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Retardation 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 100 million to toxic levels of arsenic (*1*). Holocene aquifers are the source of widespread arsenic poisoning across the region (*2, 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 water (*4*) 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 over 120 m from 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 have been delayed by the retardation of arsenic transport.

This study reconstructs the initial phase of contamination of a low-As aquifer in a village 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 where the site is located still draw water from their 30 to 50 m-deep

private wells. In the western portion of the village, the wells typically contain <10 μg/L As and therefore meet the World Health Organization (WHO) guideline for in drinking water, whereas As in groundwater from most wells in eastern Van Phuc exceeds this guideline by a factor of 10-50 (*5*). Drilling and sediment dating in the area has shown that low-As groundwater is drawn from orange-colored sands deposited over 12,000 years ago, whereas high-As groundwater is typically in contact with grey sands deposited less than 5,000 years ago (*6-7*). The key issue addressed in this study is to what extent the boundary between the low- and high-As aquifers of Van Phuc has shifted in response to groundwater withdrawals in Hanoi. This unintended full-scale experiment spanning several decades has implications for low-As aquifers throughout Asia that are vulnerable to contamination due to accelerated groundwater flow.

The collection of sediment cores and installation of monitoring wells was concentrated along a southeast to northwest-trending transect 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 rapidly respond to the daily and seasonal cycles of the river stage (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 River (*8*). In Van Phuc, however, the groundwater level was on average 40 cm below that of the Red River stage 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 centered 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 Hanoi (*9-11*), which nearly doubled from 0.55 to 0.90 x 10^6 m^3/day between 2000 and 2010 due to the rapid expansion of the city (Fig. S1).

A change in the color 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 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 ~20,000 years ago (*7, 12*).

The color of aquifer sands below the upper clay layer also changes markedly along the Van Phuc transect. Sand color 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 carbon (*13*). 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 sea level rose back to its current level, the nature of the remaining organic carbon precluded a new cycle of Fe(III) reduction (*14*).

Independently of sediment color, 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 >2,000 mg/kg

in sand cuttings to a depth of 30 m (Fig. 2A). The groundwater in this portion of the aquifer is supersaturated with respect to calcite and dolomite (*6*), suggesting that authigenic precipitation is the source of Ca in the grey drill cuttings, as previously proposed elsewhere (*12*) (Fig. S2). At a distance of 1.7 km from the river and further to the northwest, instead, the Ca content of orange sand cuttings systematically remains <100 mg/kg and the groundwater is undersaturated with respect to calcite and dolomite. Unlike surficial shallow grey clays, the Ca content of the presumed paleosol is also very low (<100 mg/kg) and consistent with extensive weathering.

The redox state of the aquifer has a major impact on the composition of groundwater in Van Phuc, as reported elsewhere in Vietnam (*15*) and across South and East Asia more generally (*3*). High Fe (II) concentrations in groundwater (10-20 mg/L) associated with grey reducing sediments are apparent to residents of eastern Van Phuc as an orange Fe(III) precipitate that forms in their water upon exposure to air (Fig. S3). Invisible, but instead constituting a major health threat, are groundwater As concentrations at 20-30 m depth within the same portion of the transect that range from 200 µg/L near the river to levels as high 600 µg/L between 1.2 and 1.6 km from the river bank (Fig. 2C). The groundwater in contact with Pleistocene sands in northwestern Van Phuc is also anaerobic but contains <0.5 mg/L Fe (II) and <10 µg/L As and shows little indication of organic carbon mineralization compared to the Holocene aquifer (Fig. S4).

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 between 25-30 m depth extending to the northwest at a distance of 1.7 to 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 color. Within the portion of the Pleistocene aquifer that turned grey and is closest to the geological boundary, groundwater As concentrations are therefore presumed to have been originally very low (<5 μg/L). Actual As concentrations of 100-500 μg/L, as high as in the adjacent Holocene aquifer, indicate contamination extending over a distance of ~120 m into the Pleistocene aquifer (Fig. 3A).

