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Abstract

One of the reasons the processes resulting in As release to groundwater in southern Asia remain poorly understood is the high degree of spatial variability of physical and chemical properties in shallow aquifers. In an attempt to overcome this difficulty, a simple device that collects groundwater and sediment as a slurry from precisely the same interval was developed in Bangladesh. Recently published results from Bangladesh and India relying on the needle-sampler are augmented here with new data from 37 intervals of grey aquifer material of likely Holocene age in Vietnam and Nepal. A total of 145 samples of filtered groundwater ranging in depth from 3 to 36 m that were analyzed for As (1–1000 μg/L), Fe (0.01–40 mg/L), Mn (0.2–4 mg/L) and S (0.04–14 mg/L) are compared. The P-extractable (0.01–36 mg/kg) and HCl-extractable As (0.04–36 mg/kg) content of the particulate phase was determined in the same suite of samples, in addition to Fe(II)/Fe ratios (0.2–1.0) in the acid-leachable fraction of the particulate phase. Needle-sampler data from Bangladesh indicated a relationship between dissolved As in groundwater and P-extractable As in the particulate phase that was interpreted as an indication of adsorptive equilibrium, under sufficiently reducing conditions, across 3 orders of magnitude in concentrations according to a distribution coefficient of 4 mL/g. The more recent observations from India, Vietnam and Nepal show groundwater As concentrations that are often an order of magnitude lower at a given level of P-extractable As compared to Bangladesh, even if only the subset of particularly reducing intervals characterized by leachable Fe(II)/Fe >0.5 and dissolved Fe >0.2 mg/L are considered. Without attempting to explain why As appears to be particularly mobile in reducing aquifers of Bangladesh compared to the other regions, the consequences of increasing the distribution coefficient for As between the particulate and dissolved phase to 40 mL/g for the flushing of shallow aquifers of their initial As content are explored.

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1. Introduction

Even though scientists throughout the world have been mobilized by the health impact of elevated As levels in reducing groundwater of southern Asia, attempts to explain the observed patterns from first principles have so far met with limited success. One difficulty is that it remains unclear which particulate phase(s) play a role in regulating the partitioning of As between the dissolved and particulate phase – be it through solubility control or adsorption. There is little doubt that microbial reduction of Fe oxyhydroxides is a precondition for significant release of As to groundwater (Nickson et al., 1998; BGS/DPHE, 2001). But as pointed out by Polizzotto et al. (2006), it is hard to reconcile the leading hypothesis linking the release of As to groundwater to the reduction of Fe(III) oxyhydroxides with the evidently very low proportion, possibly absence, of such phases even in shallow grey aquifers where dissolved As concentrations are low. Binding constants for As on Fe(III) oxyhydroxides derived from controlled laboratory studies tend to underestimate the concentration of As in solution when applied to natural conditions, even if competing ligands such as phosphate and silicate are taken into account (BGS/DPHE, 2001; Swartz et al., 2004). In the case of a particularly well characterized shallow aquifer in Vietnam and relatively simple hydrology, Postma et al. (2007) had to allow for two different stability constants for Fe oxyhydroxides, an adjustable As/Fe ratio in dissolving Fe oxyhydroxides, and a reduced density of adsorption sites for Fe (III) oxhydroxides in order to model their data. This suggests that quantitatively relating laboratory-based studies of As behavior in model systems to redox changes in the natural environment, while clearly the ultimate goal, may remain difficult to achieve for a while to come.

Over the past few years, contributors to the present study have taken a more empirical approach by trying to determine if there is a systematic relationship between As concentrations in the groundwater and a plausible reservoir of exchangeable As in aquifer particles (Swartz et al., 2004; Zheng et al, 2005). A key tool developed with this goal in mind has been the needle-sampler, a simple device that collects groundwater as well as sediment as a slurry from precisely the same depth interval (van Geen et al., 2004, 2006). Deploying the needle-sampler overcomes the problem when collecting groundwater from a well and aquifer sediment by coring nearby that the two intervals may be geochemically distinct because of the highly variable nature of fluvio-deltaic deposits. Using the needle-sampler in a broad range of settings in Bangladesh, van Geen et al. (2008) recently documented that a roughly linear relationship between dissolved As in groundwater and P-extractable As in the particulate phase held across 3 orders of magnitude in concentrations and interpreted this finding as an indication of adsorptive equilibrium. The importance of reductive dissolution as a pre-condition for As release to groundwater was acknowledged, as this relationship was shown to hold only for intervals that were sufficiently reducing.

