgl.

Fig. 3. Relation of Cl concentration to Cl/Br in groundwaters from depths > 70 m. Of 22 groundwaters from beneath the margins of palaeo-interfluves (dotted symbols), 7 fall much above the brackish mixing line. End-member compositions for mixing lines from Ref 40 as follows: uncontaminated recharge, 1.3 mg/L Cl, 9.5 μ g/L Br; waste-water, 126 mg/L Cl, 81 μ g/L Br; brackish connate water (10% seawater), 1,940 mg/L Cl, 6.8 mg/L Br. Analytical uncertainty of Cl/Br values is about the size of the symbols.

Fig. 4. a) Stable-isotopic composition of groundwaters from deep palaeo-channels and from Pleistocene aquifers beneath deep palaeo-channels. With one exception labelled SBN 11, data for Pleistocene groundwaters cluster tightly around LELs A and B, which are reduced-major-axis regression fits to the local data pools. Data for deep palaeo-channels scatter widely along the LEL for deep palaeochannel groundwaters, the LEL has a slope steeper than LEL A or LEL B, and a lower intercept on the LMWL. The local meteoric water line (LMWL) from Ref. 45 is for Barasat, 50 km south of the study area. The large yellow triangle is those authors' value of annual volumeweighted rainfall for Barasat of -6.20 for $\delta^{18}O$ and -39.9 for δ^2H . b) Stable isotopic composition of groundwaters from Pleistocene aquifers beneath palaeo-interfluvial interiors of the study area. These also tightly group around LEL A and B, especially for groundwaters deeper than 150 mbgl.

Supplementary Information

Arsenic in groundwater: the deep Late Pleistocene aquifers of the western Bengal Basin.

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S1. History of the Bengal Basin, 125 ka to Now. The sedimentology of the aquifers of the Bengal Basin is summarized from Refs. $1 - 9$. In outline, sea level declined by some 120 m between 125 ka and 18 ka, the time of the last glacial maximum $(LGM)^{10}$. During the decline, the coastline retreated southward by up to 100 $km^{5,6,11}$. The existing and newly-exposed coast, and the low-lying hinterland, was eroded into a landscape of interfluves and river channels with a relief of mostly no more than 50 $m^{3,4,8}$. The pre-LGM sediments, predominantly sands, beneath the interfluves were weathered in the zone of most active groundwater flow, largely the unsaturated zone down to depths level with river bases, which was generally no more than 30 m depth. The weathering formed the oxidised brown Pleistocene sands that now sit on underlying grey Pleistocene sands that were weathered much less. A reddish-brown clay palaeosol formed on top of the brown, weathered sand, and has been termed a laterite^{3,4} and the 'last glacial maximum palaeosol', or $LGMP¹²$.

Sea level rose after the termination of the LGM, stabilising around 6 ka close to the present level. The rise created the accommodation space for the accumulation of post-LGM sediments, largely sands, on top of the LGM landscape to form the present submarine and subaerial deltas, under which lies the buried landscape of palaeo-interfluves and palaeo-channels. River avulsion since 6 ka has reworked the upper $20 - 30$ m of the sequence, leaving large areas covered by shallow palaeo-channel fill of grey sands to $20 - 30$ m depth, interspersed with silty/clayey/peaty floodplain sequences^{8,13-15}. Historical floodplain silts now cover the succession in the basin's south and central parts, forming an upper, semi-confining aquitard of fine sediments usually $<$ 5m thick.

