Mobilization of natural arsenic in groundwater: targeting low arsenic aquifers in high arsenic occurrence areas

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Abstract：Chronic exposure to minute amounts of arsenic in drinking water has been shown to adversely affect human health. Over 100 million people, many living in poor areas of the world, are currently exposed to unsafe level of arsenic (> $10\mu g/L$) in drinking water derived from aquifers. Arsenic, sometimes known as the King of Poisons, is a group VA element commonly found as an oxyanion in aqueous environment. Since 2000, testing for arsenic when many countries moved to implement a more stringent drinking water standard of $10\mu g/L$ (the WHO recommended safe level for human consumption) has now unequivocally established the world wide occurrence of elevated As in drinking water, especially in ground water. More people are affected by arsenic poisoning in Asia than in the rest of the world combined. The most affected areas are the South and Southeast Asian Arsenic Belt, encompassing the deltas of the Ganges-Brahmaputra-Meghna river and the alluvial fan aquifers in the upstream areas of the Ganga plains, the deltas of the Red river, Mekong river and Irrawaddy river. In China, the alluvial basins of the Yellow River in Inner Mongolia, the Datong and Taiyuan basins of Shanxi, and the Dzungaria basin of Xinjiang produce groundwater rich in arsenic and fluoride, causing arsenicosis and fluorosis.

In most sedimentary aquifers, reducing conditions tend to mobilize arsenic from sediment to groundwater, although the detailed processes of hydrological and biogeochemical interactions remain to be fully understood. Cases studies from Bangladesh are used to illustrate that flushing over geological time scales lowers the sediment mobilizable As and organic matter content, resulting in low As groundwater. Such understanding has guided the As mitigation policy in Bangladesh. A worthwhile future research direction is to understand the hydrological, mineralogical, geological and biogeochemical factors that contribute to the sustainable use of low As aquifers in endemic area of As.

Key words：arsenic；groundwater；geochemistry

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1　Introduction

The US Environmental Protection Agency adopted more stringent regulations on Arsenic (As) in drinking water, lowering the maximum contaminant level (MCL) from $50\mu g/L$ to $10\mu g/L$, effective Jan. 2006 (http://www.epa.gov/safewater/ars/arsenic_finalrule. html). This new regulation is based on the established health effect of As even at<$10\mu g/L$. Chronic exposure to As in drinking water enhances the risks of a wide

range of diseases, including various internal cancers, as well as skin lesions [1].

While a reduction of As exposure from drinking water will benefit the health of the American public, it also presents a challenge because, with an average crustal abundance ~ 2 mg/kg [2], As is by no means a scarce element in the earth's crust and is highly toxic in its inorganic forms. It is often useful to recall that for a porosity of 25%, 1 mg/kg of solid phase As (if all As is dissolved in the pore space) can enrich the groundwater to~8000 μ g/L As. Such a simple back-of-the-envelope calculation illustrates that the As content of the solid phase needs not to be elevated to cause As concentrations in water to exceed 10 μ g/L. In other words, basic principles of earth science would predict that groundwater could contain > 10 μ g/L dissolved As in many locations. Indeed, since the review on geochemistry of As in groundwater [3] that included literatures prior to 2000, more basin-scale As problems in drinking water predominantly from groundwater sources that were attributed to As of natural origin have been identified and better characterized [4]. It is now clear that elevated groundwater As is found not only in Asia where the affected population was the most, but also in Europe, North and South America, Australia and Africa (see Fig. 1.1 in reference 10).

