# Groundwater quality beneath an Asian megacity on a delta: Kolkata's (Calcutta's) disappearing arsenic and present manganese.

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## Abstract

Kolkata, the capital city of West Bengal, exploits groundwater for public water-supply. The groundwater has been reported to be widely polluted by arsenic (As). Analysis for As in 280 groundwaters from across Kolkata, failed to detect As concentrations > 10 μg/L from natural processes. Arsenic concentrations between 10 and 79 μg/L found in 14 of the 280 groundwaters are remnant from a pollution-plume emanating from a single factory site where Paris Green, an arsenical pesticide, was manufactured between 1965 and 1985.

In 45% of groundwaters sampled, concentrations of Mn exceed 0.4 mg/L, a putative health guideline value for drinking water. Sporadic minor hazards are posed by Pb > 10 μg/L introduced into groundwater from well-fittings, from 4% of groundwaters with F concentrations between 0.75 and 1 mg/L, and the 14% of groundwaters containing more than 500 mg/L Na, concentrations that might contribute to excessive daily intake of Na. Compounding hazards from As, F, Mn, Na and Pb, shows that 64% of public wells and 40% of municipal wells supply groundwater of suspect quality. These species apart, groundwaters comply with WHO Guideline Values for drinking water in terms of Cr, Cu, Co, $NO_2$, $NO_3$, Sb, Se, and U. Aesthetic guideline values for Fe, Mn, $SO_4$, and Cl are exceeded for many groundwaters.

Keywords: arsenic, As, manganese, Calcutta, Kolkata, groundwater, pollution.

## 1. Introduction and Aims

Urban developments on deltas commonly exploit groundwater for water-supply. Increasing abstraction is driven by increasing populations, and increasing pollution of surface water that makes alternative sources necessary.[1-4] The increasing demand for groundwater leads to over-abstraction, a decline in groundwater levels and well-yield, deteriorating water quality, and land subsidence.[4-7]

An additional hazard in and around some Asian cities is the presence in groundwater of arsenic (As)[8-10], a colourless, odourless, tasteless, carcinogen. Kolkata, known as Calcutta before 2001, is such a city. The shallow aquifers around Kolkata are known to be widely polluted by As[11-14] and widespread pollution by As of groundwater beneath the city itself has also been reported.[15-17] Kolkata, however, taps only a late Pleistocene aquifer of brown over grey sands. This aquifer, commonly termed 'the deep aquifer', occurs across the Bengal Basin and is reported elsewhere to yield low-As groundwater[18-20]. In contrast, groundwater in the overlying, mostly Holocene, 'shallow' aquifer is commonly As-polluted across the Bengal Basin.[9,18,19]

Presented with claims that groundwater in the late Pleistocene aquifer under Kolkata is polluted by As, whilst groundwater in the late Pleistocene aquifer elsewhere in the Bengal Basin is not, we surveyed As concentrations in groundwater beneath Kolkata in order to resolve the apparent conflict. The data we collected allow us also to use Cl/Br to assess the degree to which surface pollution is being drawn into the aquifer by abstraction for municipal water supply, and to comment on other potential chemical hazards in groundwater.

We restricted our study to the 205 km$^2$ of Kolkata lying within the administrative area of the Kolkata Municipal Corporation (KMC, Fig. 1) because those reporting As-pollution beneath Kolkata did so.[15-17] Between September, 2015, and February, 2017, we sampled 206 public hand-pumped wells, 4 motor-pumped private wells, and 70 electrically-pumped municipal supply wells (Figs. 1, 2, S1). Public wells are low-discharge, hand-pumped, and installed for public use in public places *e.g.* along roadsides and in parks (Fig. S1): sampled wells have a median depth of 91 m and are fitted with screens 6 m in length and sited at the bottom of the well. Municipal wells are high-capacity wells fitted with submersible electric pumps that feed municipal supply *via* a piped-water distribution system (Fig. S1): sampled wells have a median depth to base of the hole of 121 m and are fitted with screens 20 m in length sited at the base of the well (Table S1 of the Supplementary Information). We also sampled the Hugli River at 5 sites (Fig. 1) that were distributed upstream, centrally, and downstream, of KMC, and did so on four occasions: October, 2015, and January, April, and July, 2016. Data are in the supplementary material (Table S1), with our methodology.