Across the Bengal Basin, the LGM land-surface that separates pre- and post-LGM aquifers lies at a depth that depends on location. It has been customary to separate the 'deep' aquifers from the 'shallow' aquifers of the Bengal Basin using a practical division based on a maximum sea-level lowering of 120 m. In the light of both old¹ and recent^{9,14,16} results on sedimentology and dating in the Bengal Basin, that figure is no longer tenable. For example, around the basin margin, the pre-LGM surface crops out, as do pre-LGM aquifers. Additionally, across much of the basin interior, the LGM surface lies at 30–40 m depth where palaeo-interfluves are preserved in the subsurface, and at depths between 50 and 120 m depth in the far smaller areas underlain by palaeo-channels.^{1-4,8,8,12-15,17--21}

At the LGM, the depth of river incision, relative to today's ground surface, would have been greatest at the coast and been close to the sea-level lowering of around 120 m below present sea-level, which would be around 130 m below present ground level in our area where elevations are currently no more than 10 m above sea-level. Our area was >100 km from the coast at that time^{5,6,11} so the depth of river incision in our field area would have been less than 120 m and probably no more than 70 mbgl on the basis of our drilling information¹⁵ and inferences from the cross-sections of Refs. 3 and 4. For an area some 50 km south of our study area, a depth to the LGM surface¹⁵ is around 50 m. For central

West Bengal, the depth to the LGM surface²² is around 60 m. Using our more relevant local field data, in this work we have assumed that the depth to the LGM surface is 70 mbgl. Our conclusions would not differ were we to set the LGM surface deeper at, say, 100 m, because few of the wells we have sampled have depths between 70 and 100 m bgl depth.

S2. Geology of the Field Area. Reproduced below (Fig. S1) from Ref. 15 is a cross section through the field area from West to East. The line of section is line A-B of Fig. 1.

Fig. S1 Cross-section along line A-B in Fig. 1. LGMP = last glacial maximum palaeosol, which is overlain in some locations by a pale, blue-grey, clay. PI = palaeo-interfluve. DPC = deep palaeo-channel. SPC = shallow palaeo-channel. TPI = truncated palaeo-interfluve, where river incision since 6 ka has cut downwards and through the LGMP that caps the palaeo-interfluves.

The eastern two-thirds of the profile have been schematised in Fig. S2 in order to illustrate the hypothetical vulnerability of wells in Pleistocene aquifers to downward movement of As-pollution in overlying Holocene aquifers. Groundwaters in Pleistocene aquifers beneath deep palaeo-channels

Fig. S2. Schematic cross-section of the solid part of the line of profile A–B in Fig. 1 showing conceptualised command areas of wells in three settings: A, under a deep palaeo-channel. B, under a palaeo-interfluvial margin. C, under a palaeo-interfluvial interior. The well at B draws groundwater from beneath both palaeo-interfluves and deep palaeo-channels.

(Well A in Fig. S2) are more at risk of As-pollution from this source than are those beneath palaeo-interfluves (Well C in Fig. S2). The highest risk occurs at palaeo-interfluvial margins (Well B in Fig. S2) where downward flow is focused because most recharge to palaeo-interfluvial aquifers derives from adjacent aquifers, a lesser amount deriving from upflow beneath the palaeointerfluves.

S3. Analytical Methods. Samples from wells and piezometers were

taken after purging into two 15 ml polythene tubes, one acidified in the field with 0.15 ml of 50%

Analar® nitric acid for cation analysis, one unacidified for anion analysis. Samples were filtered using 0.45 micron membrane filters only when visibly turbid because we, and others²³, have found that filtered and unfiltered analysis is indistinguishable unless turbid, and because we wished to measure the As concentration in water consumed, which is not filtered after being drawn. Chemical analysis was by ion chromatography for Cl and SO₄ and ICP-MS for As and Br on acidified samples. For ICP-MS, standards were matrix matched to an average groundwater composition for groundwater from West Bengal. Bromide standards were used and mass 79 measured. Backgrounds were high but very stable at around 2,000 cps from peak-spread on the Ar dimer at mass 80, enabling an RSD of $\leq 10\%$ RSD down to 10 μ g/L Br, and \pm 1 μ g/L Br below that concentration. Sensitivity was around 500 cps/ μ g/L Br; the detection limit was around 1 μ g/L Br. Analysis of oxygen and hydrogen stable isotopes were done on unacidified samples, filtered through 0.22 μm membrane filters, using a Picarro WSCRDS laser instrument calibrated against standards USGS 46 and 48, with USGS 47 run as a sample to provide a further check on data quality. Analytical precision was \pm 0.13‰ for $\delta^{18}O$ and \pm 0.45 for δ^2 H (2s.d.).

