A Review of Arsenic and Its Impacts in Groundwater of the Ganges-Brahmaputra-Meghna Delta, Bangladesh

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EIA statement

Arsenic in drinking water is the single most important environmental issue facing Bangladesh and dominates the list of stress factors affecting health, livelihoods and the ecosystem of the Delta region. This paper provides a background as well as an update to the arsenic problem relating to the impacts of climatic and hydrological change addressed in the ESPA Deltas project. The Government of Bangladesh adopted a National Arsenic Policy and Mitigation Action Plan in 2004 for providing arsenic safe water to all the exposed population. There is as yet no national monitoring program in place, although current statistics show that use of deep groundwater (below 150m) is the main source of arsenic mitigation.

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A Review of Arsenic and Its Impacts in Groundwater of the Ganges-Brahmaputra-Meghna Delta, Bangladesh

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Arsenic in drinking water is the single most important environmental issue facing Bangladesh; between 35 and 77 million of its 156 million inhabitants are considered to be at risk from drinking As-contaminated water. This dominates the list of stress factors affecting health, livelihoods and the ecosystem of the Delta region. There is a vast literature on the subject so this review provides a filter of the more important information available on the topic. The arsenic problem arises from the move in the 1980s and 1990s by international agencies to construct tube wells as a source of water free of pathogens, groundwater usually considered a safe source. Since arsenic was not measured during routine chemical analysis and also is difficult to measure at low concentrations it was not until the late1990s that the widespread natural anomaly of high arsenic was discovered and confirmed. The problem was exacerbated by the fact that the medical evidence of arsenicosis only appears slowly. The problem arises in delta regions because of the young age of the sediments deposited by the GBM river system. The sediments contain minerals such as biotite which undergo slow "diagenetic" reactions as the sediments become compacted, and which, under the reducing conditions of the groundwater, release in the form of toxic As^{3+}. The problem is restricted to sediments of Holocene age and groundwater of a certain depth (mainly 30-150m), coinciding with the optimum well depth. The problem is most serious in a belt across southern Bangladesh, but within 50m of the coast the problem is only minor because of use of deep groundwater; salinity in shallow groundwater here is the main issue for drinking water. The Government of Bangladesh adopted a National Arsenic Policy and Mitigation Action Plan in 2004 for providing arsenic safe water to all the exposed population, to provide medical care for those who have visible symptoms of arsenicosis. There is as yet no national monitoring program in place. Various mitigation strategies have been tested, but generally the numerous small scale technological remedies have proved unworkable at village level. The current statistics show that use of deep groundwater (below 150m) is the main source of arsenic mitigation over most of the arsenic affected areas as well as rainwater harvesting in certain location..

Introduction

Arsenic contamination in drinking water remains the single most important environmental issue facing Bangladesh and the Delta region and even at the global scale, probably the most serious in terms of the numbers of people affected (upwards of 30M). It has been cited variously as a disaster[1] and as mass poisoning[2,3]. This review focuses on the arsenic issue within Bangladesh and places the problem within a global context especially of areas with similar geology (low-lying deltaic sediments of Quaternary age). It also recognises that arsenic can be a natural baseline problem in several other types of aquifer and is a problem exacerbated by human activity, especially mining, although this aspect is not dealt with in the review.

The ESPA DELTAs Project entitled 'Assessing health, livelihoods and ecosytems, poverty alleviation in populous deltas' aims to provide policy makers with the knowledge and tools to enable them to evaluate the effects of policy decisions on people's livelihoods. This is being undertaken by a multidisciplinary and multi-national team of policy analysts, social and natural scientists and engineers. Collectively they will use a participatory approach to create a holistic approach to formally evaluating ecosystem services and poverty in the context of the wide range of changes that are occurring. These changes include subsidence and sea level rise, land degradation and population pressure in delta regions. The approach is being developed, tested and applied in coastal Bangladesh and also tested conceptually in two other populous deltas in India. Arsenic is of key concern to people in Bangladesh and this review aims to provide a baseline set of knowledge from which to review likely future changes in climate, land use, sea level and population in the deltas region of Bangladesh

The Ecosystem Services (ES) of river deltas often support high population densities, estimated at over 500 million people globally, with particular concentrations in South, South-East and East Asia and Africa. Further, a large proportion of delta populations experience extremes of poverty and are highly vulnerable to the environmental and ecological stress and degradation that is occurring.

