Retention of arsenic transport through a Pleistocene aquifer

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Groundwater drawn daily from shallow alluvial sands by millions of wells over large areas of south and southeast Asia exposes an estimated population of over a hundred million people to toxic levels of arsenic2. Holocene aquifers are the source of widespread arsenic poisoning across the region1,3. In contrast, Pleistocene sands deposited in this region more than 12,000 years ago mostly do not host groundwater with high levels of arsenic. Pleistocene aquifers are increasingly used as a safe source of drinking water4 and it is therefore important to understand under what conditions low levels of arsenic can be maintained. Here we reconstruct the initial phase of contamination of a Pleistocene aquifer near Hanoi, Vietnam. We demonstrate that changes in groundwater flow conditions and the redox state of the aquifer sands induced by groundwater pumping caused the lateral intrusion of arsenic contamination more than 120 metres from a Holocene aquifer into a previously uncontaminated Pleistocene aquifer. We also find that arsenic adsorbs onto the aquifer sands and that there is a 16–20-fold retardation in the extent of the contamination relative to the reconstructed lateral movement of groundwater over the same period. Our findings suggest that arsenic contamination of Pleistocene aquifers in south and southeast Asia as a consequence of increasing levels of groundwater pumping may have been delayed by the retardation of arsenic transport.

This study reconstructs the initial phase of contamination of an aquifer containing low levels of arsenic (low-As) in the village of Van Phuc, located 10 km southeast of Hanoi on the banks of the Red River. A key feature of the site is the juxtaposition of a high-As aquifer upstream of a low-As aquifer in an area where pumping for the city of Hanoi has dominated lateral groundwater flow for the past several decades (Fig. 1a). Many residents of the village of Van Phuc still draw water from their 30–50-m-deep private wells. In the western portion of the village, the wells typically contain less than 10 µg of As per litre of water and therefore meet the World Health Organization guideline for As in drinking water, whereas As in the groundwater from most wells in eastern Van Phuc exceeds this guideline by a factor of 10–50 (ref. 5).

Drilling and sediment dating in the area has shown that low-As groundwater is drawn from orange-coloured sands deposited over 12,000 years ago, whereas high-As groundwater is typically in contact with grey sands deposited less than 5,000 years ago10,11. We examined to what extent the boundary between the low-As and high-As aquifers of Van Phuc has shifted in response to groundwater withdrawals in Hanoi. This large-scale perturbation spanning several decades has implications for low-As aquifers throughout Asia that are vulnerable to contamination owing to accelerated groundwater flow.

The collection of sediment cores and the installation of monitoring wells was concentrated along a transect trending southeast to northwest that extends over a distance of 2.2 km from the bank of the Red River (Fig. 1b). Groundwater heads, and therefore the groundwater velocity field, within Van Phuc respond rapidly to the daily and seasonal cycles in the water level of the river (Supplementary Information). Before large-scale groundwater withdrawals, rainfall was sufficient to maintain groundwater discharge to the river, as is still observed elsewhere along the Red River4. In Van Phuc, however, the groundwater level was on average 40 cm below that of the water level of the Red River in 2010–11 and the hydraulic gradient nearly always indicated flow from the river into the aquifer. The reversal of the natural head gradient is caused by the large depression in groundwater level centred 10 km to the northwest that induces groundwater flow along the Van Phuc transect from the river towards Hanoi (Fig. 1a). This perturbation of groundwater flow is caused by massive pumping for the municipal water supply of Hanoi9–11, which nearly doubled from 0.55 million to 0.90 million cubic metres per day between 2000 and 2010 owing to the rapid expansion of the city (Supplementary Fig. 1).

A change in the colour of a clay layer capping sandy sediment along the transect defines a geological boundary between the two portions of the Van Phuc aquifer. Up to a distance of 1.7 km from the river bank, the clay capping the aquifer is uniformly grey with the exception of a thin brown interval at the very surface (Fig. 2b). In contrast, a readily identifiable sequence of highly oxidized bright yellow, red and white clays was encountered between 12 m and 17 m depth at all drill sites along the transect beyond a distance of 1.7 km from the river bank. This oxidized clay layer is probably a paleosol dating to the last sea-level low-stand about 20,000 years ago9,12.