The question then becomes: Why isn't > 10 μ g/L As found in groundwater at even more locations that are of regional significance? This is because As partitioning between the solid and liquid phase is strongly dependent on a key chemical parameter: the thermodynamic state, in this case the oxidation and reduction potential, of the groundwater system [5]. It is rare to observe > 10 μ g/L dissolved As in natural waters that contain dissolved oxygen, except in the cases of acid-mine drainages with low pH. Under oxic conditions, solid surfaces are usually coated with enough Fe-oxide phases that adsorb most of the available As onto its surface, preventing As from entering the water. This As, however, is more mobilizable than that trapped in the crystalline lattice of an unweathered mineral. Reducing environment stimulates mobilization of the As on Fe oxhydroxides from the solid phase to solution. Therefore, one usually finds elevated dissolved As concentrations in anoxic groundwater that is enriched in dissolved Fe and depleted in dissolved sulfate. Recent reviews on the occurrence of As in groundwater suggest that most major sedimentary aquifers with elevated As levels display this type of chemistry [3]. This simplified description of the As release mechanism in groundwater, the so-called Fe-oxides reductive dissolution hypothesis, has been invoked to explain As enrichment in Bangladesh groundwater [6] and various lake [7], groundwater [8] and marine pore water environments [9]. Occasionally, the oxidation of As-containing sulfides [10] results in As enrichment in groundwater, but those waters are usually enriched in dissolved sulfate and acidic.

An intriguing characteristics emerged from studies of groundwater arsenic distribution is the spatial variation on various scales (100-103 m) and with depth[11, 12]. That low As groundwater and aquifer[13] can be found in areas where As occurrence is prevalent has led to mitigation strategy such as well switching[14] and installation of community wells [15] to low As aquifer. Thus, there is a need to better understand the hydrogeological and biogeochemical factors that permit the sustainable usage of low As aquifers [16]. This paper discusses these factors using case studies from Bangladesh and points out future research need to help identify low As aquifers in high groundwater As areas.

2 Results and discussion

2.1 Processes important for As mobilization

The motivation to understand the biogeochemical and hydrogeological processes that result in elevated As concentrations (> 10 μ g/L) in groundwater derived from natural sources of As lies in the premise that such improved understanding will contribute to efforts to remove the health risks from exposure to As-containing groundwater by guiding the focus of

interventions on problematic areas. To tackle the interactions of hydrology, mineralogy, geology and geochemistry and their influence on As mobilization, a framework is provided (Fig. 1).

Hydrology, Mineralogy, Geology and As Geochemistry Interactions.
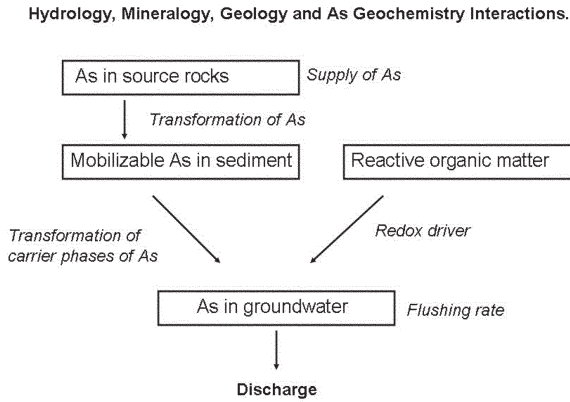

Fig.1 Schematic diagram of processes regulating dissolved As concentrations in groundwater

A key observation has been established in Bangladesh regarding biogeochemical processes for As mobilization that there is the presence of a pool of mobilizable As that can be selectively extracted in those aquifers associated with elevated groundwater As levels, and the absence of such a pool in those aquifers where groundwater As levels are typically low [13]. When organic matter, especially those that are bioavailable is present in sufficient quantity to drive the aquifer redox condition to reducing enough to allow transformation of As carrier phase, and in turn, enhance As mobility. This process usually intensifies along the groundwater flow path, with the oldest water at the end of the flow line highly enriched in As. Upon discharge, groundwater As may not leave the aquifer because a redox transition zone at the point of discharge can effectively immobilize As by sorption [17].

Another key observation suggests a very important, and perhaps dominant, role for hydrological processes on groundwater As distribution. This is the finding that As is mobilized at a rate of ~20 μ g/L per year in shallow aquifers in Araihazar, Bangladesh [18]. Alternatively, this rate may be viewed that As is flushed from the aquifer at similar rate, thus lowering

the As concentration in both sediment and water. The role of flushing on As distribution, particularly its contribution to formation of low As aquifer is discussed below.