A subset of the transect wells was sampled in 2006 and analyzed for tritium (^{3}H) 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 ^{3}H that entered the hydrological cycle (*16*). The distribution of ^{3}H 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 ^{3}He, the stable decay-product of ^{3}H, were used to calculate groundwater ages for 8 wells in the 24-42 m depth range with detectable levels of ^{3}H. In 2006, the oldest water dated by the ^{3}H-^{3}He method (Fig. S5) was sampled at a distance of 1.6 km from the river, which is the northwestern-most location along the transect where the aquifer is uniformly grey (Figs. 2B, D). Younger ages of 15 and 17 years were measured closer to the river at 1.3 and 1.5 km, respectively. Concentrations of ^{3}H, groundwater ^{3}H-^{3}He ages, and hydraulic head gradients consistently indicate that the Holocene aquifer has been recharged by the river from the southeast within the last few decades.

Drilling and geophysical data indicate that the main groundwater recharge area extends from the center of the Red River to the inland area where a surficial clay layer thickens markedly, i.e. from 100 m southeast to 300 m northwest of the river bank (Fig. S6). The relationship between groundwater ages and travel distance from the recharge area implies accelerating flow drawn by increased Hanoi pumping (Fig. S7). A simple transient flow model for the Van Phuc aquifer yields average advection rates of 38 and 48 m/yr 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 distances of 1.60 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 is derived from several decades of perturbation and is at the low end of previous estimates by other methods, typically measured within days to weeks (*17-22*), and therefore predicts greater As mobility than most previous studies. The retardation measured in Van Phuc integrates the effect of competing ions typically present at higher concentrations in the Holocene aquifer (Fig. S4) as well as the impact of Fe oxyhyroxide reduction. However, the extent to which contamination was caused by As transport 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 (Fig. S8).

The sharp drop in DOC concentrations across the geological boundary from 9 to ~1 mg/L 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 (*15*), the DOC from about 30 pore volumes of flushing 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 content (*23*), 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, the plume of grey sands would be predicted to extend 65-75 m into the Pleistocene aquifer. This is somewhat less than observed (Fig. 3), possibly due to additional reduction by H_2 advected from the Holocene portion of the aquifer (*14*). The Van Phuc observations indicate that DOC advected from a Holocene aquifer can be at least as important for the release of As to groundwater as autochthonous organic carbon (*12, 24-27*).

Contamination of Pleistocene aquifers has previously been invoked in the Red River and the Bengal basins (*11-12, 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 paleo-channels that were subsequently filled with Holocene sediments (*12*). Due to retardation, concentrations of As in a Pleistocene aquifer will not increase suddenly but over time scales of decades even in 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 (*29*). However, concentrations of As could rise more rapidly if 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. Water level data 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 25-30m 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 (^{3}H) analysis at a high flow rate using a submersible pump to avoid degassing. The samples were analyzed by mass spectrometry in the Noble Gas Laboratory at ETH Zurich. ^{3}H concentrations were determined by the ^{3}He ingrowth method (*30*). 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.

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Author contributions:

A.v.G, M.B., P.T.K.T., P.O., and B.B. conceived the study. V.M.L., N.N.M, P.D.M., P.T.K.T., and P.H.V. were responsible for organizing the field work and carrying out the monitoring throughout the study. K.R., Z.A, and B.W. participated in the field work in 2006. M.O.S. processed the hydrological data and carried out the flow modeling under the supervision of C.F.H. and P.O. J.L.M. was responsible for groundwater analyses at LDEO, C.S. at Eawag, and F.F. for noble gas measurements in R.K.'s laboratory. A.v.G drafted the paper, which was then edited by all co-authors.

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Figure captions:

Figure 1 Map of the Hanoi area extending south to the study site. (A) Location of the village of Van Phuc in relation to the cone of depression formed by groundwater pumping for the municipal water supply of Hanoi (adapted from (*10*)). Urbanized areas are shown in grey; largely open fields are shown in green. (B) Enlarged view of Van Phuc from Google Earth showing the location of the transect along which groundwater and sediment were collected, with tick marks labels indicating distance from the Red River bank in kilometers. Symbol color distinguishes the uniformly grey Holocene aquifer (red), the Pleistocene aquifer contaminated with As (yellow), the Pleistocene aquifer where the groundwater conductivity and DIC concentrations are high but As concentrations are not (green), and the Pleistocene aquifer without indication of contamination (blue), all within the 25-30 m depth interval. Three white asterisks identify the wells that were used to determine flow direction. (C) Rose diagram frequency plot of the head gradient direction based on data collected at 5 min intervals on these three wells from September 2010 through June 2011.