## 2. Kolkata's Water Supply

Kolkata lies on the east bank of the Hugli River at an altitude between 6 and 9 m above mean sea level. It is home to some 13 million inhabitants of whom 4.6 million live within administrative area of the KMC,[21] which is the historical core of the city (Fig. 1;

https://www.kmcgov.in/KMCPortal/jsp/KolkataStatistics.jsp). Groundwater provides 25% of the city's water supply and is drawn by private motorised wells operated by industry, housing estates, and high-rise apartments[22]. Another 10% is groundwater drawn from ≈ 260 electrically-pumped municipal wells that are typically 100 m to 150 m deep[23] (Fig. 2). Some 10,000 public hand-pumped shallow wells are also estimated to exist in the KMC[24]. The volume abstracted by public wells is insignificant compared to that abstracted by motorised municipal and private wells but their importance to public supply of water is great.

Decades of high-capacity pumping of groundwater has lowered the groundwater level in parts of the city by up to 14 m, creating cones-of-depression in the east, west and north of KMC (Fig. 3). The groundwater high between the eastern and western depressions arises because recharge is occurring from Tolly's Nala.

## 3. Geological and hydrological setting

***Aquifers of the Bengal Basin:*** the subsurface sediments of the upper few hundred metres of the southern Bengal Basin, including southern West Bengal, comprise a buried late Pleistocene landscape of palaeo-channels and palaeo-interfluves overlain by younger fluvial sediments. The late Pleistocene landscape formed between 125 and 18 ka when sea-level declined and the sea retreated southwards from the basin.[25] On the interfluves, weathering created a lateritic clay soil[26,27] here termed the last glacial maximum palaeosol[28,29] (LGMP). As sea-level rose to around its present level in the interval 18 to 6 ka and transgressed across this landscape[26,27,29-33], it was buried beneath mostly Holocene alluvial sediments infilling the accommodation space created (Fig. 4).

This geological development created two major aquifer systems across the Bengal Basin. Above the LGM surface, younger palaeo-channels infilled with grey sands form 'shallow' aquifers. Here we use the term 'Holocene'. Pollution of groundwater by arsenic is widespread in these aquifers. [9,12,18,19,33,34,35] Downward from the base of the LGMP and of indeterminate depth (*i.e.* typically more than several hundred metres) there is a 'deep aquifer' of brown sands over grey sands, hereinafter termed the late Pleistocene aquifer. The late Pleistocene aquifers contain groundwater that has < 10 µg/L of naturally-derived As[18-20], with trivial exceptions where strong pumping may have caused local drawdown.[36,37] Groundwaters in the late Pleistocene aquifers are low in As (< 10 µg/L) because As, held by reversible sorption to mineral surfaces, notable Fe-oxyhydroxides, was flushed from the aquifers during the period 125 ka to 18 ka[18] when groundwater flow-through was strong as sea-level fell from around its present level at 125 ka to 120 m below the present level at the LGM at 18 ka.

The late Pleistocene and Holocene aquifers are separated by the LGMP, except in those late Pleistocene palaeo-channels where it was never formed (*e.g.* the Adi Ganga deep palaeo-channel in Kolkata) because they contained active rivers, or where Holocene river incision has removed it. The LGMP is an effectively-impermeable barrier to flow between the two aquifer systems.

***The aquifer beneath Kolkata**:* the lithology of the sediments beneath the KMC is shown in Fig. 5 as a fence diagram based on cores[26] and lithological logs from 109 rotary-drilled boreholes.[38,39] In summary, an aquifer comprising ≈ 280 m of late Pleistocene sands lies between a lower aquiclude of thick clay and an upper aquitard of the LGMP and overlying floodplain silts, clays and peats. In detail, at depths between 320 and at least 600 mbgl lies a clay of indeterminate age with occasional intercalations of sand. This basal clay is overlain by a late Pleistocene sand aquifer containing laterally-impersistent clay interbeds. The sand is grey beneath 60 ± 20 m depth (location dependent) and brown above it. The sands are brown because they contain Fe(III)-oxyhydroxides that resulted from a long period of oxidative weathering during the period of declining sea-level between 125 and 18 ka.[9,18,26,27] The brown sand is capped by a hard, brown, lateritic clay, that is recognised as the LGMP. The top of the LGMP is at a median depth of 15 mbgl (mean depth 15.9 mbgl) and the median thickness is also 15 m (mean thickness 18.1 m). Overlying the LGMP are floodplain silts and clays, with widespread peats between 3 and 5 m depth, and at 12 m depth.

