

Spatial and Temporal Variations of Groundwater Arsenic in South and Southeast Asia

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Over the past few decades, groundwater wells installed in rural areas throughout the major river basins draining the Himalayas have become the main source of drinking water for tens of millions of people. Groundwater in this region is much less likely to contain microbial pathogens than surface water but often contains hazardous amounts of arsenic—a known carcinogen. Arsenic enters groundwater naturally from rocks and sediment by coupled biogeochemical and hydrologic processes, some of which are presently affected by human activity. Mitigation of the resulting health crisis in South and Southeast Asia requires an understanding of the transport of arsenic and key reactants such as organic carbon that could trigger release in zones with presently low groundwater arsenic levels.

“**T**he largest poisoning of a population in history” is how Smith *et al.* (1) described the health impact of elevated groundwater arsenic (As) concentrations in many parts of Bangladesh. Estimates of the rural population exposed to unsafe As levels by drinking untreated groundwater in India, China, Myanmar, Pakistan, Vietnam, Nepal, and Cambodia have grown to over 100 million (2). Widespread symptoms of disease in people drinking groundwater high in As in some of these countries and epidemiological studies conducted elsewhere lead to predictions of a doubling of the lifetime mortality risk caused by cancers of the liver, bladder, and lung (3, 4). Groundwater containing As also causes cardiovascular disease and inhibits the mental development of children (5, 6).

The affected areas of South and Southeast Asia are low-lying, topographically flat floodplains of rivers that drain the Himalayas (Fig. 1A) (7). Unconsolidated sands underlying these floodplains host increasing numbers of inexpensive wells made of polyvinyl chloride pipe with a cast-iron handpump mounted on top (tubewells) that are installed to avoid drinking surface water contaminated with microbial pathogens. Extensive, although by no means sufficient, testing of tubewell water for As has been carried out in most of the countries that are at risk, with Myanmar the glaring exception.

Within the arsenic-affected areas of South and Southeast Asia there is extensive variation in the depth distribution of wells (Fig. 1B). In Bangladesh and the bordering state of West Bengal,



India, tubewells extend to depths of ~350 m compared to a maximum of ~100 m in Nepal, Cambodia, and Vietnam, owing to difference in the thickness of unconsolidated sand deposits (8). More than half the wells in at least one depth interval in each of the five affected countries do not meet the World Health Organization (WHO) guideline of 10 µg/liter As in drinking water (Fig. 1B). There are also numerous wells containing <10 µg/liter As at all depths. The extensive spatial variability of As concentrations at shallow depths (9–11), even within a single village, hinders comparisons among field sites and the recognition of presumably common biogeochemical-hydrological processes that regulate As levels in groundwater. The source of As is not a mystery, however; what is less clear is how the current distribution of dissolved As in the subsurface reached its current state. This review focuses on what has been learned from a decade of field research conducted in South and Southeast Asia about the processes that resulted in the current distribution of As in groundwater and the key

factors that will control changes in the distribution of As over time.

What Drives the Release of Arsenic to Groundwater?

Weathering of Himalayan-derived sediment during erosion and transport leads to downstream deposition of As. The primary sources of As within the Himalayas are thought to be eroding coal seams and rocks containing sulfide minerals (12). Exposed to the atmosphere, the minerals contained within these deposits are oxidized, and much of their As content is transferred to secondary phases including iron (Fe) hydroxides, oxyhydroxides, and oxides, collectively referred to as Fe oxides hereafter (13, 14). There is indeed a positive relation between As and Fe extracted from hundreds of sediment samples from the Ganges-Brahmaputra-Meghna, Mekong, and Red River basins (Fig. 2) (15–18). Grain-size separation of river-borne and aquifer sediments has shown that the fine-grained, high-surface area fraction (<10 µm) contains five times as much As as bulk sediments or mica separates (9, 19–21). Destabilizing As on these Fe oxides is now recognized as a key step in the widespread contamination of groundwater, with other phases possibly playing a subordinate role (14, 22, 23).