Rural livelihoods are inextricably linked with the natural ecosystems and low income farmers are highly vulnerable to changes in ecosystem services. Their health, wellbeing and financial security are under threat from many directions such as unreliable supplies of clean water, increasing salinisation of soils and arsenic-contaminated groundwater, while in the longer term they are threatened by subsidence and sea-level rise. This study will contribute to the understanding of this present vulnerability and help the people who live there to make more informed choices about how best to reduce this vulnerability.

Within the terms of reference of the ESPA Deltas Project this review of arsenic and related elements focuses on the occurrence, the security of water quality, arsenic in the local environment, identifying occurrences of safe drinking water (especially groundwater) as well as arsenic mitigation in affected areas. There is already a very extensive literature on the subject of arsenic contamination, probably the most widely studied of all pollution issues, and the purpose of this paper is to act as a filter of the extensive material available which is of relevance to the current research topic.

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immediate and medium-term health impacts in affected areas, but the widespread introduction of high-arsenic water into the environment through irrigation can have secondary effects on food and fodder, the ecosystem and also on the economy.

As regards the specific concerns of the ESPA Project, it is the immediate coastal region of Bangladesh with very young sediments, that are of interest, where arsenic occurs extensively in the shallow aquifers. However, potable water is mainly extracted in the coastal region from older sediments tapped by deep tube wells in excess of 150m depth which is arsenic safe in almost all cases. In the coastal regions there is less dependency on shallow wells in young sediments where the arsenic problem is widespread. In these areas the main water quality problem is salinity caused by flooding and also saline intrusion caused by excessive pumping.

Global occurrence of groundwater arsenic - the specific problem of delta regions

Investigations worldwide (Fig.1) have now revealed the scale of the arsenic health problem occurring in groundwaters[5]. Some of the most common locations with extensive occurrences of high arsenic are alluvial sediments and deltaic areas as well as inland deltas and sedimentary basins in inland areas (mainly in semi-arid areas).The former occur largely in reducing sediments and the latter under oxidising groundwater conditions.

Fig.1. Distribution of documented world problems with As in groundwater in major aquifers as well as water and environmental problems related to mining and geothermal sources. By far the most serious problems in terms of those affected occur in Quaternary delta regions in south east Asia[5]

Geologically young (Quaternary) aquifers are particularly prone to developing and preserving high-arsenic groundwater. Alluvial and delta plains with recognised groundwater arsenic problems include the Bengal Basin (Bangladesh, India), Mekong Valley (Cambodia, Laos, Vietnam), Red River Delta (Vietnam and the Yellow River Plain (China). These major deltas derive sediments from tectonically active areas of the Himalayan region where geologically-rapid uplift leads readily to physical and chemical erosion of fresh bedrock. The bedrock often consists of granitic and other igneous rocks containing unweathered rock forming minerals such as biotite and other mafic (iron-rich) minerals and feldspar. Such minerals formed at high temperatures and are transported rapidly by the GBM and other rivers to the delta regions. Deltas form rapidly and the newly derived sediments quickly become buried. In the Dhaka region for example, using radiocarbon dating evidence from wood buried with the sediments, some 60m of deposits have accumulated in 60 000 yr. Under the newly-created, low temperature sedimentary environments the transported minerals are very reactive and undergo "freshwater diagenesis" during which new, more stable (secondary) minerals including clays and oxides will form and in the process release impurities not required for their stabilisation. These include various trace elements including arsenic which would have been included in minerals at high temperatures, in sulphide minerals (eg pyrite, FeS_2), or within primary mafic minerals such as biotite. The specific conditions relating to the GBM are further described below.

The nature and history of the arsenic problem

Arsenic has been used therapeutically and also as a poison and its toxicity has been recognised for centuries [6,7]. Geochemists have understood the geochemical cycle of arsenic and its potential toxicity in drinking water for half a century[8]. However, the widespread extent of its environmental distribution and occurrence of an arsenic problem is a recent phenomenon, a product of rapid global development in the late 20th century. One of the first cases recognising arsenic toxicity in water came from studies of mining areas in Taiwan[9]

The first recognitions of an arsenic problem in the GMB region came in 1983 from West Bengal[10] and in 1993 from Bangladesh[11].The earliest cases of arsenic-induced skin lesions in the sub-continent were identified in Kolkata, India[12]; the patients seen were from West Bengal but by 1987 several patients had already been identified who came from neighbouring Bangladesh. The contamination of groundwater by arsenic in Bangladesh was first confirmed by the Department of Public Health Engineering (DPHE) in Chapai Nawabganj in late 1993 following reports of extensive contamination in the adjoining area of West Bengal.