In 30% of borehole logs, no LGMP is recorded so Holocene river incision[29,40] has thinned or removed it. As lithologies were recorded in units of 5 m thickness, beds < 5 m thick would have escaped detection including the LGMP. At 90% of sites where the LGMP is not recorded, thick brown sand is logged, so most such site probably have a thinned LGMP. These brown sands are typically overlain by a thick (≥ 5 m) channel-fill of grey and/or black clay. In a few sites, intercalated grey sands occur in the channel fill but, except for the instance detailed below, these are invariably underlain by clays > 5 m in thickness. The effect of this stratigraphy is to cap the late Pleistocene aquifer over most of the KMC with either thick Holocene clays or the LGMP, or both.

We identify one deep, late Pleistocene palaeo-channel.[29,40] This marks the course of the Adi Ganga, a previous course of the Hugli River. The present Hugli River detours westward around the KMC. In past times, this detour was absent and the river flowed south through the KMC in a late Pleistocene deep palaeo-channel. Along the width and length of this deep palaeo-channel the LGMP was not developed. The grey sands that filled the palaeo-channel, as sea-level rose after the LGM. This deep palaeo-channel appears to run sub-parallel to, and possibly beneath much of, Tolly's Nala (Fig. 5) and certainly crosses beneath it in south-central Kolkata (district of Behala). Where it does so it provides a direct route for surface water from Tolly's Nala to infiltrate the underlying late Pleistocene aquifer and bypass the upper aquitard that is present elsewhere.[41]

## 4. Arsenic in KMC groundwater

***Arsenic pollution under KMC:*** of groundwaters from 280 wells, those from one municipal well (No 33) and thirteen public wells contained > 10 μg/L of As. An absence of As-pollution was expected because wells in the KMC are screened in late Pleistocene grey sands in which natural As-pollution is absent. The presence of As in 14 groundwater samples therefore needs explanation.

The As appears to be a remnant of past anthropogenic pollution. Between 1965 and 1985, Paris Green, an arsenical pesticide was made by Aceto-Chemical Private Ltd (ACPL hereinafter) at an industrial site in Behala, south-central Kolkata (Figs. 1, 6, 7).[41-43] Groundwaters in 1993 close to the ACPL site were reported to have concentrations of As up to 39,000 μg/L.[43] The ACPL site was located 200 m west of Tolly's Nala and was connected to it *via* a drain.[41] Beneath parts of Tolly's Nala, *e.g.* and at the ACPL site, the absence of the aquifer's usual capping aquitard (Fig. 5) provides a pathway into the underlying aquifer for the As-pollution.[41]

No arsenic concentrations > 5 μg/L were found upflow (*i.e.* to the southwest of) the ACPL site, the direction from which As-pollution would arrive were migrating to the site from Holocene aquifers outside of KMC. Groundwaters that contain As > 5 μg/L are found close to, or downflow of, either the ACPL site or Tolly's Nala (Fig. 6). No other site yielding groundwater with > 10 μg/L is more than 800 m from the ACPL site or Tolly's Nala. The As concentrations > 10 μg/L reported in groundwater here appear to derive from the ACPL site. The initially severe local pollution sourced from the ACPL site is now barely detectable at the spatial scale at which we have sampled.

***Arsenic's route to the aquifer under the KMC:*** the arsenic from the ACPL site was able to invade the late Pleistocene aquifer from Tolly's Nala through the window in the upper aquitard that exists where Tolly's Nala crosses the palaeo-channel of the Adi Ganga (Fig. 5, 7). Stable isotopic compositions of groundwaters reveals the extent of infiltration of river water. With trivial exceptions driven by local evaporation, the stable isotopic composition of groundwaters (Fig. 8) plot along a linear array parallel to the local meteoric water line.[44] The least-depleted groundwater compositions (− 3 to − 4‰) fall within the range of groundwaters in late Pleistocene aquifers elsewhere across the Bengal Basin[45]. Waters from the Hugli River sampled here have $\delta^{18}O$ values between – 6.1 and – 7.9 ‰, the values changing seasonally in response to varying proportions of base-flow, snowmelt, and rainfall-runoff, that reaches the river.

