Integration of aquifer geology, groundwater flow and arsenic distribution in deltaic aquifers - a unifying concept

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Abstract

Groundwater arsenic (As) presents a public health risk of great magnitude in densely populated Asian delta regions, most acutely in the Bengal Basin (West Bengal, India and Bangladesh). Research has focussed on the sources, mobilization, and heterogeneity of groundwater As, but a consistent explanation of As distribution from local to basin scale remains elusive. We show for the Bengal Aquifer System that the numerous, discontinuous silt-clay layers together with surface topography impose a hierarchical pattern of groundwater flow which constrains As penetration into the aquifer and controls its redistribution towards discharge zones, where it is re-sequestered to solid phases. This is particularly so for the discrete periods of As release to groundwater in the shallow sub-surface associated with sea level high-stand conditions of Quaternary inter-glacial periods. We propose a hypothesis concerning groundwater flow (SIHA: **S**ilt-clay layers **I**mpose **H**ierarchical groundwater flow patterns constraining **A**rsenic progression) which links consensus views on the As source and history of sedimentation in the basin to the variety of spatial and depth distributions of groundwater As reported in the literature. SIHA reconciles apparent inconsistencies between independent, in some cases contrasting, field observations. We infer that lithological and topographic controls on groundwater flow, inherent to SIHA, apply more generally to deltaic aquifers elsewhere. The analysis suggests that groundwater arsenic may persist in the aquifers of Asian deltas over thousands of years, but in certain regions, particularly at deeper levels,

arsenic will not exceed low background concentrations unless groundwater flow systems are short-circuited by excessive pumping.

Keywords: Groundwater, Arsenic, Flow systems, silt-clay, Delta, Aquifer, SIHA

1. Introduction

Groundwater providing the domestic water supply for more than 100 million people in Asian delta regions contains toxic levels of dissolved arsenic (As), in many cases exceeding by more than two orders of magnitude the 10 µg/l WHO Guideline Value for drinking water (Winkel *et al.*, 2008; Ravenscroft *et al.*, 2009; Fendorf *et al.*, 2010). The Bengal Aquifer System (BAS) of Bangladesh and West Bengal, India, is the most acutely affected. There is broad consensus that As originates in association with iron-oxyhydroxide coating of Himalayan-derived (DPHE, 1999, 2001; Fendorf *et al.*, 2010) sedimentary grains, and is released to groundwater by microbially-mediated reductive (Gulens *et al.*, 1979; Nickson *et al.*, 1998; Berg *et al.*, 2007; Fendorf *et al.*, 2010) dissolution of iron-oxyhydroxide. In the deltaic alluvial aquifers, groundwater As is prevalent, though heterogeneous, across the present-day floodplains mostly within Holocene sediments shallower than 100 m (DPHE, 2001; van Geen *et al.*, 2003b; Polya *et al.*, 2005; Berg *et al.*, 2008; Polizzotto *et al.*, 2008).

The BAS comprises Pliocene-Quaternary fluvio-deltaic sands, silts and silty-clays overlying the Mio-Pliocene Upper Marine Shale at depths of 1200 – 2000 m (Burgess *et al.*, 2010). Basin subsidence, together with cyclic periods of deposition and erosion under conditions of eustatic sea level fluctuation during Quaternary time, led to accumulation of approximately 200 m thickness of sediment over the past one million years. Each of ten eustatic cycles included an episode of widespread sedimentation of approximately 10,000 years duration associated with sea-level high-stand conditions during the inter-glacial periods. These were punctuated by periods of sustained weathering and fluvial down-cutting under falling sea levels during the on-set of glacial periods. Periods of As mobilisation to groundwater are thought to be associated with the high-stand conditions conducive of waterlogging and reducing conditions (e.g., Acharyya *et al.*, 2000; Ravenscroft *et al.*, 2001; Meharg *et al.*, 2006), leading to discrete, episodic periods of As release to groundwater over the past 1 Myr, rather than a continuous, uninterrupted, release.

At the scale of individual research studies, from single field sites to 10-20 km^2 study areas, contrasting patterns of groundwater As and its variability in specific contexts have individually been attributed to relationships with groundwater chemistry (McArthur *et al.*, 2004; Zheng *et al.*, 2005; van Geen *et al.*, 2008a; Radloff *et al.*, 2011), topography (Ravenscroft *et al.*, 2005; Shamsudduha *et al.*, 2009), local litho-stratigraphy (Aziz *et al.*, 2008; Weinman *et al.*, 2008; Hoque *et al.*, 2009), groundwater age (Stute *et al.*, 2007), sediment age (Postma *et al.*, 2012), groundwater recharge sources (Harvey *et al.*, 2002; Neumann *et al.*, 2010) and flow dynamics (Harvey *et al.*, 2002; McArthur *et al.*, 2008; Polizzotto *et al.*, 2008; Desbarats *et al.*, 2014). These explanations invoke different sources and pathways of organic matter (Harvey *et al.*, 2002; McArthur *et al.*, 2004; Neumann *et al.*, 2010), locations of As release (McArthur *et al.*, 2004; Klump *et al.*, 2006; Polizzotto *et al.*, 2008), availability of mineralogical sinks of As (McArthur *et al.*, 2004), and local patterns of groundwater flow (Harvey *et al.*, 2002; McArthur *et al.*, 2008; Polizzotto *et al.*, 2008) including transience of groundwater As flux (Polizzotto *et al.*, 2008), but each in isolation from the variety of observed patterns of groundwater As elsewhere in the affected regions and without consideration of the larger scale patterns of groundwater flow and geological structure. The absence of excessive arsenic has been recognised in groundwater of Plio-Pleistocene and older sediments (Bhattacharya *et al.*, 1997; BGS/DPHE, 2001; van Geen *et al.*, 2003b; McArthur *et al.*, 2004; McArthur *et al.*, 2008). Low-As environments in the Bengal Aquifer System (BAS), i.e., As <50 µg/L, the Bangladesh and India drinking-water standard, have also been recognized (Bhattacharya *et al.*, 1997; Burgess *et al.*, 2010; Hoque *et al.*, 2011; Hoque *et al.*, 2014) as including the northern and lateral margins of the basin, Pleistocene terraces at all depths, and at depth greater than about 150 m beneath the floodplains.

In many cases, conclusions of the local-scale studies have been extrapolated to suggest explanations of the basin-scale pattern of As occurrences (Harvey *et al.*, 2002; McArthur *et al.*, 2008; Neumann *et al.*, 2010). Only the 'palaeosol' model of McArthur et al (2008) links As pollution to geological structure at the basin scale, employing the subsurface distribution of palaeo-channel sediments (containing As-polluted groundwater) and palaeo-interfluvial sediments (containing low-As groundwater) to explain the arsenic distribution. The palaeo-interfluvial brown sediments have adsorptive capacity for As, and a clay unit of low permeability protects them from the invasion of arsenic-rich water from above (*ibid*). The palaeosol model has been validated by field observations (McArthur *et al.*, 2011a; Hoque *et al.*, 2012, 2014; Ghosal *et al.*, 2015), however it does not explain the heterogeneities of As concentration within the palaeo-channel itself, nor the effective absence of As at depth in the aquifer (ca. >150 m) irrespective of palaeo-channel / palaeo-interfluvial distinctions. These protective palaeosols are laterally discontinuous and the thickness of brown sands is limited (Hoque *et al.*, 2012, 2014).

Discontinuous silt-clay layers, irregularly distributed throughout the dominantly sandy fluvio-deltaic sediments, are a ubiquitous feature of the BAS (Michael and Voss, 2009a). Additionally, effectively impermeable palaeosols layers, formed under sub-aerial weathering at the time of the glacial maxima, have been recognised (Umitsu, 1993; Goodbred and Kuehl, 2000; McArthur *et al.*, 2008; Burgess *et al.*, 2010; Hoque *et al.*, 2014). The most recent palaeosol appears to be locally punctured by palaeo-channel sand deposits (McArthur *et al.*, 2011a; Hoque *et al.*, 2012, 2014; Ghosal *et al.*, 2015) into sections limited to a few kilometres , although the continuity of the silt-clay layers and the dimensions of the sand bodies in Bengal basin, as for alluvial aquifers in general, remain uncertain (e.g., Miall, 1996). The frequency of occurrence of discontinuous low permeability layers of the Bengal basin has previously encouraged its conceptualisation as a hydraulically anisotropic single aquifer system (Michael and Voss, 2009a).

Here we investigate the significance of the silt-clay layers in explaining the variety of local to basin-scale patterns of As occurrence. We apply a large set of lithological data to develop a description of the occurrence of silt-clay layers in BAS, which we incorporate as a simplified representation into synthetic 2D models of groundwater flow and advective transport in the aquifer. We find that the pattern of distribution of silt-clay layers exerts a considerable control on the groundwater flow systematics. We demonstrate that following a discrete period of As release to groundwater, the silt-clay layers are fundamental in determining a heterogeneous As concentration within the shallower part of the aquifer, as well as maintaining the low-As status of deeper groundwater. By integrating the distribution of silt-clay layers, the systematics of groundwater flow and the geological development of the aquifer, we seek to provide a more coherent understanding of the patterns of As occurrence for the benefit of programs of low-As groundwater extraction.

2. Materials and Methods

Our study is based in the Bengal Aquifer System (BAS) of the Bengal Basin and conceptual model outcomes are compared with the observations made by previous studies in the basin.