S4. Composition of Groundwaters from Well-Nests SP and MP

Our interpretation is that As in deep groundwaters in Pleistocene aquifers has not been drawn down from shallow aquifers, even at palaeo-interfluvial margins. This contention receives support from the vertical distribution of As, Cl, and Cl/Br in two piezometers, MP and SP, located within the

site SP is natural and essentially *in-situ*. We postulate that the As at depth at site MP has been drawn-in laterally under the palaeointerfluvial margin by pumping and derives largely from the Pleistocene aquifer underlying the adjacent deep palaeo-channel aquifer, with no contribution from shallow levels and a minimal contribution from the adjacent deep palaeo-channel. A cross-plot of compositions of groundwater from 122 mbgl

field area (Fig. 1). The well-nest SP is located at the edge of a palaeo-channel: two boreholes 10 m apart revealed thin LGMP in the western-most and only grey sand (no LGMP) in the eastern-most. The well-nest MP is 120 m westward of SP in the direction of the interior of the palaeo-interfluve.

The vertical distribution of As at MP and SP (Fig. S3) show high As at shallow depth that is typical of Aspolluted shallow palaeo-channel groundwater. At and below 90 metres depth, Cl concentrations do not exceed 4 mg/L and groundwater Cl/Br is on or below the brackish mixingline of Fig. 3, showing that at these depths, no shallow groundwater is present. Concentrations of As in both piezometers show a minimum at 90 m depth and are higher at deeper levels, a depth distribution also seen in the groundwaters (Fig. 2). This deep As is present in both MP and SP, albeit in concentrations of $\langle 70 \mu g/L \rangle$ at depth. We interpret these profiles as showing that the As at depth at

at sites SP and MP show a high degree of concordance (Fig. S4), especially for the more conservative species, supporting the hypothesis of mostly horizontal migration. The concentrations of As at depth differs little between the sites. The uppermost 30 m of the sediments comprising the palaeo-interfluvial aquifers consists of brown sand that can sorb $As^{24,25}$. At greater depths, the sand is not oxidised, is grey, and presumably contains less iron-oxyhydroxide than the brown sands. Such grey sands will retard As migration less, and possibly hardly at all.

S5. Downward Piston Flow. Drawdown occurs to replace groundwater pumped for domestic supply and irrigation. To combat As-pollution in shallow aquifers, the government of West Bengal installed at least one deep community well per village to a depth of 152 m (500 feet bgl), the abstraction from which is $\leq 10\%$ of irrigation abstraction. To develop irrigation, from the early 1960's the Government of West Bengal installed numerous high-capacity deep wells for irrigation. These typically are of a total depth between 152 and 190 mbgl, with 176 m being a common depth. Screens are long, typically 30 m. Each well typically supplies around 0.4 km^2 of Boro (winter) rice with irrigation water during the dry season (February to May) across 74 % of Nadia District and 67% of North 24 Paraganas District. There are no regulations that are effective in restricting well-spacing.

The total depth of flooding by irrigation pumping each year is typically 1 m; we assume that 50% infiltrates and 50% evaporates. Coupled to an aquifer porosity of 40% for unconsolidated sands, these figures equate to total piston-flow drawdown that has penetrated no more than 70 m across Nadia and South 24 Parganas since 1960.