The new evidence for adsorptive equilibrium may guide future studies of the specific mechanisms of As mobilization but, perhaps more significantly, provided the first quantitative estimate of the likely time scale over which an aquifer can be flushed of its initial As content by groundwater flow (BGS/DPHE, 2001). The distribution coefficient inferred from the data in Bangladesh (K_d = 4 mL/g) shows that, on average, the As content of groundwater accounts for ~3% of the combined pools in the dissolved and mobilizable particulate phase. Converted to a retardation factor, the estimated distribution coefficient indicates that As is transported through an aquifer ~40 times more slowly than groundwater because of adsorption. Using this information and a simple advection-diffusion model, van Geen et al. (2008) showed that shallow aquifers deposited during the late Holocene could be flushed of their initial As content in a few hundred to a few thousand years, depending on the velocity of groundwater flow (BGS/DPHE, 2001; McArthur et al., 2004; Ravenscroft et al., 2005; Klump et al., 2006). An argument was presented, based on a representative range of groundwater flow velocities, that

the regional and local distribution of As in shallow aquifers of the Bengal Basin could therefore reflect different flushing histories rather than a difference in the initial As content of aquifer particles (Meharg et al., 2006).

It is worth emphasizing that a subset of intervals sampled in Bangladesh characterized by leachable Fe(II)/Fe ratios <0.5 in the particulate phase or dissolved Fe <0.2 mg/L in groundwater containing <10 μg/L dissolved As did not fit the relationship corresponding to a $K_d = 4$ mL/g. The outliers, characterized by a significant deficit in dissolved As compared to the prediction from the relationship and the level of P-extracted As, were tentatively attributed to the persistence of binding sites with a higher affinity for As under insufficiently reducing conditions, possibly a very small proportion of Fe(III) oxyhydroxides. Much less reducing conditions corresponding to aquifers containing orange-colored sands of likely Pleistocene age and particularly low leachable Fe(II)/Fe ratios were not considered in this analysis (BGS/DPHE, 2001; Horneman et al, 2004; Zheng et al., 2005).

A more recent data set obtained with the needle-sampler from an As-affected region of West-Bengal, India, has shown that the relationship between dissolved As and P-extractable As can be more complex in other settings (Métral et al., 2008). This was attributed to generally less reducing conditions in grey shallow aquifers bordering the Hooghly River and, more tentatively, to mechanisms of As mobilization from freshly deposited sediment possibly distinct from the reductive dissolution of Fe oxyhydroxides such as the oxidation of As-rich Fe sulfides (Polizzotto et al, 2006). In the present study, the relationship between dissolved and P-extractable As was further tested by reporting new needle-sampler data from As-affected areas in Vietnam and Nepal. On the basis of these new observations, the sensitivity of the previously proposed flushing model to a wider range of distribution coefficients is also documented.

2. Study sites

The geomorphological setting of 3 pairs of needle-sampler profiles collected in Bangladesh and one transect composed of 7 profiles from West Bengal, India, has been described elsewhere (van Geen et al., 2006, 2008; Métral et al., 2008). In brief, an alluvial fan and an estuarine delta-plain were sampled to a depth of ~30 m in northwestern and southern Bangladesh, respectively (Fig. 1). Profiles collected in both central Bangladesh and West Bengal instead are representative of an intermediate lowland floodplain environment, with the distinction that the supply of sediment essentially ceased a few hundred years ago in the first case due to the shift of a major stream (Weinman et al., 2008), while alluvium continues to be supplied at the second site along the banks of the Hooghly River to this day. The degree of reduction of Fe oxydroxides leachable from the particulate phase varied with depth and location, but aquifer sands from intervals analyzed in Bangladesh and West Bengal were all grey in color and of known or likely Holocene age.

A transect of 7 new needle-sampler profiles was collected in Vietnam in April 2006 from Van Phuc village, located in the northern portion of the Red River delta and 13 km south of Hanoi (Fig. 1, Berg et al., 2001,2008). The Red River originates from the Yunnan Plateau in southern China, but sediment reaching the Hanoi area is derived from the entire catchment. There is a sharp contrast in As concentrations in shallow (<30 m) groundwater of the study area, with levels measured in the laboratory <10 μg/L in the northwestern portion of the village and concentrations up to 500 μg/L in the remaining portion to the south (see Fig. 6 in Berg et al., 2007; also Eiche et al., 2008). The discussion here is limited to grey sands of likely Holocene age and data are reported for 4 needle-sampler profiles extending to 30 m depth and spaced equally along the 0.5 km southern portion of the transect (Table 1).

The location of a new 1.4 km transect composed of 5 needle-sampler profiles collected in May 2007 in the alluvial floodplain of the Terai in Nepal, near the south-central border with India, was also chosen to maximize the range of groundwater As concentrations (Fig. 1, Table 1). A survey of existing wells based on laboratory measurements indicated that groundwater As concentrations range from <10 μg/L SW of Ramgram municipality, Nawalparasi district, to 500 μg/L to the SE (see p. 94 in Shrestha et al., 2003). Whereas aquifer sands recovered from depths up to 25 m in this area were also grey in color and probably deposited during the Holocene, their origin can be linked to the erosion of the poorly consolidated sedimentary rocks of the Siwalik Group that constitute the Churia hills to the north (Willis and Behrensmeyer, 1995;Upreti, 1999;Guillot and Charlet, 2007). The transect is too distant from any of the major rivers draining the Terai to receive any direct of sediment input today from the Lesser, Higher or Tethys Himalaya that lie to the north of the Siwaliks, although this may have been different in the past.