The least depleted $\delta^{18}O$ value for Hugli River water is − 6.1 ‰. Groundwaters with values more negative than this are found, with few exceptions, in two clusters close to Tolly's Nala. One is close to the ACPL site, the other is 1 km to the south at the major bend in Tolly's Nala (Fig. 9). The proximity to Tolly's Nala of these sites suggests that infiltration to the late Pleistocene aquifer beneath KMC is occurring from Tolly's Nala. The array in Fig. 8 thus results, in part, from mixing of isotopically-depleted water from the River Hugli, *via* Tolly's Nala, with less-depleted groundwater. This connection is seen directly in Well 33, which is sited 70 m east of Tolly's Nala and is screened at a depth of 102 to 122 mbgl. Groundwater composition for this well vary through the seasons (Fig. 8) and the elemental and isotopic compositions for the groundwaters from Well 33 (Table S1) fall along a linear-mixing line reflecting this seasonal change in the proportion of river water and groundwater supplied by this well. We illustrate this mixing in Fig. 10 using As *v* Cl concentrations. Similar linear (conservative) mixing is seen for most other constituents (Table S1), thus proving that this well is partly recharged by river-bank infiltration.

## 5. Reconciling conflicting claims

We find that there is no natural As-pollution of groundwater beneath the KMC and only a trace of As-pollution remnant from the ACPL site, although we caution that differences in scale makes our findings not directly comparable to the initial small-scale survey[43] at the ACPL site.

Our finding conflicts with the impression given by a published map of As pollution in groundwater beneath Kolkata[16] which shows 62% of the area of the KMC as being underlain by groundwater with > 10 μg/L of As. The map's basis is not clear and its implication conflicts with the claim[16] that groundwater containing > 10 μg/L of As was found only in 14% of 4,210 wells across KMC. The discrepancy cannot be resolved as no well locations are given, nor are they shown on the map. Another report[17] of arsenic concentrations > 10 μg/L in groundwaters across KMC, which contains only summary data, claims that As pollution has increased since 2009. How can these claims be reconciled with our data?

Previous claims[15-17] are not supported by data that could resolve the conflicts. Nevertheless, a resolution is possible. Regarding Ref 17, no GPS locations of wells were reported but the authors provided to the writers the GPS co-ordinates of three (their numbers 55, 56, and 57). We analysed groundwaters we collected from Wells 56 and 57 (55 was defunct in early 2017). Data are, in μg/L:

*Ref 17* No. 56: As = 41 Fe = 1,626. *Same well, this work*, (our 249): As = 1.2, Fe = 3,700

*Ref 17* No. 57: As = 14, Fe = 128. *Same well, this work*, (our 247): As = 1.1, Fe = 6,800

For Ref 17, ICP-AES was used to quantify As concentration without specifying analytical conditions; no quantitation limit was reported. For ICP-AES it is typically between 10 and 100 μg/L depending on instrument make, maintenance schedule, and operating mode. This work used ICP-MS with a quantitation limit around 1 μg/L. We therefore regard the summary data of Ref. 17 as being erroneous because they were obtained using an analytical method insufficiently sensitive for the task undertaken. We discount the possibility that those authors sampled mainly the limited occurrence of shallow palaeo-channel aquifers beneath Kolkata, and our essentially-random sampling did not. Our analysis of the geology underlying Kolkata (Fig. 2, 5), and the number of wells we sampled, restricts this likelihood severely. Moreover, the claim[17] that As-pollution has increased since 2009 would be valid only if the authors of that work had sampled the same wells as had the authors of Ref 15 and found that As concentrations in those wells had increased. There is no indication that they did so.

Regarding the apparently contradictory claim that 14 % of KMC wells gave groundwater with > 10 μg/l As whilst 62% of the area under Kolkata is As-polluted[16], the supplementary information for Ref 16 reveals that 57% of the samples were collected prior to 1999 and 86% were collected prior to 2009. It follows that, irrespective of inconsistency, these publications do not reflect the *current* hazard posed by As in KMC's groundwater.