Many factors influence such estimates. Estimates of drawdown will be lessened because not all deep wells are operational at any one time; many farmers prefer to use their own motorised shallow irrigation wells, which pull water from shallower depths; flood irrigation from high-capacity government wells is not applied uniformly, being used only for low ground where hydraulic gradients allow gravity flow to feed fields. Both high-yield irrigation wells and municipal high-yield supply wells have long screens, typically up to 30 m, and the flow of water at any point through the screen will be inversely proportional to its distance from the pump intake: most pumped water comes from the screen area close to the pump intake and little originates from the lowest part of the screen. Drawdown of groundwater in marginal regions of the palaeo-interfluves may be underestimated because recharge to aquifers beneath palaeo-interfluves is focused at such margins.

Migration of groundwater and As from depth to beneath the palaeo-interfluvial aquifer must be occurring in response to extraction from beneath the impermeable LGMP. Drilling shows that the base of the brown sand in the vicinity of the piezometers is at a depth of about 70 mbgl¹⁵, so it is important to note that the deep As has not passed through brown sands beneath the local palaeo-interfluve but has migrated through the underlying grey, pre-LGM, sands. We know of no data that quantifies sorption of As to pre-LGM grey sands, but speculate that such sands sorb less than do brown, palaeo-interfluvial sands, which are known to retard migration of dissolved As in the subsurface of the Bengal Basin^{24–25}.

S6. Cl mixing-models. A few groundwaters from Pleistocene aquifers beneath deep palaeochannels, and a few in Pleistocene aquifers beneath palaeo-interfluvial margins, fall above the Cl v Cl/Br mixing line for brackish water, are contaminated by shallow Cl, and so might be polluted by

shallow As. The proportion of contaminant shallow groundwater, derived from a Cl-based mixing model, ranges from 1.4% and 27% for the affected groundwaters from beneath palaeo-channels, and from 2.3% to 17% for the affected groundwaters from beneath palaeo-interfluvial margins. The As concentrations in groundwater in deep palaeo-channels $(35 - 70 \text{ mbg})$ ranges up to 640 µg/L, but 75% of concentrations are $\langle 100 \mu g/L^{15} \rangle$. Groundwater flow homogenises contaminant concentrations through hydrodynamic dispersion, so concentrations in any deep palaeo-channel groundwaters that moves downward would likely tend toward the mean or median concentrations, which are, respectively, 60 and 27 μ g/L $(n = 75;$ Ref. 15). The maximum concentration of As that groundwater in deep palaeo-channels could supply to groundwaters beneath them would thus be $16 \mu g/L$ of As, and for most of the samples discussed would be a good deal less. With groundwaters beneath deep palaeochannels containing up to 326 ug/L As, but mostly concentrations in the range 10 to 100 µg/L, the contribution to deep As from shallow groundwater is likely to be insignificant even in wells with elevated Cl/Br. Even in cases where shallow, high Cl, high Cl/Br, groundwater might migrate to depth, its high content of $NO₃$ and $SO₄$ is likely to suppress Aspollution²⁶ by preferential utilisation of $NO₃$ for oxidation of DOC, and by sequestration of As in neoformed pyrite from sulphate reduction.

Fig. S5. Relation of As concentrations to Cl/Br mass ratio. The inverse relationship arises through the addition to groundwater of waste water containing high concentrations of Cl and NO3. The NO³ suppresses reduction of FeOOH and so prevents reductive dissolution releasing As to groundwater. Data for groundwaters at depths $<$ 70m from Ref. 15.

S7. Fig. 6. Photos of Cores

The photos below are a representative selection showing the frequency and nature of clayey lenses in shallow and deep palaeo-channel sediments. For locations, see Ref 15.

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Table S1. Locations, depths, and composition of well waters. Depths with an asterix were measured after removal of the pump.

Pleistocene Aquifers at 35 - 70 mbgl under a Palaeo-interfluve

Others lacking stable isotope data can be found in Ghosal et al. 2015

Pleistocene Aquifers 35 - 70 mbgl under a Palaeo-interfluvial Margin

Others lacking stable isotope data can be found in Ghosal et al. 2015

Holocene Aquifers 35 - 70 mbgl in Deep Palaeo-channels

Others lacking stable isotope data can be found in Ghosal et al. 2015