3. Methods

The procedure followed to collect matched samples of groundwater and aquifer particles has been described (van Geen et al., 2004, 2006). Drillers in the Terai region of Nepal use the same drilling method as in Bangladesh and West Bengal. In Vietnam, however, water is forced into sections of PVC pipe with two electric pumps to flush sediment out of the hole instead of using the hand as a check-valve to rhythmically pump sediment-laden water out through the pipe. Drillers in Vietnam also use sections of thin-walled PVC that are cut with a hacksaw, softened over a flame, and glued together at every deployment rather than using threaded metal connectors, which is common in Bangladesh. The central opening of the metal cutter used in Vietnam was modified to allow the needle-sampler to pass through it.

As in the past, the small headspace remaining above the groundwater and sediment slurry in each needle-sampler tube was flushed with N_2 immediately after collection in Vietnam and Nepal. After allowing the sediment to settle for a few minutes, 5–10 mL of groundwater was gently pressure-filtered under N_2 through 0.4 μm syringe-filters and into acid-cleaned scintillation vials with PolySeal caps.

Several days before analysis for As, Fe, Mn, S, Na, Mg, Ca and K by High Resolution Inductively Coupled Plasma-Mass Spectrometry (HR ICP-MS) at LDEO, filtered groundwater was acidified to 1% Optima HCl in the laboratory (Cheng et al., 2004). The delay in acidification, which reduces the chance of contamination and eliminates the need for shipping strong acid, has been shown to entirely re-dissolve any precipitates that could have formed (van Geen et al., 2007).

On the evening of each sampling day, sediment kept in the dark and under groundwater after flushing the headspace of the needle-sampler tube with N_2 was subjected to two different extractions: (1) a hot 10% HCl leach for 30 min (Horneman et al., 2004) and (2) an extraction at room temperature in a N_2-purged 1 M NaH_2PO_4 solution (pH~5) for 24 h (Keon et al., 2001; Jung and Zheng, 2006). The acid leachate was analyzed that same evening for dissolved Fe(II) and Fe(III) by colorimetry using ferrozine and later for As by HR ICP-MS. The phosphate extracts were passed through a 0.4 μm syringe filter after 24 h and also analyzed later for As by HR ICP-MS.

4. Results

This contribution focuses on the geochemical relationships between groundwater and aquifer particles at new sampling sites in Vietnam and Nepal in the context of previous observations from Bangladesh and India based on the same sampling methods. Site-specific spatial patterns

in aquifer composition and how these may be controlled by geological history and hydrology is discussed elsewhere in the case of Vietnam (Berg et al., 2008; Eiche et al., 2008) and are under investigation in Nepal.

Concentrations of As in filtered groundwater from grey aquifers of Van Phuc village in Vietnam range widely (200±130 μg/L; n=25), with several samples at one end of the spectrum containing ~10 μg/L and several samples approaching 500 μg/L at the other extreme. Concentrations of P-extractable As (2.3±1.5 mg/kg; n=24) and HCl-extractable As (2.5±2.3 mg/kg; n=23) are comparable and vary in concert at this location, but are not related in any systematic way to dissolved As (Fig. 2a, b). Concentrations of dissolved Fe in Van Phuc span more than two orders of magnitude (<0.1 to 40 mg/L), with most groundwater samples containing >100 μg/L As associated with >3 mg/L dissolved Fe (Fig. 2c). An advanced state of reduction in the particulate phase as well as groundwater anoxia are indicated by leachable Fe(II)/Fe ratios >0.7 and dissolved Mn>0.2 mg/L, respectively, in all sampled intervals (Figs 2c, e). Comparing dissolved S concentrations in groundwater with typical SO_4^{2-} levels in the Red River (~5 mg/L, Berg et al., 2008), a likely source of recharge for these shallow aquifers, suggests considerable SO_4^{2-} reduction has taken place in at least half the groundwater samples from Van Phuc (Fig. 2e).

Whereas higher levels were expected based on a previous survey of Ramgram in Nepal, dissolved As concentration turned out to be relatively low (21±20 μg/L; n=12), with only a single groundwater sample collected with the needle-sampler slightly exceeding 50 μg/L (Fig. 2b). Excluding a (different) interval containing 15 mg As/kg, average P-extractable As concentrations in the particulate phase (0.9±0.8 mg/kg; n=11) are only a factor of two lower than in Van Phuc. There is no clear relation between As concentrations in the solid phase obtained by the two types of sediment extractions, and the P-extractable As content from 3 intervals actually exceeds more than 3 times the level of HCl-extractable As (Fig. 2a). A more systematic distinction between Vietnam and Nepal is that Fe concentrations exceeded 1 mg/L in only one sample from Ramgram (Fig. 2c). Possibly less strongly reducing conditions are also indicated by leachable Fe(II)/Fe ratios <0.5 in 3 samples from Nepal, even if dissolved Mn concentrations of 0.2–0.7 mg/L indicate that groundwater from these intervals is still anoxic (Figs. 2d, f). As in Van Phuc, dissolved S levels <1 mg/L in more than half the groundwater samples indicates significant SO_4^{2-} reduction in most shallow aquifers that were sampled in Ramgram (Fig. 2e).