Arsenic is released from Fe oxides into groundwater as a result of two potentially concurrent processes under the anoxic conditions that prevail in the subsurface. First, field and laboratory evidence suggest that microbial reduction of Fe(III) oxides liberates As into the dissolved phase (23, 24). Reduction of As(V) to more labile As(III) probably contributes to this release but is hard to distinguish

from the reduction of Fe oxides under natural conditions given the rates of groundwater flow. Second, dissolution of Fe oxides is accompanied by the release of other ligands such as phosphate that compete with As for adsorption on the remaining Fe oxide surface sites (9).

The restriction of high dissolved As concentrations to aquifers composed of gray-colored sands, indicative of coatings of reduced or mixed-valence Fe(II+III) oxides, and the absence of elevated concentrations from aquifers containing orange sands coated with Fe(III) oxides (Box 1) suggest that Fe(III) reduction is a primary factor contributing to high As concentrations in groundwater (9, 24–28). A systematic analysis of the composition of hundreds of groundwater samples from the Bengal, Mekong, and Red River basins has shown that high concentrations of As in groundwater prevail under advanced stages of reduction rather than the onset of Fe oxide reduction (29).

Microbial Fe(III) and As(V) reduction both require a supply of labile organic carbon. When the biological oxygen demand from the decom-

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position of organic carbon exceeds the rate of oxygen infusion, anaerobic metabolism prevails and, following nitrate and manganese reduction, causes microbially mediated reduction of Fe(III) to Fe(II), as well as As(V) to As(III). Elevated groundwater As concentrations that broadly correspond with increased levels of metabolic by-products in groundwater including inorganic carbon, ammonium, and methane, in addition to dissolved Fe(II), are consistent with the central role of organic-matter metabolism (18, 19, 28–30).

Where Does Arsenic Release to Groundwater Occur?

There are three environmental requirements for groundwater As concentrations to increase: water saturation (which limits diffusion of atmospheric oxygen), a limited supply of sulfur, and a source of organic carbon to drive microbial dissolution of Fe oxides. The height of the water table, typically within 5 m of the surface, indicates where oxygen supply is limited and reductive dissolution can potentially be initiated (Fig. 3B). The

domain within which As can be released to groundwater is restricted in some shallow (<20 m) aquifers where sulfate supplied by recharge has not been depleted. This is because sulfate reduction promoted by organic carbon produces sulfide that can bind As, forming sparingly soluble sulfides mineral that effectively remove As from groundwater (13, 29). Marine-influenced areas also show inhibition of As release by sulfate reduction along the coasts of Bangladesh (9) and Vietnam (31).

The availability of labile organic carbon as a driver of microbial reduction is possibly the most prominent outstanding issue limiting our ability to predict the distribution of As in groundwater. Organic carbon necessary to drive reduction of Fe(III) and As(V) can be supplied through various pathways. One is co-deposition of plant material with sediments over geologic time, also referred to as an autochthonous source of carbon (9). Dissolved organic carbon (DOC), produced by recent degradation of plants in modern soils or in buried peat layers and transported to a different

location by groundwater flow, could be an alternative allochthonous supply (26, 28). The reactivity of organic matter needs to be considered as well (32, 33), as indicated by dissolved inorganic carbon typically being younger than DOC (14, 28) and by assays of microbial decomposition (34). The relative importance of different sources of organic carbon remains undetermined and even controversial (32–34).