## 6. Fate of anthropogenic As

What is the fate of the anthropogenic As-pollution spilled at the ACPL site? The schematic cross-section through the ACPL site shown in Fig. 7 suggests that, since the ACPL site closed in 1985, > 30 years of dilution and dispersion has lowered the concentration of As in groundwater. Secondly, sorption to brown and grey late-Pleistocene aquifer sands will have contributed to the removal of As from groundwater.[31,46-48] Thirdly, As substitutes for S in pyrite[49-53] so sequestration of As into pyrite has been invoked repeatedly as a sink for As in order to explain unexpectedly low concentrations of As in anoxic groundwaters.[54-59] The ACPL factory made Paris Green, ($Cu[CH_3COO]_2{\cdot}3Cu[AsO_2]_2$), which contains acetate, so the factory effluent would likely have contained acetate or acetic acid, microbial oxidation of which would have promoted the reduction of $SO_4$ in the pollution plume and contributed to pyrite formation. That sulphate reduction has occurred in groundwaters is shown by the fact that salt-corrected concentrations of $SO_4$ are in deficit by up to 110 mg/L (Fig. S2a). To achieve this amount of reduction requires 28 mg/L of DOC. Sulphate in excess is now found in fresher groundwaters bordering Tolly's Nala (Fig. S2a), thus emphasizing the temporal element of the As-pollution; older water is deficient in $SO_4$ whilst younger water is enriched in $SO_4$ and found mostly in the vicinity of Tolly's Nala (Fig. S2b).

## 7. Other Elements

***Copper:*** Paris Green contains copper. Although Paris Green has a very limited solubility in water, the Cu salts used to make it were likely more soluble. Yet only two groundwaters contain > 10 μg/L Cu (179 and 12 μg/L for Wells 180 and 258). Neither are near Tolly's Nala or the ACPL site. Copper substitutes well into pyrite, so we hypothesise that either little Cu salt accompanied the As-pollution emanating from the ACPL site, or that Cu that might have contaminated groundwater between 1965 and 1985 has been removed by dilution, dispersion, and sulphide formation.

***Manganese:*** the presence of Mn in groundwater may be a hazard to health, especially for children.[60-64] The element is present in both Holocene and late Pleistocene aquifers across the Bengal and other Asian deltaic aquifers.[18,19,65,66] Despite this hazard, no Guideline Value (GV) for Mn was set by the World Health Organization[67] in 2017 although "*A health-based value of 0.4 mg/l can be derived for manganese based on the upper range value of manganese intake of 11 mg/day*.". Prior to 2011, WHO did set a GV of 0.4 mg/L.

Of the wells we sampled in Kolkata, 37 % of municipal wells and 47% of public wells give groundwater with concentration of Mn > 0.4 mg/L and concentrations range up to 1.4 mg/L with one outlier at 2.8 mg/L (Table S1). Only one municipal well (No 33) contains > 1 mg/L Mn. Thus, for residents of the KMC, the hazard to health from Mn in groundwater may be greater than the hazard from As. The Mn concentrations are higher than those of 0.1 to 0.4 μg/L that are typically found in groundwaters from late Pleistocene grey sands elsewhere in the Bengal Basin.[18,19,45] They are, however, comparable to Mn concentrations found in late Pleistocene brown sands, which typically range between 0.2 and 1 mg/L except in the vicinity of redox fronts where roll-fronts of Fe and Mn oxides are mobilized and drive Mn concentrations up to 6 mg/L.[33,65] Concentrations of Mn > 1 mg/L appear to form a circular distribution emanating from the ACPL site; the distribution could be interpreted as a redox front progressing downflow from the ACPL site (Fig. S3). The highest Mn concentrations occur at around 120 m depth (Fig. 11c), as do Fe concentrations (Fig. 11b), but the Mn concentrations decline at increasing depth below 120 m more slowly than do those of Fe, again suggesting a redox front of Mn-reduction progressing ahead of an Fe-reduction front.