2.2 Flushing lowers As content

Flushing refers to the removal of As from both the solute and solid phases of the aquifer over time. This is because water with low As content, when flowing through sand with mobilized As, will come to a state that can be empirically viewed as a sorption equilibrium, desorbing some As and carry with it down the flow path. In this process, the aquifer As inventory is lowered. If this process continues for many years, eventually the As will be flushed out. To gain quantitative understanding of flushing, one may consider that the partitioning of As between solute and solid phases generally follows a Langmuir type of isotherm (Fig. 2). The oxidized sediment such as the natural soils [20] or the orange colored sand from deep Pleistocene aquifer of Bangladesh [21] displays more non-linearity than the reducing sediment such as grey colored sand from shallow Holocene aquifer of Bangladesh [17]. Thus, for solute (As) ranging from 0 to ~100 μ g/L, the partitioning coefficient for the oxidized orange colored sediment is ~20-30 L/kg whereas the reducing gray colored sediment is only 0~1-4 L/kg. Indeed, that flushing history lowers As content of aquifer over time and contributes to the regional pattern of groundwater As distribution in Bangladesh was supported by field observations [19].

To illustrate the role of flushing quantitatively, a one-dimensional advection dispersion model was constructed to show that flushing history, combined with a linear isotherm dictating the equilibration of As between the dissolved and particulate phases, could explain regional as well as local patterns in the distribution of As in shallow aquifers in Bangladesh [19]. A wide range of As distributions in the shallow aquifers of Bangladesh can be reached by using the constraint on partitioning coefficient Kd of 4 L/kg between dissolved and P-mobilizable As derived from the needle-sampler data and a plausible range of

hydrogeological conditions. For a flow rate of 50 cm/d, the model suggests that As concentrations in shallow aquifers of the region can be lowered to < 10 μ g/L only a few centuries after their deposition. The model also suggests that, in contrast, flushing As out of the shallow aquifers of at slower 0.5 cm/d may require another several thousand years.

Thus, slowly flushing groundwater tends to accumulate As, as is the case found in many sedimentary basins in China. Aquifer that either has been previously flushed, or those that are presently flushed at high rate, are good candidates for low As water. That flushing lowers As content is not a new notion. The value of present work is that the role of

mobilizable As is demonstrated in relationship to flushing. Measurement of mobilizable As in sediment, in addition to measurement of groundwater As from those aquifers, should be considered together when considering sustainable use of low As aquifer.

2.3 Flushing lowers organic matter content

Flushing also lowers organic matter content of sediment in low As aquifer. Sand samples from shallow As containing aquifers from two sites, Dari and Bay, in Araihazar display higher mobilizable sediment As concentration and % organic carbon content than those from the deep low As aquifer of Pleistocene age (Fig. 3).

The low bulk organic carbon content (0.05%) of Pleistocene aquifer sand is the most likely reason for less reducing conditions commonly found in such aquifer. That These waters are not reducing enough to reduce Fe or to mobilize As sorbed on sand. Here, calculations that address the amount of time that it might take to exhaust all reactive organic matter in a sedimentary aquifer with oxidants (dissolved oxygen and sulfate) supplied through recharge are used to provide further insight on how flushing lowers organic matter content.