In principle, where As is released from aquifer sediment and in what quantity will depend on the amount of reactive organic carbon and availability of As in the sediment. Sediment with recalcitrant organic carbon and/or As-bearing Fe oxides is expected to release As slowly. In contrast, highly reactive forms of both organic carbon and labile sediment-bound As should result in the strongest release. Field evidence from Nepal, West Bengal, Bangladesh, Cambodia, and Vietnam suggests both rapid, shallow release of As as well as more gradual release at depth (9, 17, 18, 25, 28, 35, 36). The available data show that the geological setting likely plays an important role, but there

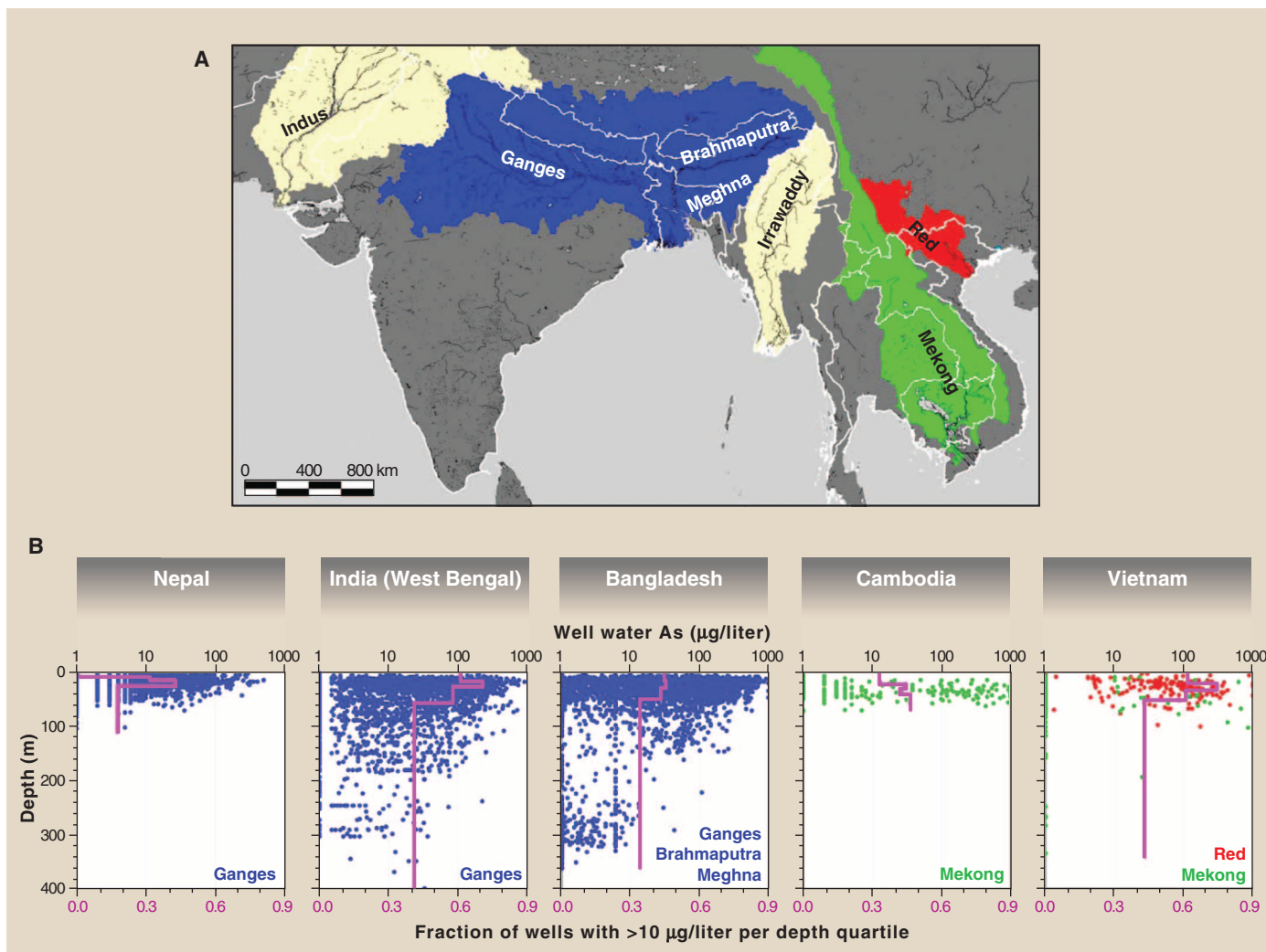


Fig. 1. Distribution of arsenic in groundwater of South and Southeast Asia. (A) Map of four major river basins draining the Himalayas. (B) Depth distribution of As in groundwater determined for five affected countries. Concentrations of As

are shown on a logarithmic scale. Symbols are color-coded according to the major river basins shown in (A). The pink line depicts the fraction of wells that exceed the WHO As guideline of 10 µg/liter for each depth quartile of the available data (54).

remain notable uncertainties regarding rates of carbon metabolism coupled to As release.