The colour of aquifer sands below the upper clay layer also changes markedly along the Van Phuc transect. Sand colour in fluvio-deltaic deposits is controlled primarily by the extent to which Fe(III) has been reduced to Fe(II) by the decomposition of organic carbon15. Up to a distance of 1.6 km from the river bank, sandy drill cuttings within the 20–40 m depth range are uniformly grey. The predominance of orange sands beyond 1.6 km indicates oxidation during the previous sea-level low-stand. After the sea level rose back to its current level, the nature of the remaining organic carbon precluded a new cycle of Fe(III) reduction15.

Independently of sediment colour, the calcium (Ca) content of sand cuttings collected while drilling along the Van Phuc transect confirms that a geological boundary extends to the underlying aquifer sands. Within the southeastern portion of the aquifer that is not capped by the presumed paleosol, X-ray fluorescence measurements indicate Ca concentrations of over 2,000 mg Ca per kg of sand in cuttings to a depth of 30 m (Fig. 2a). The groundwater in this portion of the aquifer is supersaturated with respect to calcite and dolomite9, suggesting that authigenic precipitation is the source of Ca in the grey drill cuttings, as previously proposed elsewhere16 (Supplementary Fig. 2). At a distance of 1.7 km from the river and further to the northwest, instead, the Ca
The redox state of the aquifer has a major impact on the composition of groundwater in Van Phuc, as reported elsewhere in Vietnam. The presumed palaeosol is also very low (less than 0.5 mg Fe(II) per litre and less than 10 µg As per litre) and shows little indication of organic carbon mineralization compared to the Holocene aquifer (Supplementary Fig. 4).

The Pleistocene portion of the Van Phuc aquifer adjacent to the Holocene sediment is not uniformly orange or low in As. Of particular interest is a layer of grey sand at 25–30 m depth extending to the northwest at a distance of 1.7–1.8 km from the river bank (Fig. 2b). The intercalation of grey sand between orange sands above and below, combined with the low Ca content of sand cuttings within this layer, indicate that it was deposited during the Pleistocene and therefore until recently oxidized and orange in colour. Within the portion of the Pleistocene aquifer that became grey and is closest to the geological boundary, groundwater As concentrations are therefore presumed to have been originally very low (<5 µg per litre). Actual As concentrations of 100–500 µg per litre, as high as in the adjacent Holocene aquifer, indicate contamination extending over a distance of about 120 m into the Pleistocene aquifer (Fig. 3a).

A subset of the transect wells was sampled in 2006 and analysed for tritium (3H) as well as noble gases in order to measure groundwater ages and determine the rate of As intrusion into the Pleistocene aquifer. Atmospheric nuclear weapons testing in the 1950s and 1960s is the main source of 3H that entered the hydrological cycle. The distribution of 3H indicates that only groundwater in the southeastern high-As portion of the aquifer contains a plume of recharge dating from the 1950s and later. Concentrations of 3He, the stable decay product of 3H, were used to calculate groundwater ages for eight wells in the 24–42 m depth range with detectable levels of 3H. In 2006, the oldest water dated by the 3H–3He method (Supplementary Fig. 5) was sampled at a distance of 1.6 km from the river, which is the most northerly location along the transect where the aquifer is uniformly grey (Fig. 2b, d). Younger ages of 15 years and 17 years were measured closer to the geological boundary, groundwater As concentrations are therefore presumed to have been originally very low (<5 µg per litre). Actual As concentrations of 100–500 µg per litre, as high as in the adjacent Holocene aquifer, indicate contamination extending over a distance of about 120 m into the Pleistocene aquifer (Fig. 3a).