5. Discussion

The new data for dissolved and P-extractable As concentrations in shallow aquifers of Vietnam and Nepal do not fit the relationship previously documented for shallow aquifers of Bangladesh (Fig. 2b). Applying the same criteria as in Bangladesh to identify insufficiently reducing conditions (i.e. diss. Fe <0.2 mg/L and As <10 μg/L) excludes one sample from Vietnam and 5 from Nepal, but even then dissolved As concentrations at a given level of P-extractable As for a considerable number of samples are up to an order of magnitude lower than previously observed in Bangladesh. The needle-sampler data from India also deviate significantly, even after about half the samples from the Hooghly River floodplain are excluded on the basis of either low Fe(II)/Fe ratios or a combination of low dissolved Fe and low dissolved As (Fig. 2b). Unlike the situation in Bangladesh, a single distribution coefficient does not adequately describe the equilibration between dissolved As and P-extractable As in the particulate phase in India, Vietnam, and Nepal.

It is not clear why concentrations of As in groundwater are roughly proportional to the P-extractable As content of aquifer particles across Bangladesh but not at the more recently sampled locations. One notable feature of the combined set of observations is that the

relationship established in Bangladesh appears to place an upper bound on the concentration of dissolved As expected for a given level of P-extractable As (Fig. 2b). One possible explanation is that the 1 M phosphate extraction, which constitutes merely an operational definition of the pool of exchangeable As, may be too aggressive outside Bangladesh. Laboratory experiments have shown that even As adsorbed to Fe(III) oxyhydroxides is remobilized in 1 M phosphate because of the strong affinity of P(V) for the same sites (Jung and Zheng, 2006). Thoral et al. (2005) also showed that the structure of Fe(II) oxyhydroxides is limited to very small clusters in the presence of As(III) during Fe oxidation experiments. This suggests that extraction in 1 M phosphate could also release As bound deeply within the natural Fe oxyhydroxides coatings of aquifer particles. It can only be speculated that a milder extraction procedure might be more appropriate for quantifying readily desorbable As and could perhaps have produced a more consistent relationship across a wider range of settings.

An alternative explanation is that dissolved As levels are not controlled by adsorptive exchange with an identifiable pool in the particulate phase, even when considering exclusively Fe and SO_4 reducing environments. Differences in mineralogy and/or affinity of surface sites for As are another possibility, but it is not obvious why the mineralogy of sediment reaching different regions of Bangladesh should be any less heterogeneous than sediment deposited in India, Vietnam and Nepal.

Some of the differences in the relative efficiency of HCl and P-extractions documented here are consistent with previous observations and may therefore reflect regional trends worth exploring further. BGS/DPHE (2001) reported that oxalate extractions of aquifer sands, which can be considered to target a fraction equivalent to that mobilized by the 1 M phosphate extractions, release only 10–50% of As in the sediment measured by total digestion. Swartz et al. (2004) and Zheng et al. (2005) also noted that 1 M phosphate extractions release <30% of total As present in shallow grey sediment at several locations in Bangladesh. Within the suite of samples collected with the needle-sampler in India and Bangladesh, P-extracted As concentrations in sufficiently reducing intervals are on average 0.4–0.5 times lower than HCl-extractable As levels, respectively (Table 2). It therefore appears that 1 M phosphate extractions systematically release a modest fraction of HCl-extractable As present in aquifer solids from Bangladesh – and this phase appears to be in adsorptive equilibrium with As present in groundwater. Berg et al. (2008), in contrast, report that a similar P-based extraction releases >50% of As in the sediment at several locations in Vietnam. Phosphate extractions also leaves little residual As in the solid phase extractable in HCl for aquifer solids collected with the needle-sampler in Vietnam, as suggested by the comparable P- and HCl-extractable As levels (Table 2). The average P- to HCl- extractable As ratio for aquifer solids from Nepal is similar to the one measured in Vietnam, but more variable and less well constrained. For reasons that are presently not understood, P-extractable As concentrations are significantly lower than HCl-extractable As levels in two regions that are most affected by elevated As groundwater levels, Bangladesh and West-Bengal, India, whereas the two extractions release comparable amounts of As from the solid phase in two regions where the problem appears to be less widespread. It is speculated that the underlying cause may be related to the extent of transformation of As-containing phases in aquifer particles. Observations from Vietnam and Nepal may indicate a relatively mature system, whereas the significant fraction of As contained in the solid phase in the Bangladesh and West Bengal that is not mobilized in 1 M phosphate may indicate incomplete transformation and, consequently, further delay in flushing. One practical implication is that a milder form of extraction, possibly the less aggressive extraction carried out in 0.05 M phosphate by Postma et al. (2007), might be more appropriate for identifying the exchangeable fraction of As in aquifer material across the entire affected area.