Figure 2 Contoured sections of sediment and water properties based on data collected between distances of 1.3 and 2.0 km from the Red River bank. The location and number of samples indicated as black dots varies by type of measurement. (A) Concentration of Ca in sand cuttings measured by X-ray fluorescence. Also shown are the boundaries separating the two main aquifers and the paleosol overlying the Pleistocene aquifer. (B) Difference in diffuse spectral reflectance between 530 and 520 nm indicative of the color of freshly collected drill cuttings (*13*), (C) concentrations of As in groundwater collected in 2006 with the needle-sampler and in 2011 from monitoring wells along the transect. (D) Groundwater ages relative to recharge

determining by ^{3}H-^{3}He dating of groundwater samples collected from a subset of the monitoring wells in 2006. The portion of the Pleistocene aquifer that became reduced and where As concentrations presumably increased over time is located within the large arrow pointing in the direction of flow.

Figure 3 Distribution of (A) arsenic and (B) dissolved organic carbon in groundwater within the 25-30 m depth interval along the Van Phuc transect. Symbols are colored according to the classification in Fig. 1. Grey and yellow shading indicates the extent of the grey Holocene aquifer and the portion of the Pleistocene aquifer that is still orange, respectively. The intermediate area without shading indicates the portion of the Pleistocene aquifer that turned grey. Shown as dotted lines are predicted As concentrations bracketing the observations with retardation factors of 16 and 20 and an average advection velocity of 43 m/yr over the 50 years preceding the 2011 sampling (Supplementary Discussion). Also shown are predicted concentrations for As assuming retardation factors of 5 and 50 and the same average rate of advection. For visual reference, predicted DOC concentrations are shown as dotted lines according to the same advection velocity and the same four retardation factors as for As, assuming there was no detectable DOC in the Pleistocene aquifer before the perturbation.

Methods

Drilling: A first set of 25 wells, including two nests of 9 and 10 wells each tapping the depth range of the Holocene and Pleistocene aquifers, respectively, were installed in Van Phuc in 2006 (*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 7 sites to increase the vertical resolution of both sediment and groundwater data using the needle-sampler (*31*). 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-hr extraction in a 1 M PO_4 solution at pH 5 (*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-minute 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 25-30m depth of the aquifer at Van Phuc was calculated using the barometrically adjusted and survey referenced water level data collected at 5-minute intervals from September 2010 to June 2011 in three wells located near the center 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-minute 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 (^{3}H) analysis. After purging the wells, the samples were taken using a submersible pump. To avoid degassing of the groundwater due to bubble formation during sampling the water was pumped at high rates to maintain high pressure. The samples for noble gas and ^{3}H analysis were put into copper tubes and sealed gastight using pinch-off clamps. All samples were analyzed for noble gas concentrations and the isotope ratios $^{3}He/^{4}He$, $^{20}Ne/^{22}Ne$, and $^{36}Ar/^{40}Ar$ using noble gas mass spectrometry in the Noble Gas Laboratory at ETH Zurich (*30, 33*). ^{3}H concentrations were determined by the ^{3}He ingrowth method using a high-sensitivity compressor-source noble gas mass spectrometer. ^{3}H-^{3}He ages were calculated according to the equations listed in (*34*), taking into account an excess air correction. When comparing the reconstructed original ^{3}H content of each sample as a function of ^{3}H-^{3}He age with the ^{3}H input function for South and Southeast Asia (Fig. S5), most samples follow the trend expected from simple plug flow (*34-35*).

Several days before analysis by high-resolution inductively-coupled plasma mass spectrometry (HR ICP-MS) at LDEO, groundwater was acidified to 1% Optima HCl in the laboratory (*36*). This has been shown to entirely re-dissolve any precipitates that could have formed (*37*). In most cases, the difference between duplicates was within the analytical uncertainty of ~5%. With the exception of needle-sample data and the nest of 10 wells in the Holocene portion of the aquifer, which had to yield to construction, groundwater As, Fe, and Mn concentrations reported here represent the average for samples collected without filtration in April and May 2012. Groundwater data from 2006 were previously reported in (*6*) and (*31*).