One of the main reasons for the slow recognition of the scale of the problem and its environmental significance has been the issue of its chemical analysis at the μg/l level, which may still present problems[13]. Natural baseline concentrations in groundwater are low in many geological environments due its low geochemical abundance. In many major well-developed aquifers which have been used for water supply and monitored for decades, arsenic was rarely seen as a problem. In a study of 23 European aquifers in a range of lithologies[14], the overall median As concentration was only 0.5 μg/l; only in three minor aquifers did the median reach a value of 6 μg/l. The global scale of the problem became an issue only when improved analytical procedures were applied to detailed water quality investigations in Recent and Quaternary alluvial sediments.

Until the mid-20th century rural populations in Bangladesh relied mainly on often-contaminated surface water and shallow wells for water supply. From the 1960s hand-pumped tube wells accessing purer, pathogen-free water were widely introduced especially by development agencies and this practice accelerated significantly from the 1980s onwards as the technology became very cheap and easily available all over the rural areas. This led to a vast increase in the access of rural populations to what was considered a superior and safe source of drinking water from the readily available groundwater resources contained in the shallow alluvial aquifers[15]. Of the existing shallow water wells in the country only 10% were installed by government agencies like the Department of Public Health Engineering (DPHE) and various NGOs, the remaining 90% being privately owned. The number of wells continues to increase with an annual growth rate of about 10%.

Arsenic and health issues

It is only in the past two decades that the real significance and extent of arsenic as an environmental health issue has gained prominence, now a global issue, due specifically to the situation in Bangladesh, where between 35 and 77 million of its 125 million inhabitants are considered to be at risk from drinking As-contaminated water[12]. In 2003, studies by the Bangladesh Arsenic Mitigation Water Supply Project (BAMWSP) estimated the total exposed population at nearer 20M[16]. Much has been learned of the health effects of long term human exposure to arsenic through the evidence collected in Bangladesh[12,17].

The millions of tube wells drilled mostly by the private sector and by national and international agencies to improve water quality in the 1980s and 1990s were tested mainly for pathogens and gastro-intestinal diseases; even as late as 1997, UNICEF[18] was able to claim that 97% of the population had been provided with "safe "drinking water. As noted above, arsenic was not routinely tested until the late 1990s due to difficulties in low level and routine chemical analysis.

Chronic arsenic poisoning, arsenicosis, can increase the risk of several health hazards including skin lesions, cancers, restrictive pulmonary disease, peripheral vascular disease, gangrene, hypertension, non-cirrhotic portal fibrosis, ischemic heart disease, and diabetes mellitus. Skin changes due to arsenic poisoning include a raindrop pattern of pigmentation and depigmentation that is particularly pronounced on the extremities and the trunk. Although less common, other patterns include diffuse hyperpigmentation (melanosis) and localized or patchy pigmentation, particularly on skin folds. Hyperkeratosis (hardened skin) appears predominantly on the palms and the planter surface of the feet. Skin cancer resulting from chronic arsenicosis is quite distinctive. Multiple lesions are common and involve covered areas of the body, contrary to non-arsenical skin cancers which usually appear as a single lesion and which occur in exposed parts of the body

The health effects of ingesting arsenic-contaminated drinking-water appear slowly. .Thus the problem of estimating the affected population has to take into account the past and continuing exposure to arsenic. Since large numbers of tube-wells were installed in Bangladesh over the 20 years prior to 1990 and assuming the population continues to drink arsenic-contaminated water, then a major increase in the number of cases of diseases caused by arsenic, over and above those clinically-confirmed may be predicted (Smith et al 2000). The recent investigations also predicted higher rate of cancer death in the coming years.