Drilling and geophysical data indicate that the main groundwater recharge area extends from the centre of the Red River to the inland area where a surficial clay layer thickens markedly, that is, from 100 m southeast to 300 m northwest of the river bank (Supplementary Fig. 6). The relationship between groundwater ages and travel distance from the recharge area implies accelerating flow drawn by increased Hanoi pumping (Supplementary Fig. 7). A simple transient flow model for the Van Phuc aquifer yields average advection rates of 38 m yr⁻¹ and 48 m yr⁻¹ towards Hanoi since 1951 and 1971, respectively (Supplementary Discussion). According to these two pumping scenarios,
groundwater originating from the Holocene portion of the aquifer was transported 2,000–2,300 m into the Pleistocene sands by 2011, when the transect was sampled for analysis of As and other groundwater constituents.

The sharp decline in As concentrations between 1.60 km and 1.75 km from the river bank indicates that migration of the As front across the geological boundary was retarded by a factor of 16 to 20 relative to the movement of the groundwater (Fig. 3a). Without retardation, attributable to As adsorption onto aquifer sands, the entire Pleistocene aquifer of Van Phuc would already be contaminated. The retardation measured in Van Phuc observations indicate that dissolved organic carbon advected from the adjacent Holocene aquifer or reductive dissolution of Fe(III) oxyhydroxides and in situ As release to groundwater cannot be determined from the available data (Supplementary Fig. 8).

The sharp drop in dissolved organic carbon concentrations across the geological boundary from 9 mg per litre to about 1 mg per litre indicates rapid organic carbon mineralization coupled to the reduction of Fe(III) oxyhydroxides and explains the formation of a plume of grey sands within the Pleistocene aquifer (Fig. 3b). On the basis of a stoichiometric Fe/C ratio of 4 (ref. 15), the dissolved organic carbon supplied by flushing the aquifer 30 times with groundwater from the Holocene aquifer would be required to turn Pleistocene sands from orange to grey by reducing half of their 0.1% reactive Fe(III) oxyhydroxide content16, assuming a porosity of 0.25. Given that groundwater was advected over a distance of 2,000–2,300 m across the geological boundary over the past 40–60 years, we would predict that the plume of grey sands extends 65–75 m into the Pleistocene aquifer. This is somewhat less than is observed (Fig. 3), possibly due to additional reduction by H₂ advected from the Holocene portion of the aquifer14. The Van Phuc observations indicate that dissolved organic carbon advected from a Holocene aquifer can be at least as important for the release of As to groundwater as autochthonous organic carbon12,24–27.

Contamination of Pleistocene aquifers has previously been invoked in the Red River and the Bengal basins13,12,28, but without the benefit of
a well-defined hydrogeological context. The Pleistocene aquifer of Van Phuc was contaminated under the conducive circumstances of accelerated lateral flow. Although downward groundwater flow and therefore penetration of As will typically be slower, the Van Phuc findings confirm that the vulnerability of Pleistocene aquifers will depend on the local spatial density of incised palaeo-channels that were subsequently filled with Holocene sediments. Owing to retardation, concentrations of As in a Pleistocene aquifer will not increase suddenly but over timescales of decades even in the close vicinity of a Holocene aquifer. This is consistent with the gradual increase in groundwater As concentrations documented by the few extended time series available from such a vulnerable setting. However, concentrations of As could rise more rapidly where flow accelerates beyond the rate documented in Van Phuc, closer to Hanoi for instance.

METHODS SUMMARY

A total of 41 wells were installed in Van Phuc in 2006–11. The water levels of the river and in the wells were recorded from September 2010 to June 2011 using pressure transducers and adjusted to the same elevation datum after barometric corrections. The magnitude and direction of the head gradient within the 25–30 m depth interval was calculated from water level measurements in three wells (Fig. 1b). In 2006, a subset of the wells was sampled for noble gas and tritium (3H) analysis at a high flow rate using a submersible pump to avoid degassing. The samples were analysed by mass spectrometry in the Noble Gas Laboratory at ETH Zurich. 3H concentrations were determined by the 3He ingrowth method. Groundwater As, Fe and Mn concentrations measured by high-resolution inductively coupled plasma mass spectrometry at LDEO represent the average for acidified samples collected in April and May 2012. Further details are provided in the Supplementary Information.