The pool of labile As within an interval of an aquifer sediment is finite and can become depleted despite continued reduction of Fe oxides. Such a situation has been documented for deeper aquifers of Bangladesh where dissolved As levels are low despite elevated Fe(II) concentrations in groundwater (16). In other situations, the available pool of labile organic carbon has been depleted although some labile As is still bound to sediment particles. Sediments deposited prior to about 20,000 years ago and that were well drained because of incision during the last glacial sea-level low stand, for instance, contain limited reactive organic matter. The orange color of these oxidized deposits indicates that they were deposited with a low concentration of organic carbon or that their initial organic carbon was oxidized during the low stand (9, 15, 16, 25, 26).

After the initial biogeochemical transformations that result in As release from the sediment, adsorption on residual or newly formed aquifer solids will control dissolved As concentrations. Weaker surface complexes of As(III) and the degradation of Fe oxides (9) mean that adsorption is less pronounced than for As(V) in oxidized surface environments (37). Nevertheless, adsorption of As(III) does occur within reduced aquifers, as indicated by a fairly systematic relation between dissolved and adsorbed As across a broad range of conditions in Bangladesh (38). This implies that As transport is substantially retarded relative to

groundwater flow, even if adsorption sites may be saturated in aquifer sands under certain conditions (9, 28).

How Does Groundwater Flow Affect the Distribution of Arsenic?

Groundwater flow transports dissolved As as well as DOC, oxygen, sulfate, and competing adsorbates, all of which influence As concentrations. When the system is not in a steady state, either hydrologically or biogeochemically, As concentrations can be expected to change over time. Groundwater flow therefore plays a key role in the current distribution of groundwater As and its evolution.

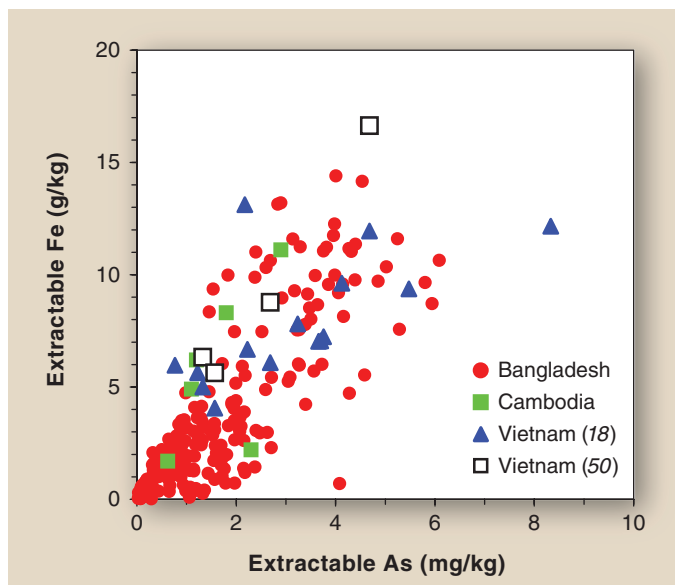


Fig. 2. Relation between As and Fe concentrations for a suite of sediment samples from three countries based on different extraction methods (9, 14, 18, 50).