2.1 Analysis of lithologs

We analysed 1573 lithological logs distributed throughout southern Bangladesh (Fig. 1) principally from the Department of Public Health Engineering (DPHE), mostly drillers' logs recorded from the washed cuttings of rotary drilling, sampled at intervals of 10 ft (ca. 3 m) (DPHE/DFID/JICA, 2006). The distance between available logs varies from <1 km to >10 km. On average, log density is 1 in *ca.* 30 km^2. The logs range in maximum depth from 87 to 380 m with a median value of 244 m; 75% of the logs contain lithological data to a depth of ≥207 m. We re-coded the lithological descriptions into four grain-size categories (silt-clay, fine sand, medium sand and coarse sand). We grouped silt and clay together as having significantly lower hydraulic conductivity (K) than sands, and we analysed the percentage occurrence, lateral continuity and spatial distribution of silt-clay layers, in Rockworks®. The discontinuous nature of the silt-clay was incorporated by interpolating mid-way to adjacent logs and the resulting 'inter-leaved pattern' of silt-clay layers (section 3.1) formed the basis of a synthetic representation of the aquifer structure.

2.2 Modelling groundwater flow and arsenic transport

We incorporated the 'inter-leaved pattern' of silt-clay layering into exploratory 2D models of steady state groundwater flow and advective transport of arsenic using the MODFLOW-2000 (Harbaugh *et al.*, 2000) and MT3D (Zheng and Wang, 1999) codes. The model represents interleaved silt-clay layering as a concept, derived from the interpretation of the lithologs illustrated in figure 1; it is not intended to represent an actual cross-section of southern Bangladesh. The scale of the model is approximately 1:20 the width of the Bengal basin. The model dimensions are 15 km wide and 100 m high, with cell dimensions of 100 m by 100 m and 27 layers of variable thicknesses in the vertical plane (Fig.2). The base and lateral boundaries of the model were assigned a no-flow condition, so the model domain represents a complete sedimentary basin. The synthetic geological structure and aquifer parameterization are indicated in Fig. 2. Hydraulic parameters were assigned values identified from previous summary and basin-scale studies of the region (Rahman and Ravenscroft, 2003; Michael and Voss, 2009a). Silt-clay (K = 6.05E-05 m/d) was treated as hydraulically isotropic, while sands (K_h = 25 m/d) were assigned a K_h/K_v anisotropy of 10. Bulk hydraulic anisotropy (K_h/K_v) for the entire model is *ca* 1000, the minimum value found consistent with vertical profiles of groundwater age by ^{14}C dating (Hoque and Burgess, 2012) and at the lower limit applied in previous basin scale modelling (Michael and Voss, 2009a). The top boundary, describing elevation of the ground surface and reproducing the relative topographic gradients of the Bengal Basin, was assigned a fixed head so as to impose topographically-driven gravitational groundwater flow as previously applied for the Bengal Basin (Michael and Voss, 2009a) and so that additional induced recharge would automatically be provided in response to pumping (Michael and Voss, 2009a; Shamsudduha *et al.*, 2011). Internal topographic low points in the model represent river valleys and/or surface depressions. An alternative representation of the aquifer as hydraulically uniform, incorporating heterogeneities as permeability anisotropy of K_h/K_v value 10^3, was also implemented (Figure A5).

Both a natural condition with no abstraction, and a scenario including steady-state groundwater abstraction for domestic and irrigation supplies were considered. For abstraction, we applied laterally extensive pumping stresses of 2 cm/yr from both a shallow and a deep level to represent domestic hand-pumped tubewells (HTWs) and deep tubewells (DTWs) respectively, and 40 cm/yr from an intermediate level to represent irrigation pumping (Fig. 2), consistent with previous studies (Michael and Voss, 2008; Michael and Voss, 2009b; Radloff *et al.*, 2011).

The geochemical processes of arsenic mobilisation are not the subject of the paper; we do not explicitly incorporate the redox reactions which release arsenic, driven by organic matter. Rather, we implicitly acknowledge its release through definition of an initial concentration source term of 500 μg/L As, a typical value for the maximum concentration of arsenic in the source zone (Cuthbert *et al.*, 2002). Simulation of As release at this concentration represents conditions at the culmination of one episode of As mobilisation to groundwater, acknowledgement that the conditions promoting As mobilisation are not continuous, but are themselves determined by the periodic imposition of high-stand conditions (e.g., Acharyya *et al.*, 2000; Ravenscroft *et al.*, 2001; Meharg *et al.*, 2006).

In representing transport we omit the retarding effect of sorption and reaction. Although several studies (van Geen *et al.*, 2008b; McArthur *et al.*, 2010; Radloff *et al.*, 2011; Jung *et al.*, 2012) show that As is retarded relative to groundwater, uniform sorption may not affect the patterns of spatial redistribution. The issue of rate of arsenic transport is complicated by likely dis-equilibrium between exchangeable As in the sediments (Swartz *et al.*, 2004; Zheng *et al.*, 2005) and groundwater (van Geen *et al.*, 2008a; van Geen *et al.*, 2008b), as evidenced by temporal variation of dissolved As induced by pumping (McArthur *et al.*, 2010). An important simplification of the models is that they treat arsenic as being chemically conservative. Therefore, our models indicate relative rather than absolute values of As concentration and time, our principal concern being to reproduce the spatial patterns of groundwater arsenic distribution from its source following release and mobilisation. We employed the models (Table A1) over a 1000 year modelling timescale. First, the model was used to simulate re-distribution under natural (non-pumping) conditions. and we tested contrasting views of the As source distribution, representing the arsenic as an initial concentration (500 μg/L) distributed across the interior of the basin over three alternative depth intervals proposed as original As source distributions, *ie* a surface source (e.g., Polizzotto *et al.*, 2008), a buried source (e.g., Ahmed *et al.*, 2004) and a source uniformly distributed throughout the full thickness of the aquifer (e.g., DPHE, 2001). Subsequently we applied the models to explore the influence of the inter-leaved pattern of silt-clay layers on the patterns of As re-distribution, and the effects of groundwater pumping.

An alternative representation of the As source at constant concentration was also implemented (Figure A9); while the details of groundwater As distribution in the shallow regions of BAS can only be explained by a discrete, non-continuous As source, conclusions relating to the deeper regions apply equally to a continuous source..

3. Results

3.1 Silt-clay layers and the concept of inter-leaving

At the scale of the available data, the silt-clay layers cannot be traced laterally (Fig. 1). Their spatial extent is therefore unknown, but they are numerous in each log and variable in thickness from a few metres to 10s of meters. As the position and frequency of silt-clay layers varies from log to log, the depth to the topmost silt-clay varies spatially (Figs. 1-3), in a manner typical of alluvial aquifers (e.g. Zeito, 1965; Sneider *et al.*, 1978; Miall, 1996). We interpolated silt-clay layers half-way between the actual field observations to investigate whether these sparsely-distributed data provide a useful description of the aquifer system, and this resulted in a pattern we called the 'inter-leaved pattern' (Fig. 1). In fact, this is geometrically a fractal pattern, i.e. with more lithological data the pattern of heterogeneity remains the same but with increased conglomeration. In the modelling, we show the influence of the inter-leaved distribution of silt-clay layers on groundwater flow (Figures A2 and A4). This inter-leaved pattern forms the basis of a synthetic representation of the aquifer structure, in which the depth to the shallowest silt-clay varies across the region (layers A to D in Fig. 2a).

The lithological logs (Fig. 3 and Supplementary Material, hereafter SM Fig. A1) indicate that almost the entire southern part of the Bengal basin has >10% cumulative silt-clay fraction within the top 140 m thickness of sediments. Although no quantitative relationship between thickness and spatial extent of silt-clay has been established (Zeito, 1965), we assumed that a cumulative thickness of 10 m silt-clay in a 100 m thickness of sediment would have a sufficient spatial extent to produce an inter-leaved pattern effective to that depth. Note that in the western and north-western part of the region, the silt-clay component of the aquifer sediments is relatively less, as previously reported by JICA (2002).

3.2 Silt-clay layers and patterns of groundwater flow

In the case of a homogeneous aquifer, hierarchical groundwater flow and the depth of groundwater penetration were shown to be a function solely of the ground surface topography in classical studies by Tóth (2009). Our results show that when explicit representation of low permeability layers is made, groundwater flow follows tortuous paths and both the imposed hydraulic anisotropy (Zijl, 1999) and surface topography determine the patterns and depth of groundwater penetration (Fig. 4). Steady-state 2D groundwater flow simulations using a synthetic inter-leaved representation of silt-clay layering demonstrate (Fig. 4) that even the very subdued topography typical of the Bengal delta is sufficient to generate 'hierarchically-nested groundwater flow systems' (Tóth, 2009), within the depth of the exploited aquifer (*ca.* 350 m). The pattern of hierarchically-nested groundwater flow systems can be ordered as *local* if recharge and discharge areas are contiguous, *intermediate* if these areas are separated by one or more local systems, and *regional* if it occupies the main divide or valley bottom (Tóth, 2009), as has been proposed for Bengal basin by Ravenscroft et al. (2005).