Despite the scatter, the new data can be used to place some constraints on the rate at which shallow aquifers are likely to be flushed of their mobilizable As content, assuming it is

relatively uniform initially. The simple one-dimensional advection-diffusion model recently presented by van Geen et al. (2008) is used with one modification: the distribution coefficient K_d is varied between 4 and 40 mL/g to accommodate the new observations (Fig. 2a). Assuming that dissolved and particulate-phase As concentrations are initially equilibrated along the entire flow path at a concentration C_i and that recharge water entering the aquifer at one end of the flow path contains no As, the solution of the governing equation is:

$$C(x,t) = Ci \left[1 - \tfrac{1}{2}\mathrm{erfc}\left(\frac{Rx - vt}{2\,(DRt)^{1/2}} \right) + \tfrac{1}{2}\exp\left(vx/D\right)\mathrm{erfc}\left(\frac{Rx + vt}{2\,(DRt)^{1/2}} \right) \right]$$

where C is the concentration of As in the dissolved phase, x the distance along the flow path, v the advection velocity, D is a hydraulic dispersion coefficient, and R the retardation factor, which is related to the distribution coefficient K_d by the expression $R = 1 + \rho\, K_d/\theta$ where ρ is the aquifer bulk density, K_d is the ratio of the As concentration in the particulate phase on per mass of sediment divided by the As concentration in the dissolved phase, and θ is the aquifer porosity (van Genuchten and Alves, 1982).

The focus is on the sensitivity of the model between distances of 50–500 m, i.e. within the range of length of likely flow paths that lead from an area of recharge to the depth range of shallow aquifers and eventually to a discharge area, typically a local stream (Stute et al., 2007; Aziz et al., 2008). Only the central scenario based on a groundwater flow velocity 5 cm/ d (5.8×10^{-7} m/s) and a dispersion coefficient $D = 5.8 \times 10^{-6}$ m^2/s are considered here. Justification for these parameters and model sensitivity to these choices were discussed previously by van Geen et al. (2008). For K_d of 4 and 40 mL/g, retardation factors R = 36.8 and 359, respectively, are calculated from an aquifer bulk density of 2.24 g/cm^3, derived in turn from a porosity of 0.25 and a particle density of 2.65 g/cm^3.

The model assumes a uniform initial P-extractable As concentration of 4 mg/kg, which corresponds to dissolved As concentrations of 1000 and 100 µg/L for K_d = 4 and 40 mL/g, respectively. Under conditions of greatest As mobility, representative of shallow aquifers in Bangladesh, the model shows that a considerable portion of the 50–500 m range of distances along the flow path is already flushed by 0.5 ka and entirely so by 5 ka (Fig. 3). Whereas As concentrations start at a lower level under the alternative scenario associated with a 10-fold higher K_d, flushing of the aquifer is also considerably slower. The model predicts elevated As concentrations across the 50–500 distance range, and significant but incomplete flushing of the same shallow aquifers after 5 ka. The scatter in the needle-sampler data suggests that the reality under natural conditions is probably somewhere in between these two extreme scenarios, assuming all sampled deposits are of Holocene age (this has been confirmed in Vietnam and Nepal on the basis of optically stimulated luminescence dating, B. Weinman and A. Singhvi, pers. comm.). The only upside to the fact that As appears to be particularly mobile in groundwater of Bangladesh is that shallow aquifers are likely to be flushed more rapidly in Bangladesh compared to India, Vietnam and Nepal. This is, however, not relevant in terms of human exposure since, hopefully, much of the population in affected regions will no longer consume untreated groundwater within the next few decades. Flushing would be delayed further if, in addition, the fraction of As in the solid phase released in hot HCl is gradually converted to exchangeable As.

No claim is made here that the mechanisms underlying the observed relationships between dissolved and particulate phase As are understood. The new results merely provide some constraints on the range of situations that a more mechanistic model will eventually have to represent. Such a model, possibly based on a more accurate measure of the exchangeable As fraction in the particulate phase, will have to explain why adsorption equilibrium appears to

control groundwater As concentrations in Bangladesh more systematically than at the other locations that were sampled. From a practical perspective, it would also be important to understand under what conditions the considerable pool of P-extractable As stored in the particulate phase in less reducing aquifers characterized by leachable Fe(II)/Fe ratios<0.5 or dissolved Fe <0.1 mg/L could potentially be released to groundwater in the future.