The main river basins affected by As (Fig. 1A) share similar hydrogeologic features, most notably a monsoonal climate and rapid sediment accumulation. Groundwater flow systems range in scale from the local (tens of meters) to the regional (hundreds of kilometers). Studies of local-scale flow systems (39–42), which are most relevant to the distribution of As in shallow aquifers, illustrate the complex, site-specific, and transient nature of natural patterns of recharge and discharge (Fig. 3B). Further, abundant surface water bodies such as rivers, ponds, and wetlands interact with the groundwater systems. Monsoonal rains and dry-season irrigation pumping cause reversals in hydraulic gradients that can transform a water body from a source to a sink of groundwater and back over a year (39–42). Constructed ponds, for instance, are numerous

in the Bengal Basin and vary in their contribution to aquifer recharge (34, 39, 43), depending on the accumulation of fine-grained bottom sediment. Such seasonally and spatially variable forcing can result in highly complex groundwater flowpaths connecting recharge and discharge areas.

High groundwater pumping can substantially alter natural flow patterns. In Bangladesh, the rate of groundwater pumping for irrigation is at least an order of magnitude higher than integrated flow from hand pumps (16, 39, 44). Irrigation pumping and return flow through fields rearrange recharge and discharge areas, increase recharge rates, and modify regional and local flow patterns (34, 39, 44–46). Groundwater use for irrigation is greatest in the Bengal Basin and the Terai Basin along the southern border of Nepal, less in the Red River Basin (17), and least in the Mekong River Basin (41). Because elevated As concentrations are observed in all these areas (Fig. 1B), processes associated with irrigation pumping, though potentially important, cannot be the only trigger of As release to groundwater.

The time since recharge, or groundwater age, is also an important factor that influences groundwater As concentrations. Groundwater age, measured by two different radioactive clocks, ranges from less than 1 year to a few decades in shallow (<20 m deep) aquifers in Bangladesh and Vietnam and from centuries to thousands of years in deeper strata of Bangladesh (50 to 400 m deep) (Fig. 3A). The vertical gradient in groundwater ages reflects regional flow systems and flowpaths that link distant recharge and discharge areas beneath more vigorous shallow and local groundwater circulation (Fig. 3B). Irrigation water is typically drawn from shallow (<100 m) depths and may be partly responsible for the pronounced difference in age between shallow and deeper aquifers (39, 45).

Box 1: The color of aquifer sands is a useful visual indicator of the redox state of an aquifer. (Bottom) Orange sands from Vietnam indicate the presence of Fe(III) oxides that are consistently associated with low-As water, whereas gray sands with reduced or mixed-valence Fe(II+III) oxides (top) are often, though not always, associated with higher dissolved As. Sand color has been used by drillers to target low-As groundwater in spatially heterogeneous aquifers. [Photo courtesy of Benjamin Bostick]



Within the river basins considered here, the highly variable As concentrations in young groundwater in shallow strata may be due to differences in topography on multiple scales. Slightly elevated, often coarse, sandy deposits appear to be associated with lower As concentrations in Bangladesh and Cambodia (47–49). Such observations suggest that rapid recharge through these deposits locally inhibits the release of As, possibly by supplying oxygen, nitrate, or sulfate as alternatives to Fe oxides for oxidizing organic carbon (34, 48). Similar processes prevent release of arsenic in water recharged through rice field bunds (34). In contrast, low-lying areas in the river basins are typically covered with finer-grained sediment, frequently flooded, and associated with high dissolved As concentrations at shallow depths. Rapid release of As under these conditions is attributed to co-deposition of labile carbon and As-bearing Fe oxides in the seasonally saturated surface sediments (18, 30), infiltration of recharge with abundant DOC (17, 39), or simply slow flow of water through As-releasing sediment (48).

Along the pathway of groundwater flow, changes in As concentration will depend on local partitioning (adsorption/desorption) with the sediment as well as reductive release. Arsenic can be released from the sediment and eventually flushed from the aquifer in areas where the concentration of As in inflowing water is below that dictated by partitioning, even within reduced gray sands depleted in Fe(III) (38). Along anaerobic, shallow

flowpaths containing organic carbon, As concentrations typically increase. This is consistent with a correlation between As and groundwater age or flow rate within shallow aquifers (21, 40), and with As plumes that originate from natural wetlands high in organic carbon (18, 30) or constructed ponds (34). The subsurface maximum in groundwater As frequently observed within shallow gray reduced aquifers is likely the result of layering of groundwater flow having different evolutionary histories. High-As groundwater indicates a plume evolved from active Fe/As reductive dissolution/desorption; low-As water can reflect flowpaths that lack Fe/As reduction, secondary As-sulfide precipitation, various extents of sediment flushing, or mixing near irrigation well intakes (16, 28, 34, 38, 45).