***Iron:*** in groundwater from late Pleistocene aquifers of the Bengal Basin, of both grey and brown sand, concentrations of Fe > 3 mg/L are uncommon. [18,19,45] In contrast, beneath the KMC concentrations of Fe > 10 mg/L are common and are concentrated around and to the north of the ACPL site (Fig. S3). The highest concentrations of up to 23 mg/L are at 120 m depth (Fig. 11b, Table S1). Concentrations > 10 mg/L indicate influx to the aquifer of a reducing agent of unusual power or concentration; we speculate that it was acetate from the ACPL site. Although organic matter from sewage disposal into Tolly's Nala might contribute to reduction, the data suggest the effect is minor because, around 1 km south along Tolly's Nala from the ACPL site, the stable isotope data (Fig. 9) reveal a window into the late Pleistocene aquifer for water from Tolly's Nala, yet in that vicinity Fe concentrations > 10 mg/L are all but absent (Fig. S3).

***Other trace elements:*** Mn apart, few elements of health concern[67] are present in amounts that pose a serious threat to consumers, although local, minor, hazards exist. They are summarised here; details are in the supplementary information, Section S3. Nitrate is present at concentrations > 0.5 mg/L only in groundwater from motorised wells (5 municipal, one private), of which 3 are < 200 m from Tolly's Nala; all have values of $\delta^{18}O$ more negative than −5.9 ‰. Concentrations of F are between 0.75 and 1 mg/L in 10 groundwaters and are inversely related Ca concentrations, suggesting a control by equilibria with a Ca-mineral, possibly fluorite or apatite (Fig. S4). Sodium concentrations have been increased by ion-exchange with Ca (Fig. S5a); Na concentrations > 500 mg/L (mostly in western KMC; Fig. S5b) might promote hypertension in consumers.[68-70] If hazards from As (> 10 μg/L) and Mn (> 0.4 mg/L) are compounded with uncommon hazards from F (10 wells, assuming a GV of 0.75 mg/L), common high Na (>500 mg/L), and minor exceedances for Pb (> 10 μg/L), then 64% of public wells and 40% of municipal wells are supplying groundwater of questionable quality because of one or more of these species.

***Chloride:*** high concentrations of Cl in groundwater beneath large cities is often taken to indicate the presence in groundwater of sewage effluent, which typically contains Cl concentrations in the range 300-600 mg/L.[59,71,72] In coastal settings, high Cl could also derive from salt-water either *via* modern intrusion or from brackish connate water. These two influences can be distinguished using Cl/Br values[71-73] and these are shown in Fig. 12a.

Around 10% of groundwaters plot below the marine-mixing line; all are at a depth of 120 mbgl (Fig. 12b). These groundwaters contain excess Br from organic degradation.[59,74,75] A further 33% of public wells and 14% of municipal wells plot above the marine-mixing line and are contaminated by Cl of anthropogenic origin (Fig. 12a; Table S1; Cl/Br > 308, the upper limit of 288 ± 20, to allow for analytical uncertainty). These figures are lower limits, as small additions of high-Cl sewage effluent would be masked by the high Cl concentration of many groundwaters (> 500 mg/L). Depth profiles of Cl/Br (Fig. 12b) shows that surface contamination by anthropogenic Cl has been drawn down to around 130 m depth by pumping. All wells deeper than 130 m, however, remain unaffected by surface-derived Cl, and so, by implication, other surface derived pollution given that Cl is more mobile in groundwater than are other contaminants or pollutants. Most of the groundwaters plot close to the marine mixing-line, proving that their Cl is derived from seawater (or brackish water of marine origin), rather than being of anthropogenic origin[59]. The depth profile of predicted-Cl *i.e.* Cl concentrations predicted from Br so discounting anthropogenic Cl (Fig. 11a), shows that the interval 80 to 120 mbgl is the most affected by seawater.

Although elevated Cl/Br is seen in scattered localities elsewhere across KMC, most elevated values are located in south central Kolkata near the ACPL site and along Tolly's Nala (Fig.

12 c). This is unsurprising, as it is in the vicinity of the ACPL site that river incision along Tolly's Nala provides a conduit from the surface to the underlying late Pleistocene aquifer. The implication for groundwater supply is that wells should not be located near the intersection of the Adi Ganga palaeo-channel and Tolly's Nala. Until the subsurface route and extent of the Adi Ganga palaeo-channel is better known, the precautionary principle suggests that wells in Behala and all near Tolly's Nala should be tested for known surface-derived contaminants/pollutants.