Full Methods and any associated references are available in the online version of the paper.

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 METHODS

Drilling. A first set of 25 wells, including two nests of nine and ten wells tapping the depth range of the Holocene and Pleistocene aquifers, respectively, were installed in Van Phuc in 2006 (ref. 6). Another 16 monitoring wells were installed between December 2009 and November 2011. Three additional holes were drilled to collect cuttings without installing a well. All holes were drilled by flushing the hole with water through a rotating drill bit.

Needle sampling. In 2006, drilling was briefly interrupted at seven sites to increase the vertical resolution of both sediment and groundwater data using the needle sampler31. Groundwater was pressure-filtered under nitrogen directly from the sample tubes. As a measure of the pool of mobilizable As, sediment collected with the needle sampler was subjected to a single 24-hour extraction in a 1 M PO4 solution at pH 5 (ref. 32).

Water level measurements. A theodolite elevation survey of the well and river measurement points were carried out in June 2010 by a surveying team from Hanoi University of Science. Water level data in both the wells and river were recorded using Solinst Levelogger pressure transducers. A barometric pressure logger was also deployed at the field site. Water level and barometric data were recorded at 5-min intervals and all water level data was barometrically corrected. The barometrically corrected water level data from each logger was then adjusted to the surveyed elevation of their respective measurement point so that all of the data was referenced to the same elevation datum.

Groundwater flow. The magnitude and direction of the head gradient within the 25–30-m depth of the aquifer at Van Phuc was calculated using the barometrically adjusted and survey- referenced water level data collected at 5-min intervals from September 2010 to June 2011 in three wells located near the centre of the transect (Fig. 1b). A least-squares fit of a plane was calculated for each set of simultaneous water levels at these three wells, and from this set of planes the magnitude and direction of the head gradient at 5-min intervals was directly computed.

Groundwater analysis. In 2006, a subset of the monitoring wells was sampled along a vertical transect for noble gas and tritium (3H) analysis. After purging the wells, the samples were taken using a submersible pump. To avoid degassing of the groundwater owing to bubble formation during sampling the water was pumped at high rates to maintain high pressure. The samples for noble gas and 3H analysis were put into copper tubes and sealed gastight using pinch-off clamps. All samples were analysed for noble gas concentrations and the isotope ratios 3He/4He, 20Ne/22Ne and 36Ar/40Ar using noble gas mass spectrometry in the Noble Gas Laboratory at ETH Zurich33,34. 3H concentrations were determined by the ingrowth method using a high-sensitivity compressor-source noble gas mass spectrometry at LDEO, groundwater was acidified to 1% Optima HCl in solution at pH 5 (ref. 32).

Dissolved organic carbon samples were collected in 25-ml glass vials combusted overnight at 450 °C and acidified to 1% HCl at the time of collection. Dissolved inorganic carbon concentrations were analysed on a Shimadzu TOC-V carbon analyser calibrated with K phthalate standards. Methane (CH4) samples were filled up to about half of the pre-vacuumed glass vials and immediately frozen in dry ice. The analyses were performed no longer than ten days after sampling. Headspace CH4 in the vials was measured on a Shimadzu 2014 gas chromatograph with a Porapak T packed column35.

Sediment analysis. As a measure of the redox state of Fe in acid-leachable oxy-hydroxides, the diffuse reflectance spectrum of cuttings from all sites was measured on samples wrapped in Saran wrap and kept out of the sun within 12 hours of collection using a Minolta 1600D instrument36. Starting in 2009, the coarse fractions of the drill cuttings were analysed by X-ray fluorescence for a suite of elements including Ca using an InnoX Delta instrument. The drill cuttings were resuspended in water several times to eliminate the overprint of Ca-enriched clays contained in the recycled water used for drilling. The washed samples were run as is, without drying or grinding to powder. Analyses of NIST reference material SRM2711 (28,800 ± 800 mg Ca per kg) analysed by X-ray fluorescence at the beginning and end of each run averaged 30,200 ± 400 mg Ca per kg (n = 16).

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