How Vulnerable Are Low-Arsenic Zones?

Low-As zones within the aquifer systems of the affected basins are rarely distinct aquifers and can be associated with reduced gray [Fe(II) dominated] or oxidized orange [Fe(III) dominated] sands (16). Zones of low dissolved As occur in gray sands where As is removed by sulfide (13) and along flowpaths where adsorbed As has been flushed by sustained recharge or has never been released (16, 38). Low-As zones associated with oxidized orange sands are often deeper (>100 m) but, depending on the local geology, are occasionally preserved at shallower depths (9, 10, 50). Groundwater is typically anoxic throughout the

affected region, even within orange sand deposits. The vulnerability of shallower and deeper low-As zones to human perturbation must be understood because millions of households in Bangladesh have switched their consumption to a nearby low-As well identified by testing in the field (51).

Low-As zones can be protected against intrusion of high-As groundwater by favorable hydraulics or geochemical processes. Hydraulic protection occurs where the source area that contributes water to a particular zone is not high in dissolved As or solutes that can mobilize As. Geochemical protection occurs because of As adsorption or precipitation (e.g., As-bearing sulfides). Experiments and modeling indicate that breakthrough of As through 10 m of orange sands may lag groundwater flow by hundreds of years because of adsorption (37).

Shallow low-As zones are particularly vulnerable to As invasion owing to complex and rapid flow combined with the patchy distribution of dissolved and solid-phase As (Fig. 3B). The adsorption capacity of gray sands that prevail at shallow depths is lower than that of orange sands and further contributes to the vulnerability of shallow low-As zones. A primary threat is advective transport from adjacent high-As zones because groundwater flows much more easily laterally than vertically through stratified sediments.

Deeper groundwater (>100m deep) is more uniformly low in As (Fig. 1B) and already a