6. Conclusions

The proportionality between dissolved and P-extractable As concentrations documented for shallow aquifers of Bangladesh does not appear to hold in other more recently sampled regions of southern Asia. Even after excluding intervals where conditions may not be sufficiently reducing, As concentrations in groundwater of India, Vietnam and Nepal are frequently up to an order of magnitude lower at given levels of P-extractable As than in Bangladesh. One possible explanation is that the 1 M phosphate extraction releases As from a less labile fraction in the particulate phase that, for reasons presently unclear, is more important outside Bangladesh. To a first approximation, much of the needle-sampler data obtained from grey aquifers throughout the affected region can nevertheless be ascribed to adsorptive equilibration according to a distribution coefficient that ranges from 4 to 40 mL/g. Using this formulation and a simple model of groundwater flow, it is estimated that late Holocene aquifers have been, or will be, flushed of much of their initial As content 0.5 to 5 ka after their deposition. The uncertainty of such estimates is considerable. More robust is the conclusion that the elevated As content of groundwater throughout southern Asia is probably a transient feature, although on a time scale that extends considerably beyond the lives of the presently exposed population.

Acknowledgments

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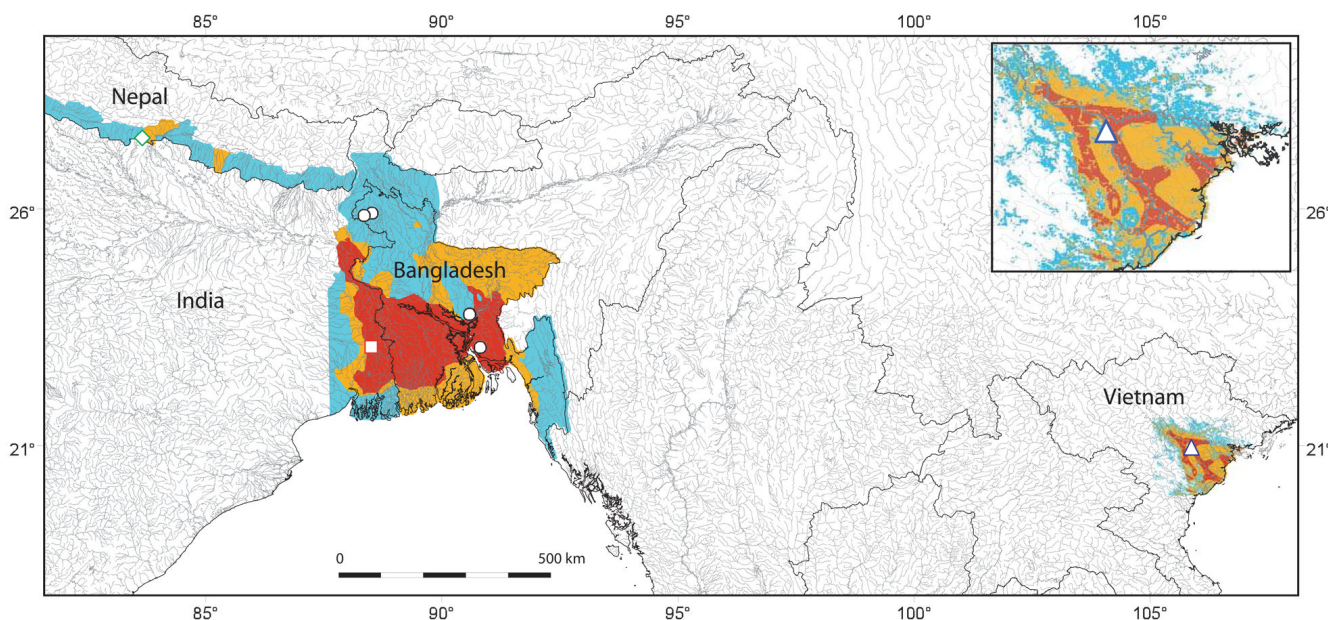
Fig. 1.
Provenance of needle-sampler material from Bangladesh, India, Vietnam and Nepal shown on a map of As-affected areas in southern Asia. The majority of tubewells sampled and analyzed by Dr. Dipankar Chakraborti's group at Jadavpur University located within red (dark grey in the printed copy) and light blue (lightest grey) areas in India and Bangladesh contain >50 μg/L As, respectively. Orange (intermediate