Dissolved organic carbon (DOC) samples were collected in 25 mL glass vials combusted overnight at 450 ^{o}C and acidified to 1% HCl at the time of collection. Dissolved inorganic carbon (DIC) samples were also collected in 25 mL glass vials with a Teflon septum but were not acidified. Both DOC ("NPOC") and DIC (by difference of "TC-NPOC") were analyzed on a Shimadzu TOC-V carbon analyzer calibrated with K phthalate standards.

Ammonium samples were collected in polypropylene bottles after passing through 0.45 um cellulose acetate membrane filters and preserved by acidifying to pH<2 with HNO_3. NH_4^+ concentrations were analyzed on a spectrophotmeter (UV-3101, Shimadzu) at a wavelength of 690 nm after forming complex with nitroferricyanide (*38*).

Methane (CH_4) 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 10 days after

sampling. Headspace CH_4 in the vials was measured on a Shimadzu 2014 gas chromatography with a Porapak T packed column (*14*).

Sediment analysis: As a measure of the redox state of Fe in acid-leachable oxyhydroxides, the diffuse spectral reflectance spectrum of cuttings from at 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 instrument (*13*). Starting in 2009, the coarse fraction of the drill cuttings were analyzed by X-ray fluorescence for a suite of elements including Ca using an InnovX 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/kg Ca) analyzed by X-ray fluorescence at the beginning and end of each run averaged 30,200 ± 400 mg/kg (n=16).

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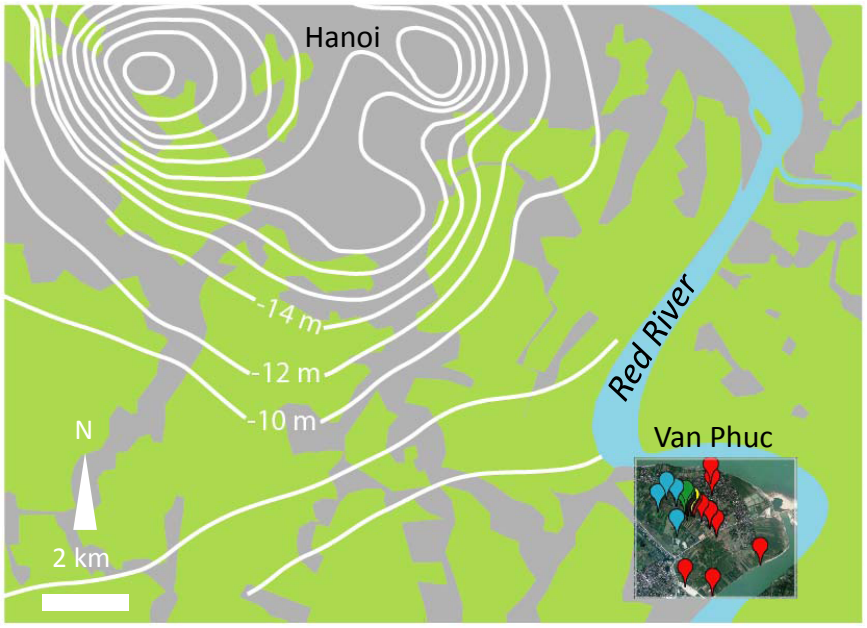
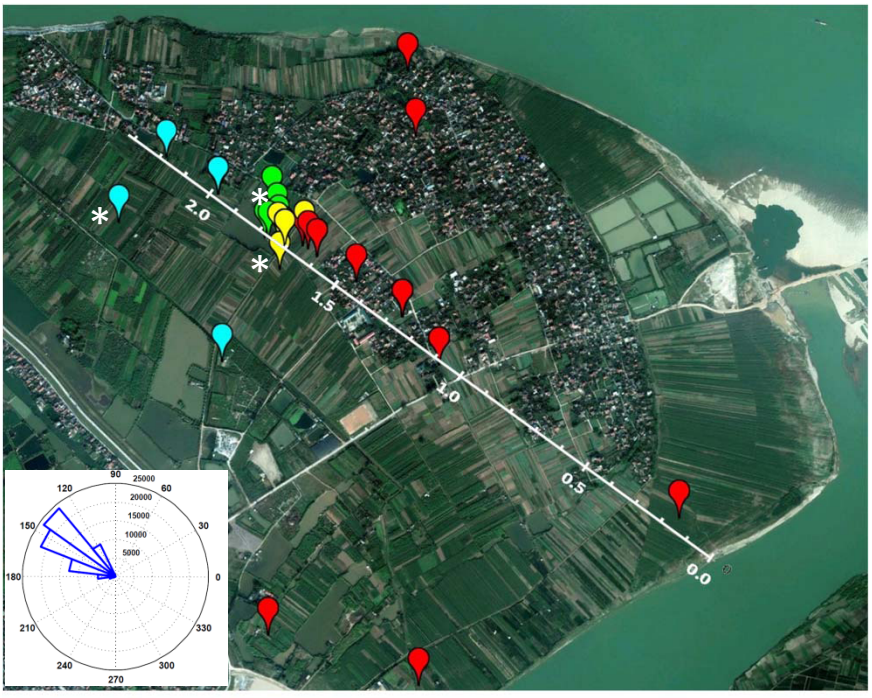
(A)