The main manifestations of the disease are skin lesions (keratosis),which appear typically around 10 years following first exposure, although these may appear in children younger than 10 years old. Other significant manifestations are black lesions (discoloured skin) on the feet and hands in particular. This is a peripheral vascular disorder with similarities to gangrene. The affected skin gradually thickens, cracks, and ulcerates. The skin discolouration led to the term "black-foot disease" from the localised disease occurrence in groundwaters of Taiwan from where it was first well documented[19]

Table 1. Key statistics on arsenic poisoning in Bangladesh (after UNICEF 2010)[18]

	Number	%
Household drinking water tested for arsenic in 2009[a]	***13 423***	**100**
Household drinking water exceeding Bangladesh standard in 2009		12.6
Household drinking water exceeding WHO guideline in 2009		23.1
Estimated number of tube wells in Bangladesh in 2002	***8 600 000***	**100**
Tube wells tested for arsenic in 2002 and 2003[b]	*4750 000*	55
Tube wells marked green (safe)	*3 300 000*	39
Tube wells marked red (unsafe)	*1 400 000*	16
Estimated total villages in country	***87 319***	**100**
Villages screened for arsenic	*54 041*	62
Villages where<40% of the wells are contaminated	*70 610*	81
Villages where 40-80% of the wells are contaminated	*8 331*	10
Villages where 80-99% of the wells are contaminated	*6 062*	7
Villages where all wells are contaminated	*2 316*	3
Active public safe water options in arsenic affected areas[c]	***705 094***	**100**
Shallow tube well with hand pump (safe)	*417 960*	59.3
Deep tube well with hand pump	*154 264*	21.9
Shallow well with Tara pump (safe)	*82 880*	11.8
Deep tube well with Tara pump	*10 350*	1.5
Dug well	*9 163*	1.3

a) Source: Multiple Indicator Cluster Survey, Bangladesh Bureau of Statistics/UNICEF 2009.
b) Source: National Arsenic Mitigation Information Centre, 2005.
c) Source: Situation Analysis of Arsenic Mitigation 2009, JICA/DPHE.//

The impact of arsenic on children's nutritional status and intellectual development has been studied by Minamoto et al. [20]. Small numbers of skin cancer had started to appear in Bangladesh by the end of the millennium but no long term studies of the disease were available at that time [12]. Previously, a study of a large population in Taiwan[9] found a clear dose-response relationship between arsenic concentrations in drinking-water and the prevalence of skin cancer. In this latter study the average concentration of arsenic in water was about 500 mg/l and by age 60 more than 1 in 10 had developed skin cancer. The lifetime risk of developing skin cancer from a daily intake of 1 mg/kg body weight of arsenic in water ranges from 1 per 1000 to 2 per 1000. Using geostatistical studies, Yu et al.[21] predicted that long-term exposure to present arsenic concentrations will result in approximately 125,000 cases of skin cancer, and 3000 fatalities per year from internal cancers. It is also reasonable to expect marked increases in the incidence of the other health effects[12].

Causes of the problem – the hydrogeochemistry of arsenic

Despite the numerous papers on the subject, there is still not complete agreement on the causes of the high As concentrations, which result from a combination and interaction of geological, hydrological and geochemical controls. It is important to stress that arsenic is not a particularly rare element (52nd in terms of geochemical abundance) and is quite widely distributed in the earth's crust, especially associated with iron. Nevertheless as discussed above it is the nature of the sediments, with above average concentrations of micaceous minerals, the amounts of colloidal-sized iron oxides, combined with their geologically young age that provide the setting for a reactive environment.

The aqueous geochemistry of arsenic is among the most complex of any of the metals and other toxic elements, being controlled by a very wide range of geological, physicochemical as well as biogeochemical processes. The environmental and especially the aqueous geochemical behaviour of arsenic is now well documented as a result of the intense interest in its health significance and occurrence in groundwater[5,15,22,23]. A summary of the main features of arsenic hydrogeochemistry are summarised here drawing heavily on the comprehensive review by Smedley and Kinniburgh[15]. It should be noted that arsenic mobility is unlikely to be controlled by a single geochemical factor and therefore routine prediction of its occurrence and behaviour is exceedingly difficult.