We assume that the rate-limiting step of organic matter oxidation is the supply of dissolved oxidants to
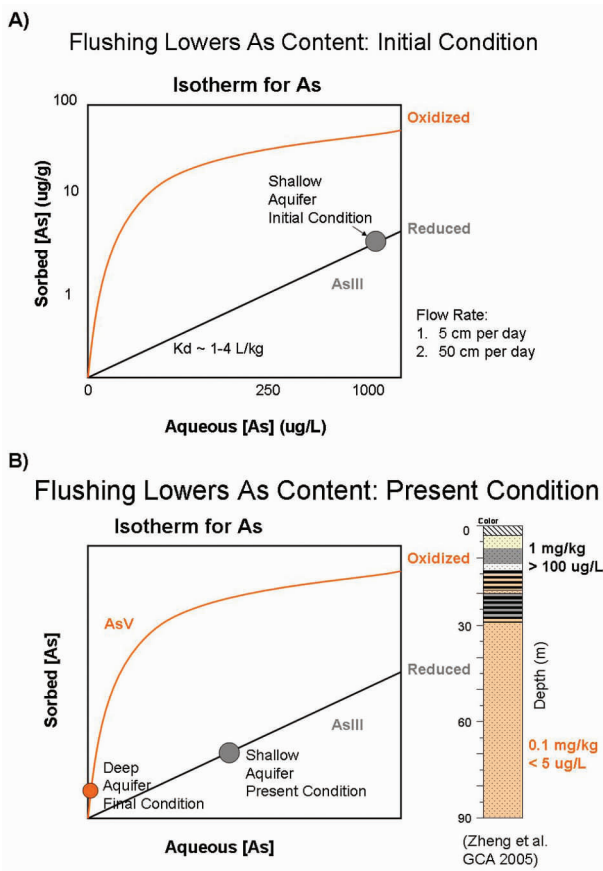

Fig.2 Groundwater flow at a rate of 5 cm per day or 50 cm per day, or flushing, lowers groundwater As from~1000 g/L (A) to a few hundred g/L in a few thousand to a few hundred years, respectively [19]. Even longer flushing time of > 100,000 years will result in a final condition found in deep aquifer of Bangladesh, with low mobilizable sediment As of ~0.1 mg/kg and groundwater As of < 5g/L, as shown in lithological sketch of a core from Araihazar, Bangladesh [13]
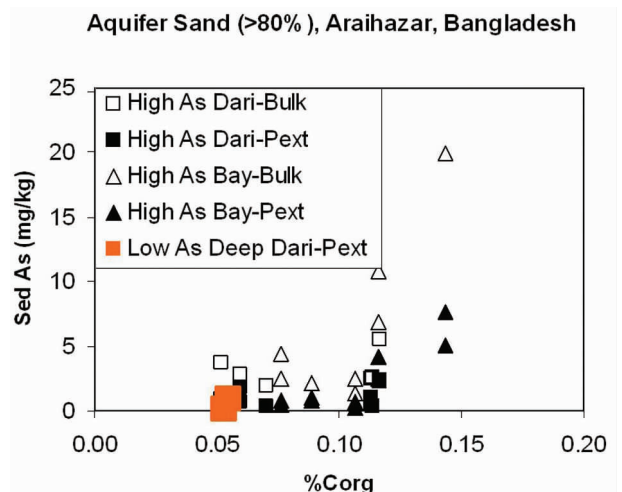

Fig.3 Sediment bulk As and phosphate−extractable As concentrations vs. percent organic carbon content from high As and low As aquifers in Bangladesh[13]

the aquifer, i.e. the rate of organic matter consumption equals the rate of dissolved oxidants supply.

The supply of dissolved oxidant to the aquifer is：

$$C_{ox} \times F$$

Where C_{ox}：dissolved oxidant concentration, mole/L

F：flux of recharged water, L/yr

The amount of organic matter that it can oxidize at a

$$\frac{\alpha \times C_{ox} \times F}{M} = \frac{\alpha \times C_{ox}}{t_{res}}$$

given time is:

Where α：stoichiometric ratio of oxidants, mole reductant/mole oxidant

M：size of the aquifer, L^3

t_{res}：residence time of aquifer, $t_{res} = M/F$

Thus, the rate of organic matter consumption can be

$$\frac{dC_{org}(t)}{dt} = -\frac{\alpha \times C_{ox}}{t_{res}}$$

estimated by：

Where C_{org}：concentrations of organic carbon, mole/L

Integration over time gives a linear decrease of the amount of C_{org} with time：

$$C_{org}(t) = C_{org}(0) - \frac{\alpha \times C_{ox}}{t_{res}} \times t$$

The dissolved oxidant concentrations include 0.2 mM of dissolved oxygen based on solubility equilibrium, and 0.1 mM of dissolved sulfate, a value representing the average composition of GBD river waters [22,23]. Accordingly, with an initial labile organic matter content of 1% or 0.1%, the time it would take to exhaust labile organic matter is 60,000 years or 2000 years if the groundwater residence time was 10 years, and is > 100,000 years or 16,000 years if the groundwater residence time was 100 years, respectively. In this calculation, an aquifer porosity of 30%, and particle density of 2 g/cm³ are assumed. For simplicity, the stoichiometric ratio of oxidants, is assumed to be 1 in the case of oxygen reduction, and 2 in the case of sulfate reduction.

Residence times of groundwaters in aquifers under the uplifted Pleistocene Madhupur terrace [24], such as sites in Sripur and Dhaka, are likely to be approximately 10 to 100 years based on observation that groundwater in such systems contained detectable amounts of tritium [6]. Whereas we do not know the concentration of reactive organic matter in such systems, the assumption that the system has a homogeneously distributed concentration of 1% labile organic carbon is probably a reasonable upper limit case. Such a calculation illustrates that one prerequisite for low As concentrations in the Pleistocene or Pliocene aquifers is that these sediments probably need to have been previously high-standing relative to sea level for a considerable period of time to allow oxidation from relatively rapid flushing of oxygenated groundwaters through the system, i.e., water residence time < 100 years. Such conditions clearly existed during the Pleistocene when sea levels were much lower than that of the present.

3　Conclusions

In Bangladesh, the deep Pleistocene aquifer currently with low As groundwater has benefited from extensive flushing that lowered both the mobilizable As and organic matter content of the aquifer sand, removing the substance and the substrate that promote As release to groundwater. Such flushing requires high groundwater flow rate, e.g., short residence time that is made possible during the glacial low sea level stand. Understanding of the depositional history of the aquifer and determination of residence time of groundwater, as well as measurement of key sedimentary properties such as mobilizable As and organic matter content can help identify low As aquifer for sustained use.

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地下水中天然砷的迁移：以高砷地区中低砷含水层为例

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提要：研究表明饮用水中微小数量的砷会对人类健康产生不利影响。世界上居住在贫穷地区的人数超过了 100 万，目前他们正直接饮用来自含水层中砷离子含量($> 10 \mu$g/L)非安全标准的地下水。砷有时称为毒中之王，在水环境中常常以五价氧化物形式出现。自 2000 年以来，许多国家开始执行更为严格的 10μg/L（WHO 认可的居民安全饮水标准）饮用水标准，可以确定地说，在世界范围内的饮用水中检测到砷的情况越来越多。亚洲地区砷中毒的人数比世界其他地区总和还多。最受影响的地区位于南亚和东南亚富砷带，环绕恒河—雅鲁藏布江—梅克纳河三角洲及恒河平原上游的冲洪积扇含水层、红河三角洲、湄公河和伊洛瓦底江；在中国境内包括内蒙黄河冲积盆地，山西大同盆地、新疆准噶尔盆地，其中的地下水富含砷和氟化物而引发砷中毒和氟中毒。

　　尽管还未完全掌握其中的水文地质及生物地球化学作用的详细过程，但对大多数沉积介质含水层，在还原条件下砷离子容易从沉积介质转移到地下水中。孟加拉研究实例表明地质时期尺度的冲刷降低了沉积介质中的 As 和有机物含量从而形成低砷地下水。这一认识为孟加拉国的降砷策略提供了科学指导，是未来水文学，矿物学，地质学和生物地球化学方面很有意义的研究方向，并有利于地砷病区低砷地下水的可持续利用。

关键词：砷；地下水；地球化学