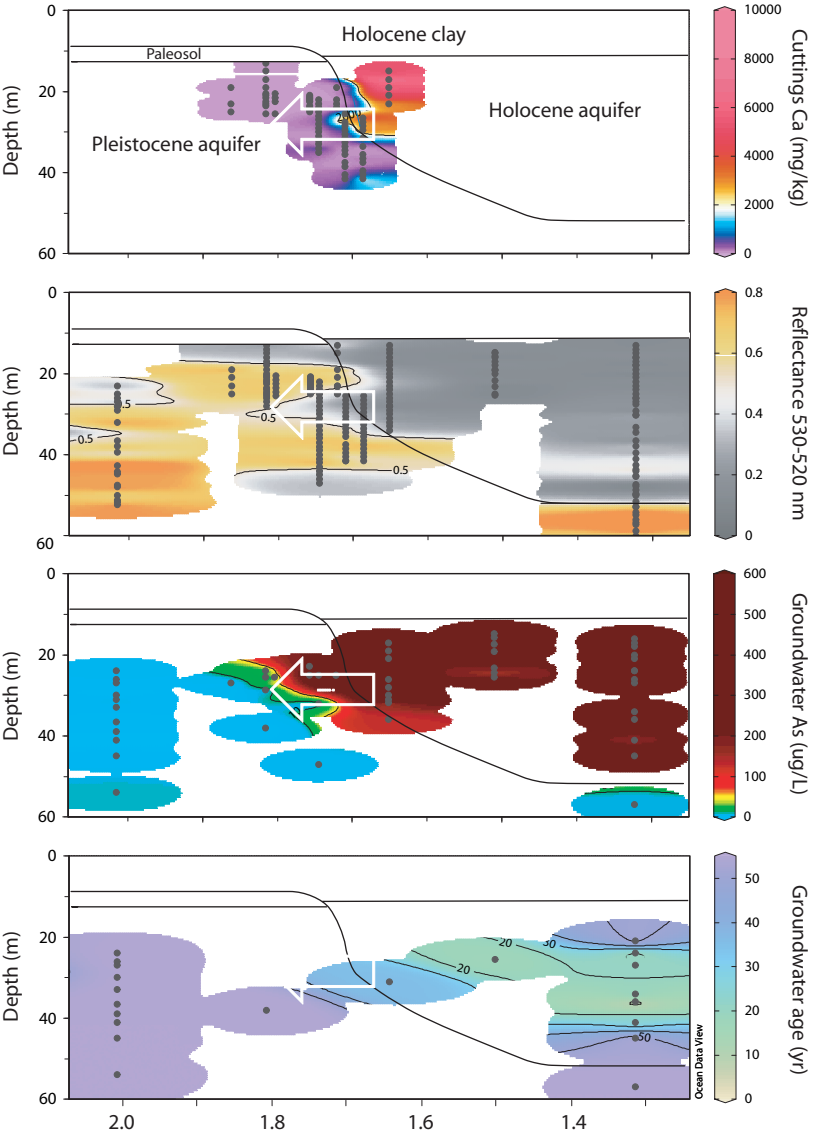

Hanoi
-14 m
-12 m
-10 m
Red River
Van Phuc
N
2 km

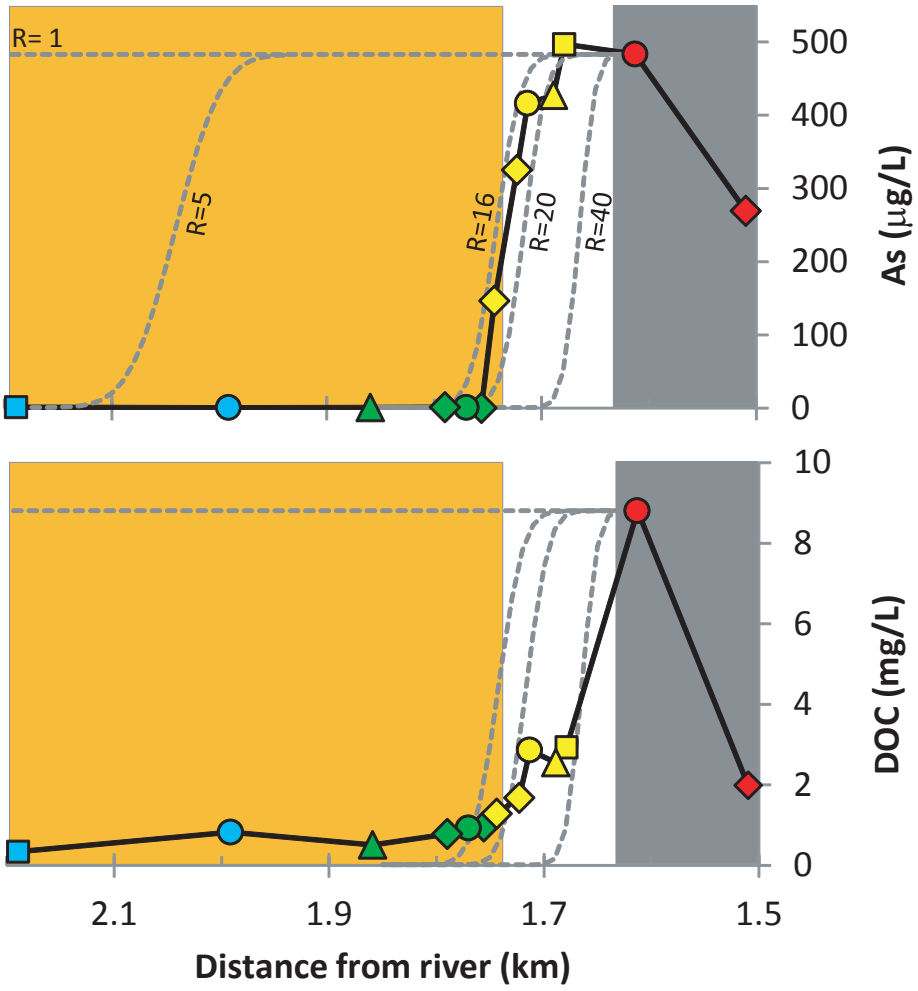
(B)


2.0
1.5
1.0
0.5
0.0

(C)

90
25000
60
20000
120
15000
30
150
10000
5000
180
0
210
330
240
300
270


Holocene clay
Paleosol
Holocene aquifer
Pleistocene aquifer
Depth (m)
0
20
40
60
Cuttings Ca (mg/kg)
10000
8000
6000
4000
2000
0
Reflectance 530-520 nm
0.8
0.6
0.4
0.2
0
0.5
Groundwater As (ug/L)
600
500
400
300
200
100
0
Groundwater age (yr)
50
40
30
20
10
0
20
30
50
Ocean Data View
2.0
1.8
1.6
1.4
Distance from river bank (km)


R= 1
R=5
R=16
R=20
R=40
500
400
300
200
100
0
As (µg/L)
10
8
6
4
2
0
DOC (mg/L)
2.1
1.9
1.7
1.5
Distance from river (km)