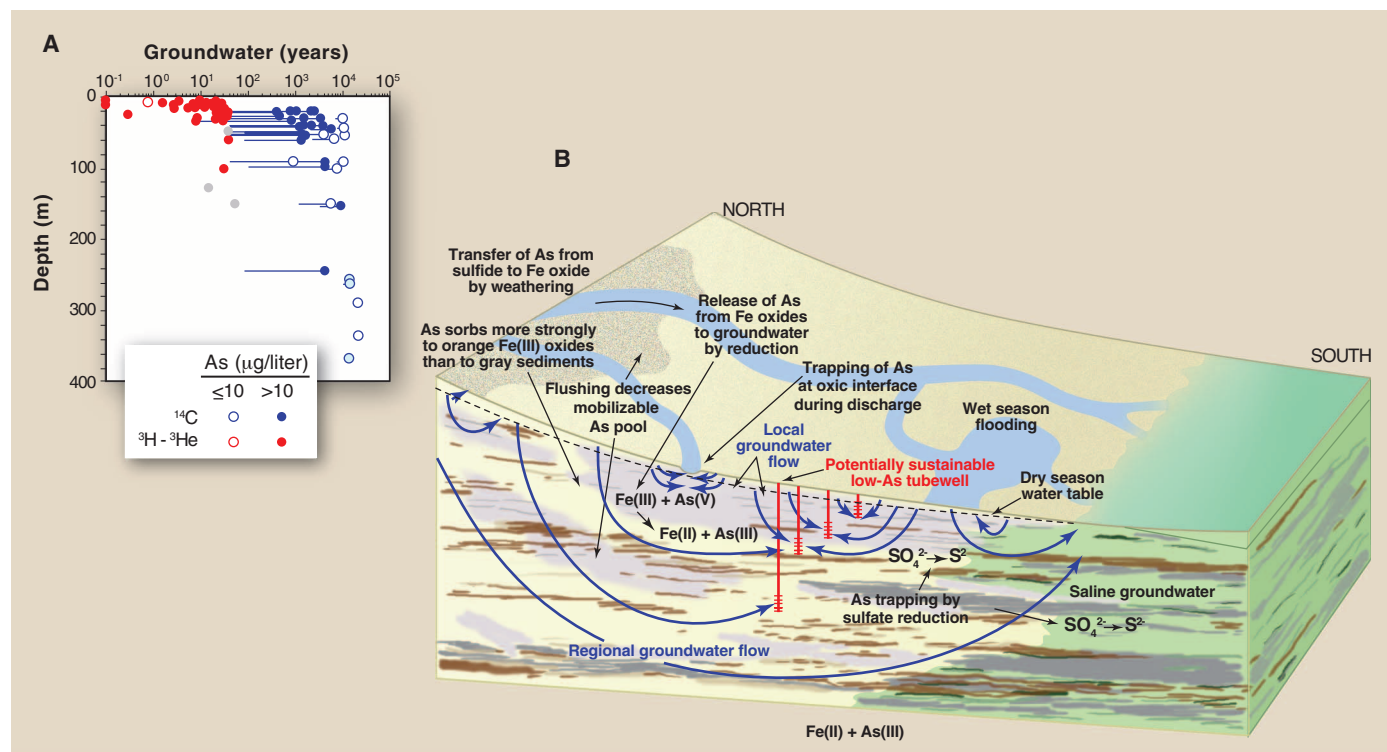


Fig. 3. (A) Depth distribution of groundwater ages in Bangladesh determined by either the ^3H - ^3He method (red symbols) or radiocarbon in those cases where ^3H was measured and not detected (blue symbols) (54). Concentrations of As were not reported for three deep samples shown as

light blue circles but are likely to be low; the age of samples shown as gray circles is uncertain owing to their low ^3He content. **(B)** Conceptual diagram modified from (9) showing the key processes affecting the distribution of As in groundwater.

widely used and potentially sustainable source of safe water in certain portions of the Bengal Basin. Hydraulic protection of deep groundwater requires geologic separation of high- and low-As strata or a regional flow system in which the recharge location is low in As. Deep, regional systems likely occur in much of the Bengal Basin despite low regional hydraulic gradients because of its large extent, depth, and extreme vertical heterogeneity (44, 52). Hydraulic gradients in the Mekong (41), Red River (42), and Terai basins are similarly low, but the basins are smaller and shallower, and thus may have more limited regional flow. Numerical modeling of groundwater flow in the Bengal Basin (44) has shown that hydraulic protection may last for at least 1000 years in much of the As-affected area if wells are deeper than 150 m and pumping rates from deep aquifers are limited to domestic supply. In contrast, deep pumping for irrigation occurs at order-of-magnitude higher rates compared to hand pumps and could induce much earlier and larger-scale downward migration of As (44).

Human-induced changes have and will continue to threaten low-As zones. Whereas hydraulic heads and flow velocities respond quickly to changes in physical forcing, solute concentrations require a period at least equivalent to the groundwater residence time to reach a new equilibrium. This applies in particular to shallow aquifers where the duration of human-induced change, such as irrigation pumping or the digging of ponds, has been approximately equivalent to the residence time of groundwater (39). Raising villages above flood level using low-permeability clay also creates a cap that inhibits recharge and could lead to a buildup of As in shallow aquifers previously suitable for drinking (49). Transport of reactive DOC by irrigation pumping into a zone of either gray or orange sands that currently lacks a source of organic matter could also lead to the onset of reductive dissolution and As release into groundwater (28, 34).