## 8. Comparisons to other Asian Megacities

The sedimentological setting of Kolkata is similar to the setting of the megacity of Dhaka, Bangladesh. These two cities exploit a late Pleistocene aquifer protected from downward movement of pollution by a thick upper aquitard. The major difference is that for Dhaka, the city sits directly on an equivalent of the LGMP, whereas Kolkata sits on thick floodplain silts, clays, and peats, that are mostly underlain by the LGMP. Both cities have a local short-circuit that connects the aquifer to the surface. In Dhaka, it is a fault at the city's western side that throws the top of the late Pleistocene aquifer into the bed of the River Buriganga, so allowing river-bed infiltration to contribute to recharge of the late Pleistocene aquifers beneath the city.[45] In Kolkata, it is, possibly, Tolly's Nala; it is certainly the point where the palaeo-channel of the Adi Ganga crosses Tolly's Nala. In contrast to Dhaka and Kolkata, the city of Hanoi exploits Holocene and late Pleistocene aquifers that are shallower (typically < 70m depth), more connected vertically and laterally, and well-connected to surface sources of recharge such as the Red River.[8,76,77] The open system under Hanoi has resulted in widespread As-pollution occurring in the aquifers beneath the city.

## 9. Summary

1. For groundwater supply, Kolkata exploits a late Pleistocene aquifer of brown over grey sands that sits beneath a late Pleistocene palaeosol, termed the last glacial maximum palaeosol.
2. In common with late Pleistocene aquifers across the Bengal Basin, the groundwater in the late Pleistocene aquifer beneath Kolkata is not polluted by naturally-occurring As.
3. A deep palaeo-channel cuts north-to-south through southern Kolkata and marks the course of the ancient Adi Ganga river, a precursor to the present Hugli River that now flows in a channel to the west of the Adi Ganga palaeo-channel.
4. In the vicinity of Tolly's Nala, a minor distributary channel of the River Hugli, river incision has cut into the palaeo-channel sands of the Adi Ganga and connects the late Pleistocene aquifer to the surface waters in Tolly's Nala, forming a recharge window into the aquifer.

5. Between 1965 and 1985, a factory making Paris Green, an arsenical pesticide, was sited directly on the window into the late Pleistocene aquifer. Arsenic from the factory polluted groundwater. That pollution has now almost vanished from the groundwater through a combination of dilution, dispersion, absorption, and sequestration into pyrite.
6. Values of Cl/Br reveal that surface contamination of Cl has penetrated to 130 m depth.
7. Of groundwaters sampled from beneath Kolkata, 45% contained > 0.4 mg/L of Mn, so naturally-occurring Mn poses a bigger threat to health than does As.

Our finding that natural As-pollution appears to be absent from Kolkata's groundwater clarifies and downgrades previous claims of wide pollution by As beneath the city. The apparent conflict between these previous claims and our data illustrates the need for an understanding of the aquifer under investigation when undertaking a water-quality investigation. Credibility may have been given to the apparent presence of natural As-pollution in KMC groundwater[15-17] because such a finding would have been consistent with the common As-pollution in Holocene, shallow, aquifers around Kolkata. Had it been known that the aquifer beneath Kolkata is late Pleistocene in age and unpolluted elsewhere in the Bengal Basin, previous interpretations might have been different.

Those previous reports [15-17] might have been interpreted differently had they contained the data on which they were based and had they given full details of analytical methods. With such data, one[17] might have had its methodology questioned in review. Two others[15,16] might have established that the As pollution was anthropogenic and waning. No better examples could be found of the need for scientific reports to contain all of the data on which they are based.

## ■ ASSOCIATED CONTENT

*Supporting Information. The Supporting Information is available free of charge on the ACS Publications website at DOI:******************. Included in tables and supporting figures are well-locations, chemical and stable isotopic composition of groundwater.

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Notes: the authors declare no competing financial interest.

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## LIST OF FIGURES

Fig 1. Map showing the boundary of the Kolkata Municipal Corporation (KMC) and the locations of sampled wells, 4 of 5 river-sampling sites (the fifth is 13 km north of the map limit) and the location of the ACPL factory (red filled triangle at 88.339° E, 22.496° N) that manufactured Paris green, an arsenical pesticide, between 1965 and 1985. GPS of all locations are in Table S1 to WGS84, as used in Google Earth.