grey) areas indicate a mixed distribution of high- and low-As wells. Modified from Métral et al. (2008) with additional well As data for Nepal from Shrestha et al. (2003). In the case of Vietnam, the 3 shaded areas correspond to high, medium and low risk of groundwater exceeding 50 μg/L As, as inferred from geological information by Berg et al. (2007). The inset is an expanded view of the Red River delta area. The shape of the symbols corresponds to the symbols used to distinguish different locations in Fig. 2. The map was created from the Digital Atlas of South Asia of Hearn et al. (2001).
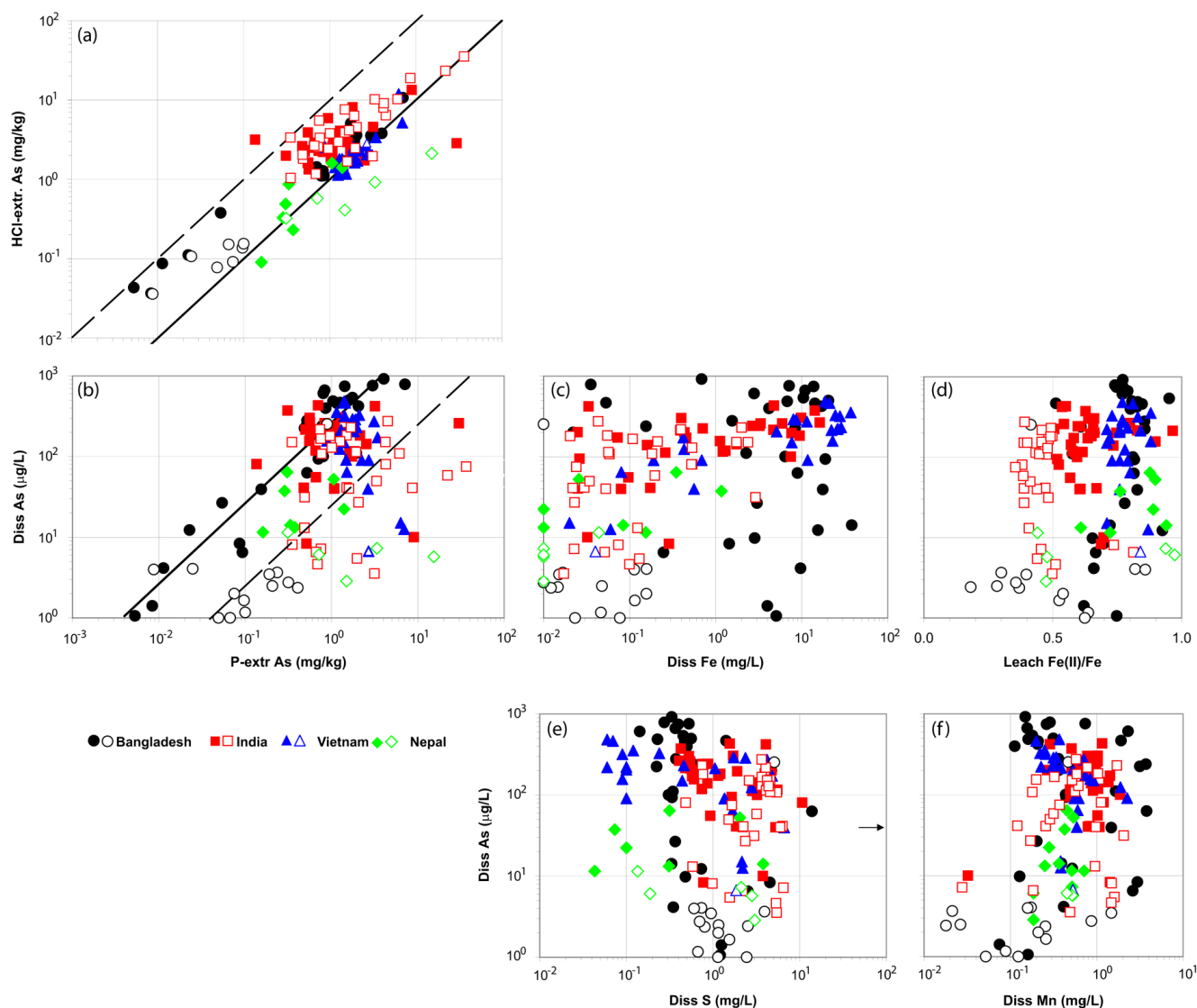
Fig. 2.
Scatter plots of groundwater and aquifer particle properties for material collected with the needle-sampler in Bangladesh, India, Vietnam and Nepal. Note the logarithmic scale of all properties, with the exception of leachable Fe(II)/Fe ratios. Open symbols identify samples collected from insufficiently reducing samples, as identified in van Geen et al. (2008) by either leachable Fe(II)/Fe <0.5 or dissolved Fe concentrations <0.2 mg/L in samples with dissolved As <10 µg/L. Solid and dashed lines in (a) correspond to equal and 10-fold higher As concentrations in HCl-extractions, respectively, compared to As levels in P-extractions. Solid line and dashed lines in (b) correspond to $K_d = 4$ and 40 cm^3/g, respectively. The arrow in (d) points to a single sample from Bangladesh containing an unexplained and extremely elevated level of 190 mg S/L.
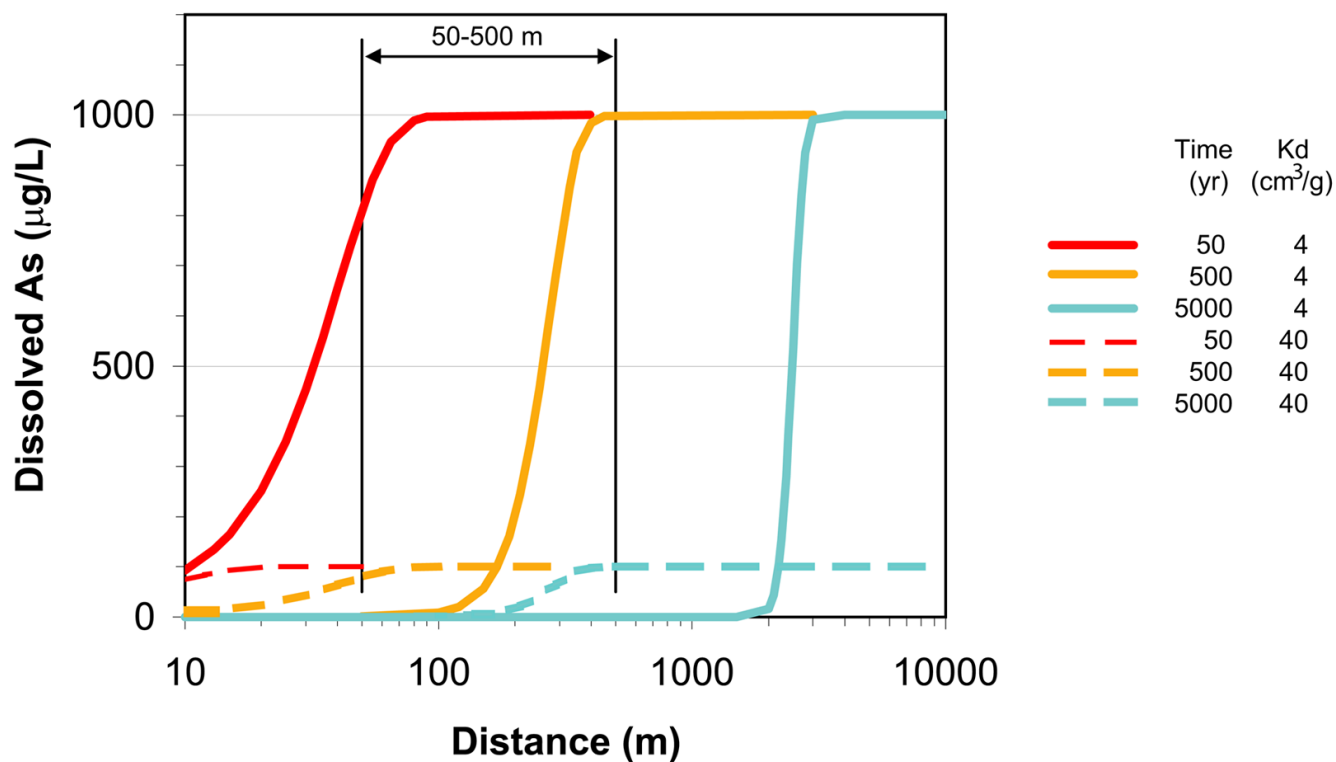
Fig. 3.
Predicted distribution of groundwater As concentrations along a flowpath according to the advection-diffusion model described in van Geen et al. (2008) after 50, 500 and 5000 a for K_ds of 4 and 40 cm^3/g. Note the logarithmic scale of distance along the flow path. Also shown is the likely 50–500 m range of lengths of flow paths from recharge to discharge areas within shallow aquifers.