Of the hydrological, geological, and topographic features included in the model, the inter-leaved pattern of silt-clay layering was the single most important factor controlling the flow pattern under natural conditions (SM, Fig. A2-A5). Only under an 'inter-leaved' pattern of silt-clay layers a series of flow systems is maintained (local, intermediate and regional), with depth of flow penetration determined by the permeability anisotropy imposed principally by silt-clay layering. Under these conditions, deep groundwater is seen to originate from the basin margins and to discharge to the major rivers. Shallow (i.e., local) groundwater flow systems, of more restricted spatial extent, originate from local topographic high points and discharge to streams or wetland areas in nearby topographic depressions. This general pattern of groundwater flow (shallow local, and deep regional flow) is also evident in models which realise the influence of discontinuous silt-clay layers by applying effective, anisotropic hydraulic parameterisation (Michael and Voss, 2009b). However, these representations are unable to reproduce the patterns of As redistribution reported from field studies in as full detail as does the 'inter-leaved' representation (see that neither the exceptional case of deep penetration of excessive groundwater As (Case II of Fig. 4), nor the variability of patterns of shallow As distribution (Cases III-VI) is captured in SM Fig.A5).

3.3 Groundwater flow systems and the distribution of arsenic

Among the As source distributions tested (SM Fig. A6-A7, A9) we find that only a relatively shallow and non-continuous As source allows reproduction of the variety of spatial and depth distributions of groundwater As described from field observations (DPHE, 2001; Harvey *et al.*, 2002; McArthur *et al.*, 2004; Berg *et al.*, 2008; Dhar *et al.*, 2008). Further, we find that hydraulic anisotropy on its own as an effective parameter cannot reproduce the observed variety of patterns of groundwater As occurrence (SM Fig. A5). We find that advective redistribution by groundwater following the hierarchy of flow patterns naturally determined by the inter-leaved pattern of silt-clay layers alone is able to reproduce the full range of contrasting As distributions observed across a number of individual field research sites in the Bengal basin (cases I to VI in Fig.4). The distributions are represented at a modelling time of 60 years, equivalent to >1000 years at the scale of BAS, although it is emphasised that the modelled time is relative rather than absolute as explained above. From a shallow As source, hierarchical groundwater flow explains the common observation that (Case I) excessive As is not normally present in ‘deep groundwater’ at >150 m in Bangladesh (DPHE, 2001), with rare exceptions (Case II) only where absence of silt-clay layers over an extended depth range has enabled deeper penetration of groundwater (Ravenscroft *et al.*, 2009). More generally, hierarchical groundwater flow explains a constraint on the depth penetration of As-bearing groundwater (Cases III to VI) commonly observed to be within the top 50 to 100 m (Dhar *et al.*, 2008), and the sharp transition from As-bearing to As-free groundwater in depth profile (Dhar *et al.*, 2008). Hierarchical flow explains how the combined influences of topography and surface silt-clay layering can result in zones of relative groundwater stagnancy (Case IV) leading to the maintenance of shallow regions of consistently excessive As (Stute *et al.*, 2007). Elsewhere, shallow groundwater is essentially free of excessive As (Cases V) where elevated topography focusses recharge and imposes greater hydraulic gradients which drive more effective groundwater flushing (Stute *et al.*, 2007; Aziz *et al.*, 2008; Weinman *et al.*, 2008; Hoque *et al.*, 2009). Notably, hierarchical flow explains the steep lateral gradients in As concentration on the boundaries of separate flow cells (Case VI) where juxtaposition of older and younger groundwater has previously been described as paradoxical (Klump *et al.*, 2006). Of these findings, only Case V depends on a time-limited As source. Therefore, taken together, the effect of the inter-leaved silt-clay layers in imposing a hierarchical groundwater flow system becomes a unifying concept which explains the variety of disparate patterns of groundwater As occurrence established by field observation.

3.4 Future trends in progression of arsenic

Modelling indicates that the present day occurrence of groundwater arsenic may largely be explained by the geometry of naturally-determined groundwater flow cells, and the pattern of aquifer arsenic redistribution, regionally, is little affected by groundwater pumping; though the bulk rate of flushing increases (Fig. 5 and SM Fig. A10). At the scale of the BAS it would still take thousands of years to completely flush the aquifer arsenic. Modelling also indicates where As concentration is low it will, in general, decrease over time or remain low for a long duration unless excessive localised pumping induces influx of As from adjacent regions.

4. Discussion

4.1 The SIHA hypothesis and aquifer evolution

We propose the SIHA (**S**ilt-clay layers **I**mpose **H**ierarchical groundwater flow patterns constraining **A**rsenic progression) hypothesis, which in combination with previous descriptions of the evolution of the BAS (e.g., Burgess *et al.*, 2010), explains how the naturally-determined distribution and depth penetration of As in Asian delta regions proceed as a consequence of geological development and topographic evolution.

The aquifer framework is made up of channel sands inter-bedded with laterally discontinuous layers of low permeability; these low permeability layers have an inter-leaved pattern of occurrence, which coupled with the basin surface topography, imposes and maintains a hierarchy of groundwater flow systems, from shallow to deep. The groundwater flow redistributes contaminants mobilised from shallow sources across the delta surface. Even under the marine high-stand conditions of the present time at the Bengal delta, the inter-leaved pattern of low permeability layers is sufficient for the subdued basin topography to maintain this hierarchy of groundwater flow systems. A hierarchy of flow systems may also have existed under the low stand conditions coincident with times of glacial maxima, determined by the inter-leaved pattern of silt-clay layers in the BAS at that time too. A similar inter-leaved pattern of occurrence of shale lenses in hydrocarbon reservoir sands is found to be important in analysing fluid flow and petroleum production (e.g. Haldorsen and Lake, 1984). However, the direct influence of an inter-leaved pattern of silt-clay layers on groundwater flow has not previously been described, although its influence, through imposing an effective hydraulic anisotropy, has been explored in many alluvial aquifers (e.g., Williamson *et al.*, 1990; Keating *et al.*, 2005) including the Bengal basin (Michael and Voss, 2009a; Hoque and Burgess, 2012).

Throughout the Pleistocene, Asian deltas (Woodroffe *et al.*, 2006) have experienced cyclical, glacioeustatically-controlled fluvio-deltaic sedimentation and erosion leading to aquifer frameworks made up of channel sands inter-bedded with floodplain silt-clay layers including a late-Pleistocene palaeosol clay horizon, and likely deeper remnants of earlier palaeosol horizons. Sedimentation and hence dispersion of solid phase As together with organic matter through fluvio-deltaic reworking to floodplains is widespread during sea-level high-stand stages and near nil during sea-level low-stands leading to discrete, episodic periods of As release to groundwater over the past 1 Ma. During transgressive to high-stand phases of the glacioeustatic cycles, arsenic available at crustal-ambient abundance from the source regions of the Asian rivers is widely and continuously dispersed across the floodplain surface, in association with iron oxy-hydroxide coating of sedimentary grains and together with organic matter (Meharg *et al.*, 2006). The penecontemporaneous release of As to groundwater is a consequence of sediment burial and anoxia. Arsenic penetrates the aquifer with groundwater recharge and re-incorporated to authigenic and/or suspended Fe-oxyhydroxides (Datta *et al.*, 2009) where oxidizing conditions are imposed at points of groundwater discharge (Fig. 6). Between regions of recharge and discharge, to depths dependant on topography and the disposition of low permeability layers, As remains in solution, except where groundwater encounters oxidized brown sediments capable of adsorbing As to ferric oxyhydroxides (McArthur *et al.*, 2004; Stollenwerk *et al.*, 2007). Repeated erosion of As-enriched sediments accumulating at regions of groundwater discharge enables further transportation as river sediment reworked (Polizzotto *et al.*, 2006) and re-deposited in the floodplains of lower reaches of the delta. These mechanisms provide the link between As flux in groundwater and with suspended/redeposited sediment in/from surface water as it is progressively transported through the basin.

Arsenic accumulation and land surface evolution can be linked with periods of slackening sea-level rise and development of high-stand conditions during Holocene time. During the late high-stand, reductions in basin accommodation space may result in an increased lateral dispersal, rather than vertical accretion, and the formation of laterally-interconnected and amalgamating channel and meander belt systems with poorly preserved flood-plain deposits (Shanley and McCabe, 1993). This phase is likely associated with the co-dispersal of As-bearing FeOOH and organic matter (Meharg *et al.*, 2006), leading to release of As to shallow groundwater in the deltaic environment. Studies *(e.g., Winkel et al., 2008)* show that high As concentration in groundwater is associated with deltaic deposits of repeated re-working across the Asian deltas. The process of deposition facilitates formation of less stable Fe(III) (hydr)oxide leading to an increase of As in the aqueous pool through reduction (Nickson *et al.*, 1998). In the Bengal Basin, prolonged and comparatively more recent deltaic processes *(Allison et al., 2003)* are found associated with the high arsenic region (SM Fig. A8), indicating the link between As release and deltaic processes.

4.2 Field observations reconciled by the SIHA hypothesis

The implications of the SIHA hypothesis are consistent with the results of individual field investigations (Fig. 4), and additionally reconcile a wide range of observations, some of which have previously appeared contradictory. SIHA determines the principal characteristics of the distribution of groundwater As in the Bengal basin, for which the occurrence of silt-clay forms a clear basis.

4.2.1 Spatial distribution and variability of groundwater arsenic

At a scale of 100s km, groundwater As concentrations are observed to be highest in the distal regions of the Bengal Basin (BGS/DPHE, 2001). At a scale of 0.01 km, adjacent wells separated by just a few meters may yield water from the same depth yet of contrasting high and low As content (Burgess *et al.*, 2002; McArthur *et al.*, 2004).

Previous explanations of the basin scale distribution have referred to sediments in the distal region being finer, and associated with a greater abundance of organic matter, thus the solid-phase As content is greater and conditions are more conducive to reduction of Fe-oxyhydroxides and release of As (BGS/DPHE, 2001; Ravenscroft *et al.*, 2005). In addition, the lower topographic (and hence hydraulic) gradients in the south of the Basin have been linked to a lower rate of groundwater flushing of the As source (Ravenscroft *et al.*, 2005; Shamsudduha *et al.*, 2009). The SIHA hypothesis additionally emphasises that sediments in the delta region, where the more recent deposition has occurred, have undergone less groundwater flushing.