Where hydraulic protection does not exist, in shallower strata or where pumping rates are high, a zone may remain low in As for extended periods because of retardation by adsorption (37). The delay in the appearance of elevated levels of As should decrease with increasing velocity and increase with flow distance, particularly through orange sands. The lower rate at which water is drawn from a community hand pump is therefore preferable to a mechanized pump connected to a piped-water supply system. Where feasible, wells should extend as deep as possible into deep orange sands rather than into gray sands or shallow orange sands. These recommendations are consistent with the outcome of monitoring a set of hand-pumped community wells in Bangladesh during which a few increases in As concentrations were recorded during the initial years (mostly in wells <60 m deep) and none since (53).

Priorities for the Future

The laterally and vertically heterogeneous distribution of As has one advantage—many vil-

lagers in the affected regions live within walking distance of a well that is low in As or within drilling distance of such a zone. Governments and international organizations should therefore reinvigorate moribund well-testing campaigns and encourage periodic monitoring of wells using field kits. Better use should also be made of existing geological data and compiling test results to target those zones that are low in As for the installation of community wells. Even if wells tapping deeper strata are more likely to be hydraulically and chemically protected, tens of thousands of deep wells installed throughout Bangladesh (51) should be retested, which currently happens rarely.

As outlined in this review, the downside of patchiness is poor predictability and potential sensitivity of those aquifers that are low in As to changes in flow and/or related biogeochemical reactions. At a limited number of judiciously selected locations, analysis of organic matter and As reactivity should therefore be coupled with more detailed evaluation of the local hydrology. Another topic that deserves closer study is the viability of rural piped-water supply systems, currently favored by some governments and international organizations, as opposed to community hand pumps. Mechanized pumps concentrate deep pumping and are more likely to draw in high-As water from shallower aquifers.

Every effort should be made to prevent irrigation by pumping from deeper aquifers that are low in As. The accumulation of As in paddy soil and rice grains is a source of concern, but deep aquifers should not be compromised by abstraction for irrigation. This precious resource must be preserved for drinking—the most direct and efficient route of exposure to As.

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Supporting Online Material for
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References

Spatial and Temporal Variations of Groundwater Arsenic in South and Southeast Asia

Supporting material

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For displaying the data in Fig. 1 from Nepal, a subset of 3,855 wells was randomly selected from a total of 11,570 measurements accompanied by depth information compiled in ref. (S1). In West-Bengal, a random subset of 3,572 measurements was selected from a total of 131,440 with depth information reported in ref. (S2). These data were obtained by PHED, Government of West Bengal/UNICEF with funding from AusAID and DFID. In Bangladesh, the entire set of 3529 wells accompanied by depth information reported in ref. (S3) was included. For Cambodia, the data include all 222 measurements with depth information reported in ref. (S4). Finally in the case of Vietnam, the 275 measurements with depth information included data from refs. (S4-S7). The map including river basins shown in Fig. 1A was drawn using the Digital Atlas of South Asia CD-ROM (S8).

The sources of groundwater age estimates shown in Fig. 3 are refs. (S3, S9-S14). In the case of ³H-³He ages, the underlying assumption is that of unidirectional “pipe-flow” and negligible mixing with an older end-member without bomb-³H, which doesn’t necessarily hold (S12-S13). Radiocarbon ages were adjusted for “dilution” of the original carbon by dissolution of old

carbonate along the flow path. To estimate the upper limit for the radiocarbon age, simplifying assumptions include a purely closed system with respect to gas exchange with the atmosphere (i.e. no carbonate dissolution within the soil zone, before recharge), no isotopic exchange between groundwater and carbonate, and a correction factor accounting for dissolution of radiocarbon-dead carbonate along the flow path determined by groundwater pH (S15). The correction assumes there is no significant input of DIC to groundwater from the mineralization of organic carbon. Error bars extending to lower ages correspond to various (and unknown) degrees of gas exchange between soil/groundwater before recharge in an open system (S15). In many cases, corrections based on open system conditions are too large and the lower limit for radiocarbon ages is instead set by the ages reported to correspond to the detection limit for ^3H by various labs.

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