Fig. 2. Composite lithological section compiled from 109 borehole logs used for Fig. 5 (data from Ref 38) together with a histogram of the number of wells sampled for this study compiled into 10 metre bins using depths to mid-screen.

Fig. 3. Modelled depth to the water table, relative to mean sea level, of groundwater beneath Kolkata outlining cones of depression caused by abstraction of groundwater for public supply. Model of Ref 79; Table 2 of that reference gives measured water levels used to calibrate the model.

Fig. 4. Schematic cross-section E-W through the Bengal Basin, showing, not to scale, the approximate distribution of pre- and post-LGM sediments. Pollution of groundwater by As is confined almost exclusively to post-LGM sediments. Updated from Ref. 29.

Fig. 5. Geology beneath KMC and borehole locations ($n$ = 109) used to map the distribution of facies. Borehole data from Ref 38. The deep palaeo-channel of the Adi Ganga, a previous course of the Hugli River, is shown as a dotted line in the lower figure.

Fig. 6. Distribution of As in groundwater beneath the KMC. Sample locations in Table S1. Groundwaters with > 5 µg/L As are close to Tolly's Nala and/or the ACPL factory site, where Paris green, an arsenical pesticide, was manufactured between 1965 and 1985.

Fig. 7. Schematic E-W cross-section through southern KMC, showing the disposition of major sedimentary units: floodplain deposits over a palaeosol over a late Pleistocene aquifer of brown sand over grey sand. Channels from Holocene river incision are filled largely by clays. One pre-glacial (deep) palaeo-channel marks the old course of the Adi Ganga river and is infilled with mostly sand, thereby forming a conduit for recharge to the late Pleistocene aquifer. The site of historical As-pollution at the ACPL factory is next to Tolly's Nala, which may be vestigial remnant of the Adi Ganga.

Fig. 8. Isotopic compositions of groundwaters compared to the local meteoric water line, LMWL, for the region.[44], which is essentially the same as the global MWL. Groundwaters plot along a mixing line between isotopically less-depleted late Pleistocene groundwaters with $\delta^{18}O$ of around −3 to −4 ‰, and river waters ranging from − 6.1 to − 7.9 ‰.

Fig. 9. Map of the distribution of groundwaters with values of $\delta^{18}O$ less than − 6.2‰, the heaviest value recorded for Hugli River water. The isotopically-light groundwater is located close to Tolly's Nala and cluster around the ACPL site and a site on Tolly's Nala about 1 km

south of the ACPL site. These distribution proves the existence of a direct route for recharge between Tolly's Nala and the underlying late Pleistocene aquifer.

Fig. 10. Seasonal changes in As and Cl in groundwater from Well 33, sited 70 m east of Tolly's Nala. Water from this well comprises varying proportions of groundwater and river water from Tolly's Nala. Linear mixing is shown by most constituents (Table S1). The mixing line shows that Well 33 is partly recharged by river-bank infiltration from Tolly's Nala. For river data, we use the river sample RC of Table S1, which was the nearest river sample to the confluence of the River Hugli and Tolly's Nala, some 2.0 km upstream of the confluence.

Fig. 11. Depth profiles of Predicted-Cl (a), Fe (b), Mn (c), and As (d), in groundwater beneath the Kolkata Municipal Corporation. Depths given to mid-screen. Predicted-Cl is Cl predicted from Br concentrations, a measure that emphasises the influence of marine-derived waters by removing anthropogenic Cl. Values are not plotted for the 24 groundwaters with Cl/Br below the marine-mixing line in Fig. 12a.

Fig 12. a) Cross plot of Cl and Cl/Br in groundwater beneath the KMC and for septage in West Bengal.[59] Groundwaters contaminated by sewage and septage plot above the marine-mixing line; b) depth, to mid-screen, of Cl/Br; values > 308 are not present beneath 130 m depth - we use 308 rather than the marine value of 288 to allow for analytical uncertainty; c) distribution across KMC of Cl/Br of groundwater, showing that most Cl/Br values > 308 occur close to Tolly's Nala.