At the scale of individual shallow well catchments, it has previously been suggested that the As source is depth-specific, yet discontinuous on account of sedimentological variability, and that the catchments of neighbouring tubewells may intersect the As source to different extents (Burgess *et al.*, 2002). Furthermore, the transience of As movement in a tubewell catchment may cause similarly positioned wells of different ages to yield groundwater of different As content, and it may take years or decades for an equilibrium As concentration to be established (Cuthbert *et al.*, 2002). The SIHA hypothesis adds that in the undisturbed, natural condition of the aquifer, instances of extreme spatial variability in groundwater As concentration are to be expected, associated with the juxtaposition of well-flushed and poorly-flushed zones of aquifer, and with the confluence of distinct groundwater flow pathways at regions of discharge.

4.2.2 Depth distribution of groundwater arsenic

Vertical profiles of groundwater As have been described at many individual sites of investigation (Harvey *et al.*, 2002; van Geen *et al.*, 2003b; McArthur *et al.*, 2004; Zheng *et al.*, 2005; Dhar *et al.*, 2008; Itai *et al.*, 2008; Libner, 2008; McArthur *et al.*, 2008; van Geen *et al.*, 2008a) as well as at a national level in Bangladesh (DPHE/BGS/MML, 1999; BGS/DPHE, 2001). The national level survey data show that wells >100 m in depth generally have low As content while shallow wells have a spatially variable range of As concentrations. The spatial variability is highest at the shallower level, and in general the As concentration forms a bell-shape distribution with a maximum at around 20 to 45 m bgl, reported to vary from region to region (Harvey *et al.*, 2006). At a basin-wide scale, excessive As is in general restricted to depths <100 m. At depths >150 m, fewer than 5% of wells exceed 10 μg/l, and in wells >200 m the As concentration is generally negligible (Bhattacharya *et al.*, 1997; BGS/DPHE, 2001; McArthur *et al.*, 2001; van Geen *et al.*, 2003b; Ravenscroft *et al.*, 2005) despite Fe(II) concentrations in groundwater being elevated in places (Zheng *et al.*, 2005;

Halim *et al.*, 2010). 'Anomalous' excessive groundwater As is nevertheless found in some places in deep groundwater >150 mbgl (Ravenscroft *et al.*, 2009; Burgess *et al.*, 2010; Mukherjee *et al.*, 2011), but appears to be entirely absent from groundwater at all depths within the oxidized Plio-Pleistocene inliers (BGS/DPHE, 2001; Ravenscroft *et al.*, 2001; van Geen *et al.*, 2003b; McArthur *et al.*, 2004; Zheng *et al.*, 2005). Site-specific observations (Harvey *et al.*, 2002; McArthur *et al.*, 2004; Dhar *et al.*, 2008) have shown that high As groundwater is constrained by silt-clay layers, which may be organic-rich (Fig. 7). Data from these individual research sites are compared to expectations from the SIHA hypothesis below, as a preliminary test of the hypothesis, despite the data having been collected for other purposes.

The basin-scale depth distributions have been related to geochemical stability at depth and the scarcity (McArthur *et al.*, 2004) or refactory nature (Harvey *et al.*, 2002) of organic carbon preventing mobilization of As to groundwater. Diagenetic pyrite may act as a mineralogical sink (Lowers *et al.*, 2007). In addition, groundwater penetrating more deeply in the aquifer has a greater likelihood, at least in some areas (Hoque *et al.*, 2014), of passing through oxidized sediments (at some depth), in which As would be sequestered to Fe-oxyhdroxides (Swartz *et al.*, 2004; Stollenwerk *et al.*, 2007; Radloff *et al.*, 2011). Alternatively, it has been suggested (Zheng *et al.*, 2005; Fendorf *et al.*, 2010) that labile As within the deep aquifer sediment has been depleted, but reduction of Fe oxides continues. Others have proposed that arsenic was effectively flushed from the deeper parts of the aquifer during pre-existing sea-level low stands (BGS/DPHE, 2001; Ravenscroft *et al.*, 2005). In explanation of the 'anomalous' deep groundwater As, thick Pleistocene channel sands of the proto-Ganges have been suggested to allow deep penetration of groundwater As (Ravenscroft *et al.*, 2009). In addition, excessive groundwater pumping from deeper regions of the BAS may cause hydraulic short-circuiting of the shallow flow system (Michael and Voss, 2008; Burgess *et al.*, 2010; Mukherjee *et al.*, 2011) as has been proposed for the Red River Delta aquifer, Vietnam (Winkel *et al.*, 2011).

In relation to the Plio-Pleistocene inliers, sorption on Fe oxy-hydroxides present in these oxidized sediments has been posited to prevent the mobilization of As to groundwater (Ravenscroft *et al.*, 2001; McArthur *et al.*, 2004; Stollenwerk *et al.*, 2007). A hydraulic explanation proposes that repeated flushing of the Plio-Pleistocene tracts by groundwater during the Quaternary has removed any As previously present (Ravenscroft *et al.*, 2001; Ravenscroft *et al.*, 2005).

At a site-specific scale, peat or organic matter associated with silt-clay has been suggested to provide the reducing capacity of the aquifer sediments (Ravenscroft *et al.*, 2001; McArthur *et al.*, 2004), but this explanation is inconsistent with the generally lower values of dissolved As observed in reality below the organic-rich silt-clay layers (Fig. 7a).

SIHA provides an over-arching explanation of the general absence of excessive groundwater As at depth in the aquifer (case I of Fig. 4), demonstrating that the depth of As occurrence is constrained by the depth of penetration of groundwater flow, which is limited by the topographic relief and inter-leaved occurrence of silt-clay layers in BAS.

By the SIHA hypothesis, natural ‘anomalous’ occurrences of As in groundwater at depth >100 mbgl are due to the local-regional absence of silt-clay layers, enabling deeper penetration of the shallow groundwater flow system (case II of Fig. 4). There is a pattern to the distribution of high As in deep groundwater which follows palaeo-channels of the Ganges in the west (Sarkar *et al.*, 2009) and centre (Umitsu, 1993) and a palaeo-channel of the river Gumti in the east (Hoque *et al.*, 2011). Along the palaeo-channels, deposition of sand predominated during the early stage of Holocene delta formation with a sedimentation rate ca. 10 times higher than the present (Sarkar *et al.*, 2009). If the rate of sedimentation was too great for groundwater to flush palaeo-channel deposits, As-rich groundwater could have also been hydraulically trapped. Moreover, stagnation points (Tóth, 2009) in the palaeo-groundwater flow system, where As could not be flushed, are also possible.

The SIHA hypothesis would allow Plio-Pleistocene sediments originally to have contained As-bearing groundwater, within the topmost ca 100 m. However the present-day remnant Plio-Pleistocene tracts, inliers surrounded by Holocene floodplain sequences, have experienced many phases of groundwater flushing under Quaternary sea level low-stands, under which conditions the sediments would have been oxidised (Davies, 1995; Hoque *et al.*, 2012) and As originally present would have been removed or immobilised. Arsenic subsequently invading from an adjacent shallow groundwater flow system would be immobilized by adsorption in these oxidized sediments.

At local-scale, SIHA shows that groundwater flow is channelled above the shallow silt-clay layers, leading to a relative concentration of dissolved As above the silt-clay layer (case IV of

Fig. 4), and relative absence below and hence As-bearing groundwater (Cases III to VI) is commonly constrained to the uppermost 50 to 100 m.

Three well-defined site-specific vertical profiles of groundwater As, and the corresponding lithological profiles (Harvey *et al.*, 2002; McArthur *et al.*, 2004; Zheng *et al.*, 2005; Dhar *et al.*, 2008), separately invoking different sources and pathways of organic carbon, act as an empirical demonstration of SIHA. In each case an As maximum occurs above the locally present silt-clay layer, consistent with SIHA as a unifying theme (Fig. 7a). In addition, the regional restriction of elevated groundwater As concentration in southern Bangladesh to depths shallower than 140 m coincides with the abundance of silt-clay layers, which demonstrate the attainment of inter-leaved layering of silt-clay by that depth (Figs. 3, and Fig. 7b).

4.2.3 Geomorphological relationships

Elevated As concentrations in shallow groundwater of BAS have been associated with low topographic slope (Ravenscroft *et al.*, 2005; Shamsudduha *et al.*, 2009). Beneath surficial sands, often of slight ground surface elevation, groundwater has been reported to have low As concentration, whereas regions of surficial silt-clays are underlain by high As groundwater (Aziz *et al.*, 2008; Weinman *et al.*, 2008; Hoque *et al.*, 2009).

Low topographic slope has by implication been associated with low hydraulic gradient in the aquifer, and hence slower rate of groundwater flushing (Ravenscroft *et al.*, 2005; Shamsudduha *et al.*, 2009). Surficial sands are more vigorously flushed by recharging groundwater (Aziz *et al.*, 2008; Weinman *et al.*, 2008; Hoque *et al.*, 2009). ‘Rapid’ recharge of surficial sands may locally inhibit release of As possibly through the supply of oxygen, nitrate or sulphate (Aziz *et al.*, 2008; Neumann *et al.*, 2010). High As concentration in groundwater at shallow depth beneath fine-grained sediments has been attributed to co-deposition of organic matter with As-bearing Fe oxides (Postma *et al.*, 2007; Polizzotto *et al.*, 2008) and lesser groundwater flux through the fine grained sediments (Aziz *et al.*, 2008; Weinman *et al.*, 2008; Hoque *et al.*, 2009). Also, at this local scale near-surface sediments in the down-gradient of groundwater flow i.e. wetlands are younger compared to recharge zone, therefore likely to be enriched in iron, arsenic and reactive organic matters (Postma *et al.*, 2012) leading to release of arsenic to aqueous pool.