Table 1

Location of new needle-sampler profiles

Vietnam (April 2006)		
Label	Latitude (oN)	Longitude (oE)
VPNS-1	20.92326	105.89198
VPNS-2	20.91982	105.89751
VPNS-3	20.92081	105.89613
VPNS-4	20.92205	105.89338
VPNS-5	20.92156	105.89491
VPNS-6	20.92429	105.89043
VPNS-7	20.91848	105.89861
VPNS-8	20.91864	105.89187
Nepal (May 2007)		
Label	Latitude (oN)	Longitude (oE)
PNS-1	27.51512	83.67187
PNS-2	27.51706	83.67490
PNS-3	27.51594	83.66876
PNS-4	27.51648	83.66119
PNS-5	27.51553	83.66561

Table 2

Average ratio of P-extractable to HCl-extractable As concentrations in aquifer particles collected with the needle-sampler in 4 countries. Also shown are the corresponding standard deviations in this ratio for each country along with, in parentheses, the uncertainty of the mean calculated by dividing by the square root of the number of determinations. Only sufficiently reducing intervals defined by leachable Fe(II)/Fe >0.5 or dissolved As>10 μg/L if dissolved Fe <0.2 mg/L are included.

Country	P-extr. As/HCl-extr. As	nReference
Bangladesh	0.5±0.3 (±0.07)	21van Geen et al., 2008
India	0.4±0.3 (±0.05)	33Métral et al., 2008
Vietnam	1.0±0.3 (±0.06)	22this study
Nepal	1.0±0.5 (±0.2)	7this study