SIHA, in associating low topographic slope with minimal groundwater flow, is consistent with these previous explanations. In addition, SIHA identifies the significance of shallow silt-clay layers, beneath which groundwater stagnates and elevated groundwater As persists, particularly in regions of topographic depression (Fig. 4, Case IV). In addition, differential flushing is a result of groundwater flow which in turn is determined by surface topography and the distribution of low permeability layers; groundwater flushes the elevated surficial sandy areas, carrying As towards regions of local groundwater discharge, where fine predominated wetland sediments are located.

4.2.4 Relationships with groundwater age

Arsenic content has been considered in relation to the age of shallow groundwater, with the more modern shallow groundwater having a lower As content than older groundwater (Klump *et al.*, 2006; Stute *et al.*, 2007). This has been attributed to modern groundwater being at sites of active recharge and hence more vigorous groundwater flow, leading to removal of labile As (Stute *et al.*, 2007). SIHA is consistent with this explanation (cases V of Fig 4), and can additionally explain the juxtaposition of older and younger groundwater as an expected outcome (case VI of Fig. 4), when it has previously been considered paradoxical (Klump *et al.*, 2006).

4.2.5 Relationship with recharge sources

There has been a vigorous debate concerning the role of irrigation in drawing carbon from irrigation return flow (Harvey *et al.*, 2002; Aggarwal *et al.*, 2003; Harvey *et al.*, 2003; van Geen *et al.*, 2003a) or from constructed ponds (Sengupta *et al.*, 2008; Neumann *et al.*, 2010; Datta *et al.*, 2011; McArthur *et al.*, 2011b; Neumann *et al.*, 2011) to fuel As mobilisation.

At sites of irrigation pumping in southern Bangladesh, mixing of young and older groundwater has been recorded at ~30 m bgl, where groundwater As is at a maximum in the vertical profile (Harvey *et al.*, 2002; Klump *et al.*, 2006). It has been suggested that infiltrating irrigation water carries young organic matter to that depth (Harvey *et al.*, 2002) driving reduction of the aquifer sediments and hence releasing As to groundwater. Alternatively, advective convergence of groundwater flow is related to As release, but the irrigation water is not itself the driver (Klump *et al.*, 2006). Controversy has surrounded the alternative sources and pathways of organic matter (Harvey *et al.*, 2002; McArthur *et al.*, 2004; Neumann *et al.*, 2010; McArthur *et al.*, 2011b; Neumann *et al.*, 2011), the precise locations of As release (McArthur *et al.*, 2004; Klump *et al.*, 2006; Polizzotto *et al.*, 2008), and the significance of local patterns of groundwater flow (Harvey *et al.*, 2002; McArthur *et al.*, 2008; Polizzotto *et al.*, 2008; Desbarats *et al.*, 2014).

Common to the conflicting views on the processes, reactants and their flow pathways leading to As mobilisation in shallow groundwater in BAS is the acceptance that mobilisation occurs within the uppermost 50 m of floodplain sediments. This consensus view of the As source is all that is required by the SIHA hypothesis, hence the validity of SIHA is independent of the variety of OM sources and pathways proposed, and they need not be mutually exclusive. Sedimentary OM may be augmented and/or supplanted by paddy-derived OM as the driver to maintain the aquifer reducing condition. However, groundwater flow pattern suggests that arsenic generally has been always released from the shallower subsurface (ca. <10-20 m), most likely from chemically less altered near-surface juvenile sediments (Postma *et al.*, 2012). The maximum depth of penetration of the shallow flow system is coincident with the dissolved As maximum (cases III and IV of Fig. 4), below which occurs the deeper, older groundwater flow of regional extent. SIHA explains how groundwater flow redistributes As such that dissolved As is at a maximum around the base of the shallow flow system.

4.3 The future of arsenic in the BAS groundwater systems

4.3.1 Long term evolution and fate of As in deltaic aquifers

The interplay of basin subsidence and eustatic sea level changes determines the development of the aquifer systems, and causes the delta locations to migrate alternately towards the ocean and towards the land. Penecontemporaneous groundwater flow and delta reworking have operated to keep As at relatively shallow levels of the aquifer in the deltaic region over much of Quaternary time (Fig. 6). Current conditions may have been initiated following delta development during the last episode of eustatic transgression in the early Holocene. In addition to regional delta-building, the landscape is actively modified on a local scale in these settings, with consequent small scale changes to the shallow, local groundwater flow systems. Release and flushing of As thereby occur on a geological time scale. However, if groundwater pumping occurs, the flow system is modified and there is concern that rapid transport of As may be induced (Polya and Charlet, 2009; Burgess *et al.*, 2010; McArthur *et al.*, 2010). Tube-well age as a proxy for pumping time has been applied to suggest that As concentration in general increases with time at pumping wells (Ravenscroft *et al.*, 2005; Burgess *et al.*, 2007). However, the older, deeper, wells may be concentrated in southern Bangladesh where groundwater As concentrations are generally higher. Moreover, older wells may have been installed in sands above silt-clay layers because of the difficulty of drilling the silt-clay, and SIHA shows this to be one of the contexts for elevated As (case IV of Fig. 4). Site-specific 3-year monitoring data for shallow groundwater has not identified any temporal changes in central Bangladesh (Dhar *et al.*, 2011). Deep groundwater consecutively re-sampled over a 13 year period at 46 sites across southern Bangladesh also shows no indication of changes in As concentration, or indeed overall chemistry, even though deep pumping has increased substantially in the region over this time (Ravenscroft *et al.*, 2013). Therefore it is difficult to be conclusive about how As concentration will change over time at pumping tube-wells.

The simple 2D model, a conceptual representation of the aquifer, does not capture the full extent of geological heterogeneity, and hence must underestimate the timescale of groundwater circulation. Sorption, which would further retard the progression of As in the aquifer at basin scale (Radloff *et al.*, 2011; van Geen *et al.*, 2013) is not included. The SIHA hypothesis does not address future predictions at individual tubewell catchments, which are subject to major limitations due to uncertainty in the extent of geochemical dis-equilibrium at this scale. The long duration (ca. 100 ka) of successive lowstand sea-level conditions may nevertheless be sufficient for the complete flushing of groundwater As and its incorporation into solid-phases.

4.3.2 Impact of pumping on the groundwater As distribution

Where As concentration is low at a shallow tube-well it should decrease with time because the well is located in a favourable zone where As has naturally been flushed away over time. Pumping (for irrigation or other purposes) should facilitate the flushing further. Where As concentration is low but the tube-well is screened between a high-As region (local groundwater discharge area, or areas covered by silt-clay layers) and an irrigation pumping well, the As concentration in the tube-well discharge may increase with time (Cuthbert *et al.*, 2002) as observed at Araihazar in Bangladesh (Dhar *et al.*, 2008). The increase should be slow however because groundwater will flow to the tube-well predominantly through the more permeable sandy zones of the aquifer which will naturally allow a higher flow rate containing less As. Therefore it is considered according to the SIHA hypothesis presented here that As concentration in tube-wells with low As concentration will, in general, decrease over time or remain low for a long duration. Understanding the local details of the flow-system would help in identify the wells which might be under greater threat due to irrigation pumping. Note that a prevalent belief has been that As concentration will increase in most tube-wells with time (JICA, 2002; Ravenscroft *et al.*, 2005; Burgess *et al.*, 2007). Currently, >70% of shallow tube-wells are found to contain As below <50 μg/l, the Bangladesh regulatory limit (BGS/DPHE, 2001; Ravenscroft *et al.*, 2001) and some of these could be used for As-safe water for a long duration.

5. Conclusions

The occurrence of As in the Bengal Aquifer System reflects release from younger near-surface sediments of the aquifer, as the anoxia developed after the sedimentation and burial, and redistribution by groundwater flow, moderated by silt-clay layering in the basin sediments, as described by the SIHA hypothesis. Redistribution by groundwater under reducing conditions is linked over a time-scale of tens of thousands of years to transport as a sorbed phase under the oxidizing environment of fluvially suspended sediment and bed-load. In this manner, arsenic migrates in multiple consecutive stages from the upper reaches of the basin to the marine environment. The SIHA hypothesis is a mechanistic explanation which suggests that groundwater As has been restricted to the shallow levels of the Bengal Aquifer System since the early stages of basin/aquifer development, and will remain so for as long as high-stand sedimentation continues in the basin. The concept of silt-clay inter-leaving should be incorporated into the predictive modelling of As concentration at local and/or basin scale, for better management of the As crisis in the region. Deeper levels of the aquifer should remain As-free, unless As is locally re-distributed by excessive pumping. Assessments of the security of deep groundwater abstraction should attempt to make explicit reference to the presence of low permeability silt-clay layers, rather than effective averaged hydraulic properties, as only the explicit presence of silt-clay layers enables groundwater flow pathways, under natural or pumping conditions, to be represented in sufficient detail for consideration of arsenic transport.

Supporting Information

Attached

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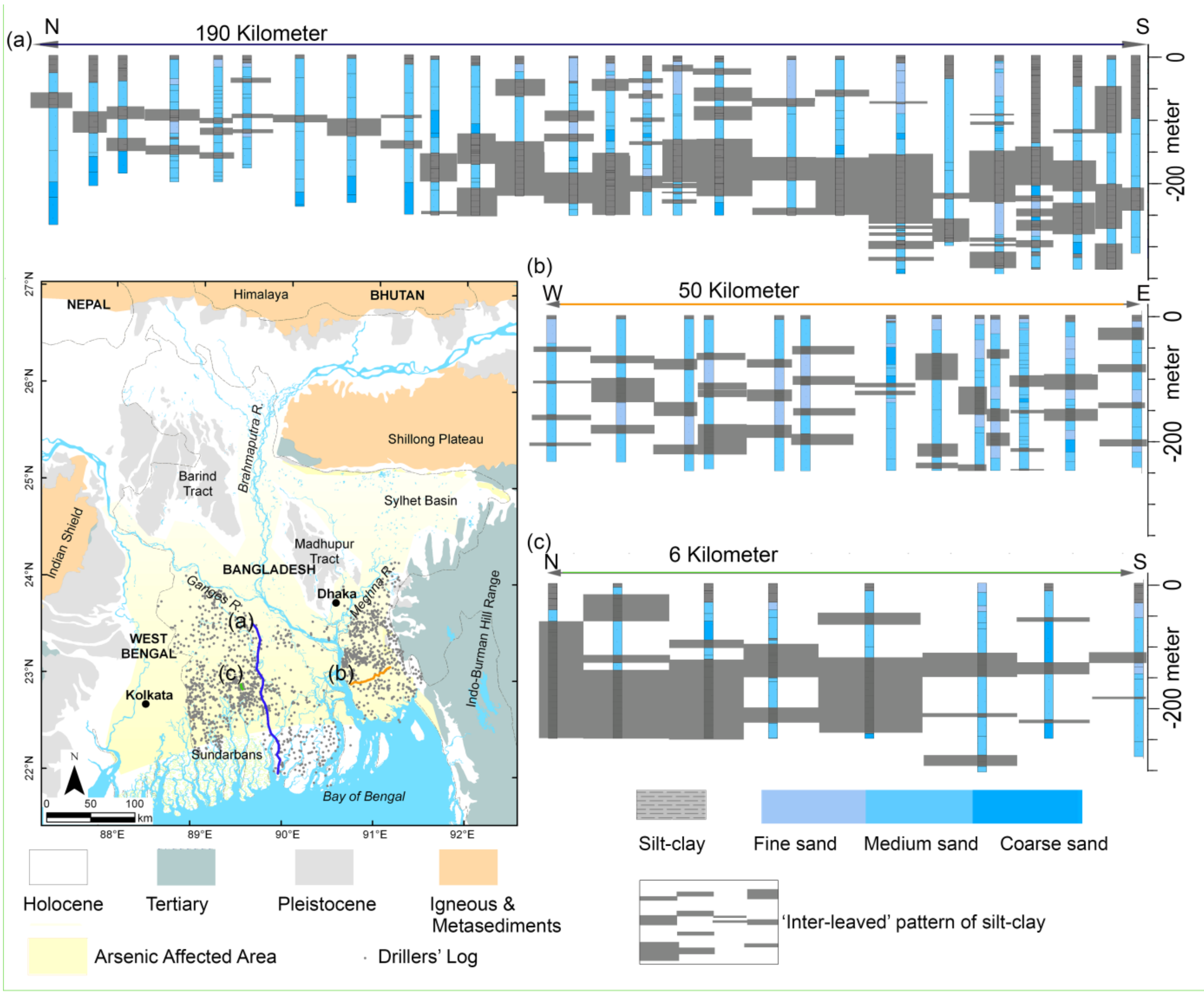

Figure 1: Lithological variability within the Bengal Aquifer System (a)-(c) cross-sections (as indicated on the map) of lithological logs. Discontinuous silt-clay layers interpolated mid-way to adjacent logs form a continuous layer in places, demonstrating the 'inter-leaved' pattern of silt-clay layering. Note the difference in horizontal scale of the cross-sections.

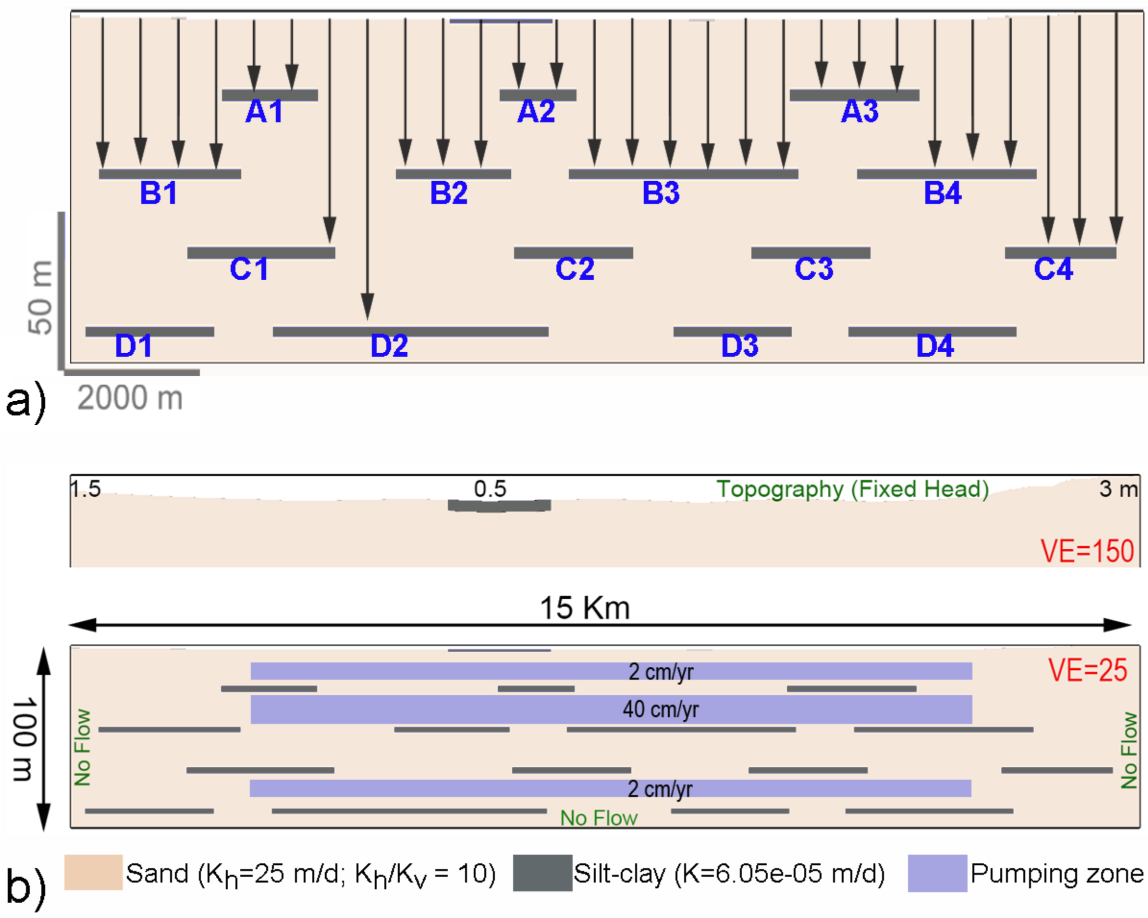

Figure 2: Conceptualisation of aquifer framework and model development. a) illustrative aquifer framework based on fig. 1, composed of sand with inter-leaved silt-clay layers. In the diagram gray horizontal discontinuous blocks (A-D) are silt-clay layers, embedded in sands. On the left, silt-clay lenses A to D form the uppermost inter-leaved layer, while on the right the lenses A to C form the uppermost inter-leaved layer. Arrows indicate the variation of depth of inter-leaved from left to right from the surface or from the base of surface silt-clay layer (note surface silt-clay layer above A2). b) Model development was based on the conceptualisation. The model is 15 km in width, 100 m thick. The depth and extent of groundwater abstractions are indicated in light blue rectangles. Topography is shown in the upper illustration. (VE: vertical exaggeration).

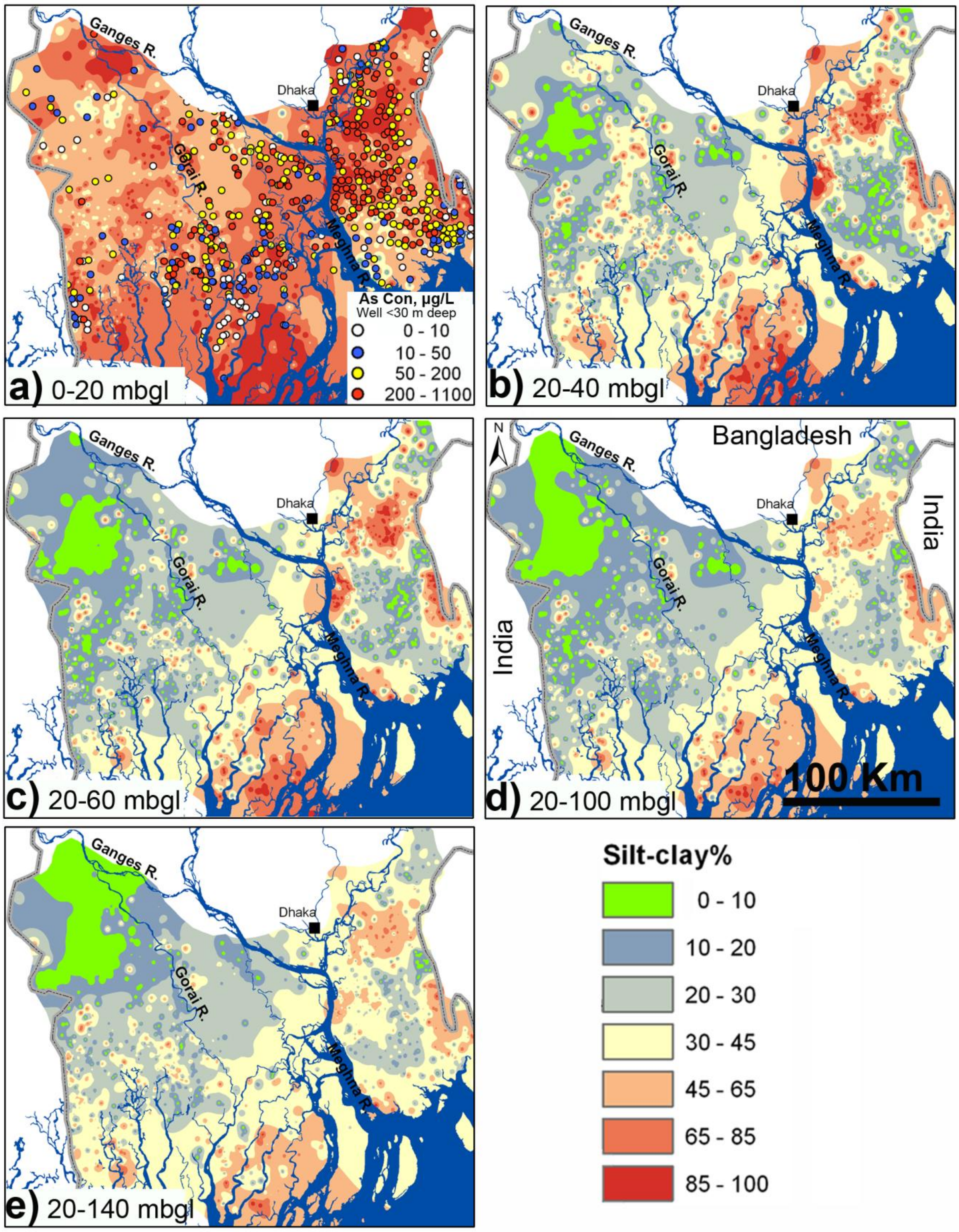

Figure 3: Cumulative thickness of silt-clay in southern Bangladesh. a) Silt-clay fraction in top 20 m and As concentration (BGS/DPHE, 2001) for wells <30 m are shown. b) to e) Silt-clay fraction is indicated for increasing thickness of sediment from 20 mbgl (20–40 m, 20–60 m, 20–100 m, 20–140 m); by 100 m most of southern part of the basin has a silt-clay fraction >10%, and an 'inter-leaved' pattern of silt-clay layers is likely to exist by that depth. Note that the interpolation was carried out using linear Kriging.

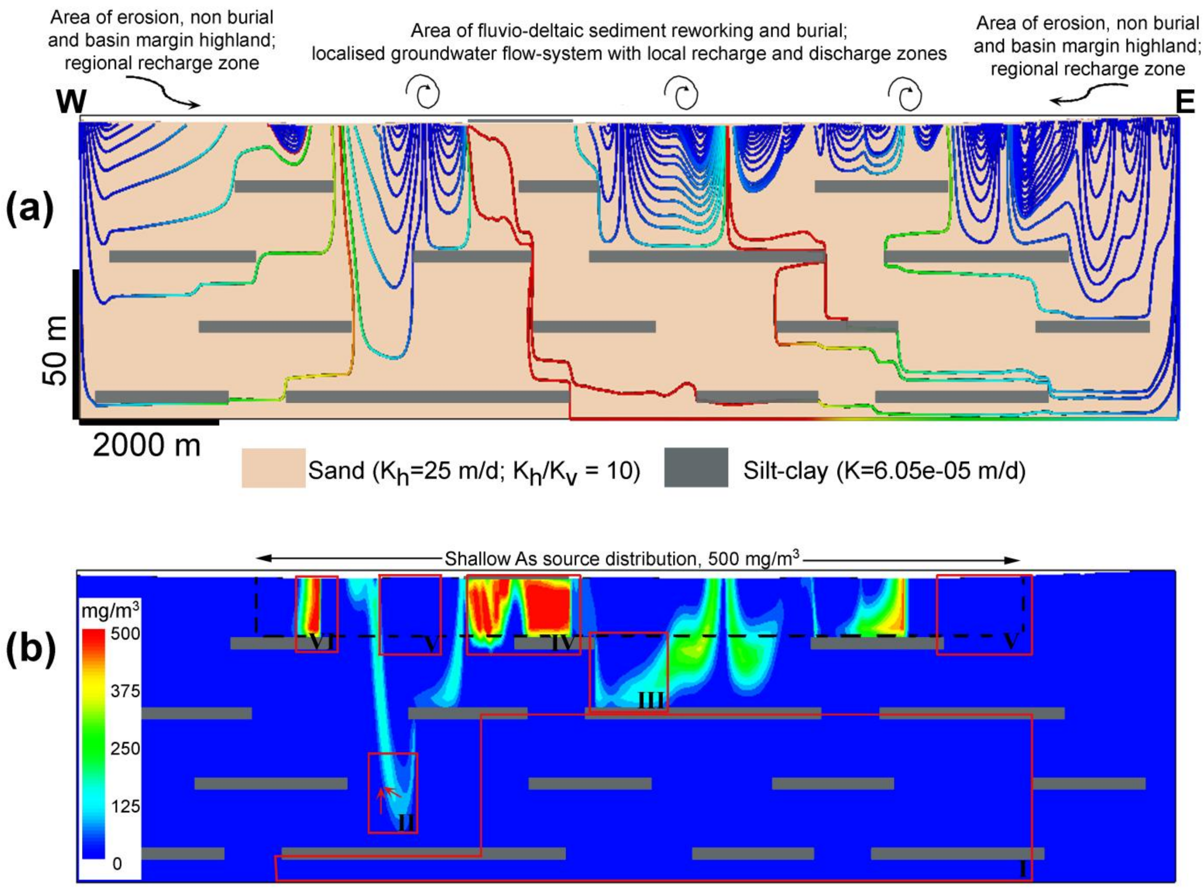

Figure 4: Groundwater flow and redistribution of dissolved-phase arsenic. (a) Geological framework of the 2D model, and simulation of groundwater flow lines. Groundwater flow from regions of recharge to discharge is indicated as flow lines grading from blue (0 years) to red (500 years) at the scale of the model; (b) Simulated As concentration in groundwater, resulting from advective redistribution over a 60 year modelled period (i.e. ca >1000 years at basin scale) from a source region initially containing 500 mg/m3 (~500 µg/L) As in the top 20 m (indicated by dashed outline). Note that the model reproduces the variety of contrasting patterns of spatial and depth distribution of groundwater As which have individually been described from field observation (DPHE, 2001; Harvey et al., 2002; McArthur et al., 2004; Berg et al., 2008; Dhar et al., 2008) (i.e. cases I to VI as outlined in the text). The twinned arrows in box II illustrate one example of older and younger water in close juxtaposition.

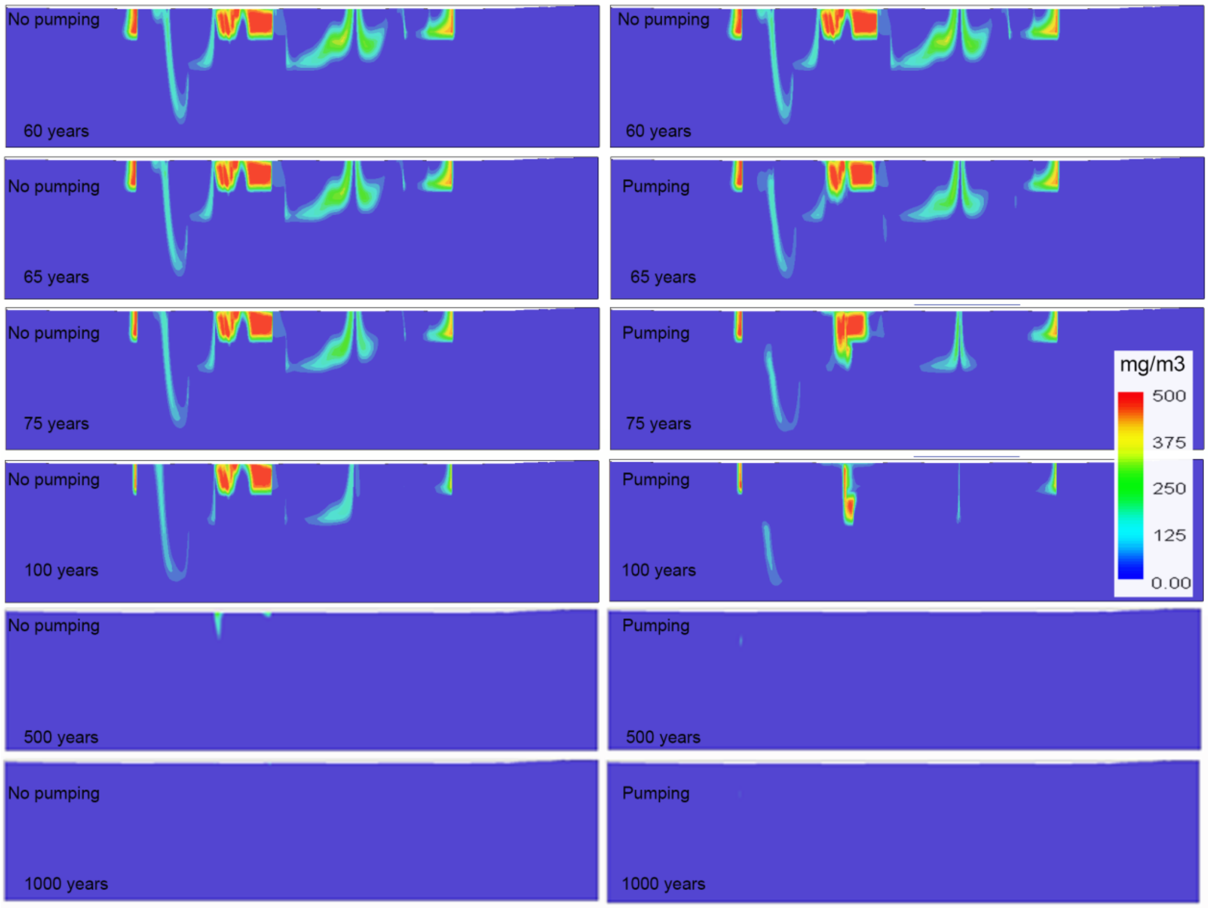

Figure 5: Impact of pumping on groundwater As distribution. Modelling indicates that the pattern of arsenic re-distribution and the scale of aquifer flushing have, regionally, been little affected by groundwater pumping.

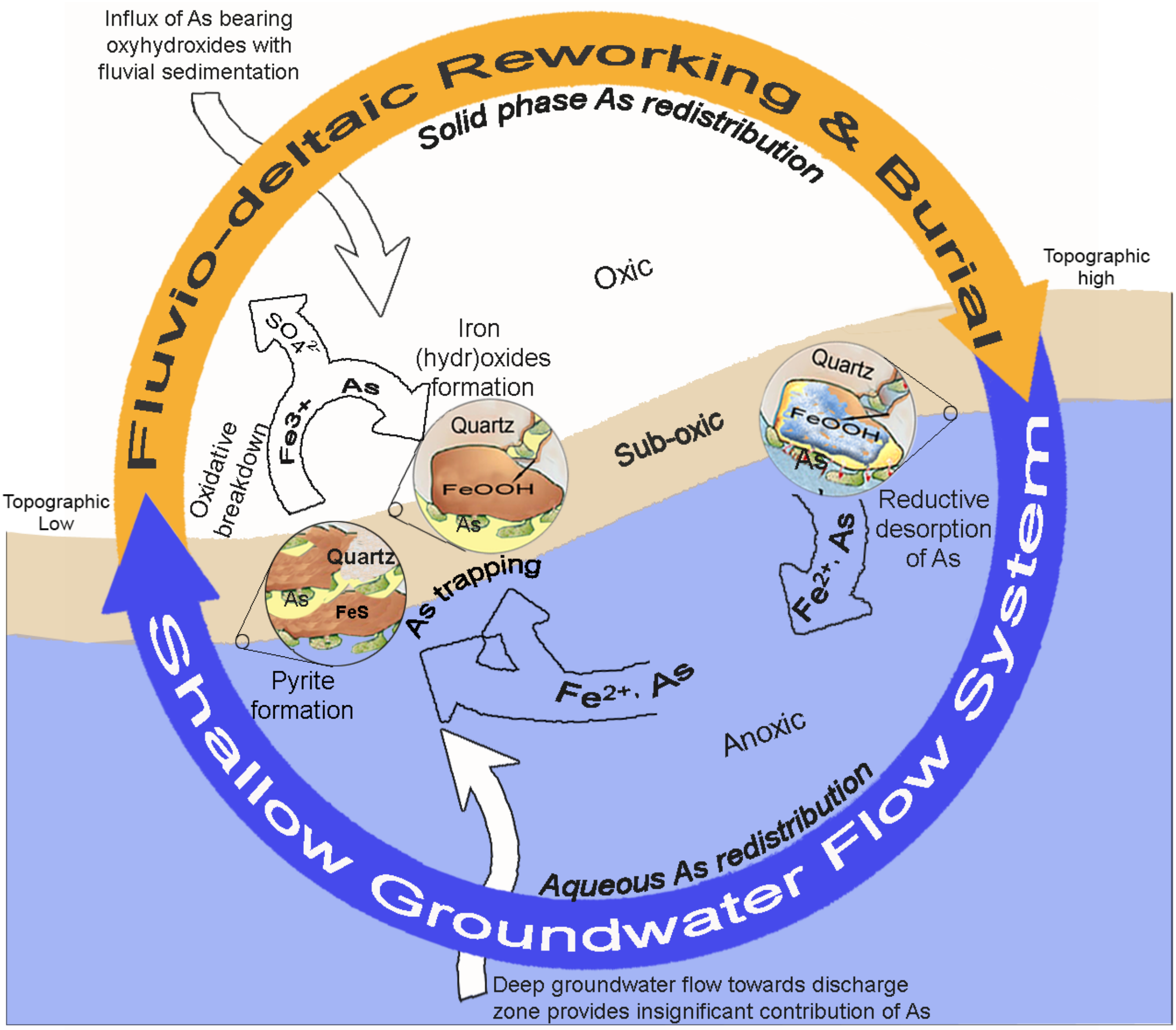

Figure 6: Geological cyclicity of arsenic in a fluvio-deltaic system. In this diagram changes of arsenic phases (aqueous-solid-aqueous) over geological time along a landscape transect (topographic high to low) is shown. Arsenic is released to groundwater in the shallow sub-surface, as reducing conditions are imposed following sediment burial. Dissolved As is conveyed within the groundwater flow field (see Figure 4) to regions of groundwater discharge, where As is sequestered by Fe(III)oxides/metastable pyrite. Hence As is re-incorporated into mineral/solid phases associated with suspended sediment and/or shallow sediment, which may be reworked and re-deposited in the floodplain locally or in a more distal position. Under suitable conditions As may then be released again into the groundwater flow-field (see text).

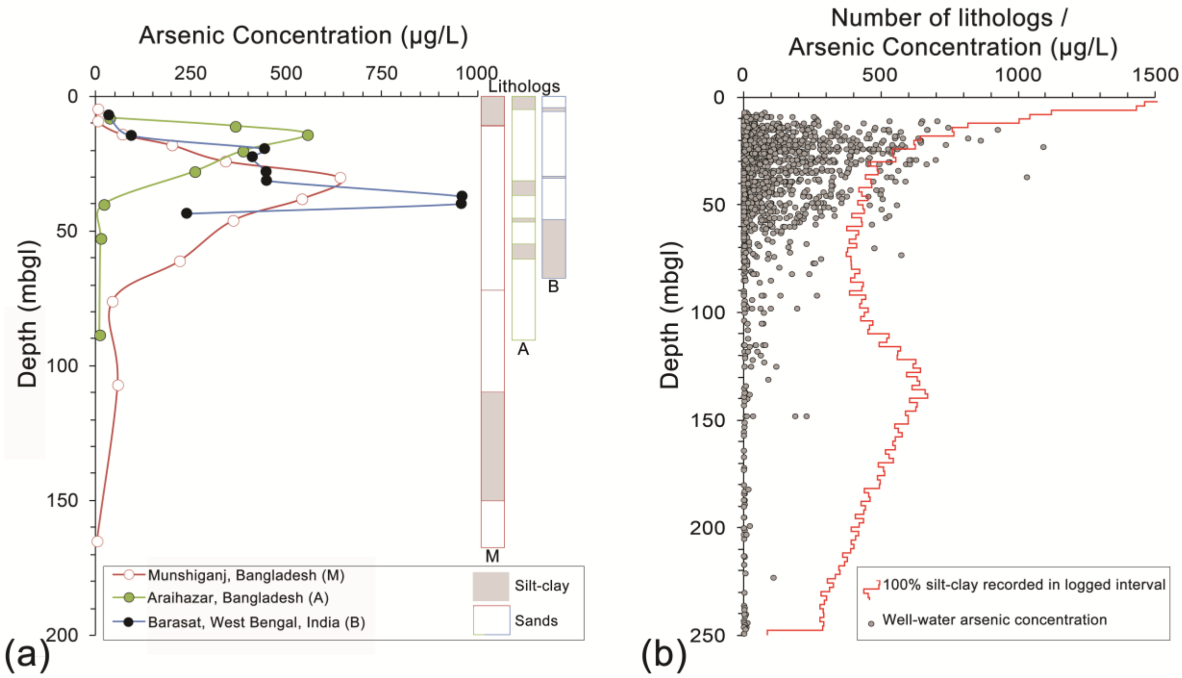

Figure 7: Local-scale and regional-scale field evidence consistent with the SIHA hypothesis. (a) Well-defined vertical profiles of pore water As from Bangladesh and West Bengal indicate that peak/high concentrations of As are constrained by the position of silt-clay layers (data from Harvey et al., 2002; McArthur et al., 2004; van Geen et al., 2004; Dhar et al., 2008); (b) Elevated groundwater As concentrations (data from, DPHE, 2001) in southern Bangladesh are regionally restricted to depths shallower than ca. 100 mbgl, consistent with the rise in abundance of silt-clay layers at that depth, and most of the high concentration data are confined within 100 mbgl by which depth an inter-leaved pattern of silt-clay layer is attained in most part of the basin (Fig. 3).