Redox properties and speciation of arsenic

The development of a strongly reducing environment is probably the single most important factor leading to mobilisation of the arsenic. Arsenic is one of a number of metals (As, Se, Mo, V, Cr, U) forming oxyanions (eg AsO_3^-) and which are mobile at the pH values typically found in low temperature groundwaters (pH 6.5–8.5). Arsenic can occur in several oxidation states but in natural waters is mostly found in inorganic form as oxyanions of trivalent arsenite [As(III)] or pentavalent arsenate [As(V)]. Organic As forms may be also be produced by biological activity especially in surface waters. It can also form ligands with other anions especially carbonate and reduced sulphur.

The ration of As (III) to As (V) has been used for some time as a redox indicator[22,24]. This ratio depends on the abundance of the redox-active solids, including organic carbon and iron/manganese oxide, the flux of potential oxidants (oxygen, nitrate and sulphate) and on microbial activity[15]. As (III) is the dominant species under reducing conditions such as the deltaic groundwater environment and is oxidised rapidly on mixing with surface conditions. As(V) is predominant under aerobic conditions typical of semi-arid environments.

Arsenic concentrations and mobility are influenced by changes in redox conditions measured by redox potential (Eh) and pH. Speciation in aqueous solution will also vary. Under oxidising conditions,$H_2AsO_4^-$ is dominant at low pH (less than about pH 6.9), whilst at higher pH, $HAsO_4^{2-}$ becomes dominant. Under reducing conditions at pH less than about pH 9.2, the uncharged arsenite species $H_3AsO_3^0$ will predominate[25]. In the presence of extremely high concentrations of reduced sulphur, dissolved As-sulphide species can also be significant.

Role of sorption

At near-neutral pH arsenic mobility is severely limited by adsorption reactions, precipitation, or co-precipitation with oxide or hydroxide minerals (eg FeOOH) and/or with clay minerals or organic matter. Hydrous ferric oxide (HFO), a high surface area form of iron oxide, often forms when Fe is precipitated rapidly[5].This oxide is able to adsorb As on its surface (HFO-As) and can then become the dominant form of As. HFO is subject to both acid dissolution at low pH and reductive dissolution at low pe (redox potential or Eh) which results in the release of As to solution. Adsorption of arsenate to hydrous Fe oxides is particularly strong and sorbed loadings can be appreciable even at very low As concentrations[26]; most oxyanions including arsenate tend to become less strongly sorbed and more mobile as the pH increases[27]. However as the sediments undergo diagenesis, the HFO tends to transform slowly to more stable forms of iron oxide with lower specific surface area, such as goethite and this tends to lower the sorption at higher pH. As pointed out by Smedley and Kinniburgh[15] adsorption reactions are responsible for the relatively low (and non-toxic) concentrations of As found in most natural waters.

Role of organic carbon

It is widely known that deltaic sediments contain significant quantities of organic debris as remnant vegetation and smaller particles including humic and colloidal substances, some of which may be reactive. Dissolved organic matter is generally the control on removal of oxygen and with reduced iron, maintaining reducing conditions. There had however been little discussion until recently of the role of TOC in the control of arsenic. It has been shown[28] that there was a correlation between peat lenses and arsenic concentrations but peat horizons are not widespread in the delta region. Debate was triggered from evidence of the shallow groundwater environment [29,30] that pollution sources, drawn down by pumping abstraction were the source of reactive organic matter causing arsenic mobilisation. This hypothesis was reviewed and has been strongly refuted by Meharg et al.[31] who showed from core material from deep profiles from widely separated sites, that arsenic and organic carbon were co-deposited and provide the reducing conditions to dissolve iron(III) oxides and release arsenite into the porewater. Klump et al[32]. among others, also question the drawdown hypothesis showing that the irrigation water does not coincide with the depths where the arsenic peaks occur.

Arsenic in soils

The background level of As in non-irrigated soils in Bangladesh is around 5-10 mg/kg but, in irrigated soils concentrations are regularly several tens of mg/kg[33]. Most of the arsenic in soils of the GBM (West Bengal Delta Plain) is derived from the Fe-bearing silicates of the delta sediments (biotite and chlorite) and concentrated especially in the newly formed oxyhydroxides[34]. Although much lower in amount, the oxyhydroxides hold almost as much arsenic as the silicate fractions (within which the As is much less mobile). During the irrigation cycles more arsenic is then taken up by the oxyhydroxide fraction of the soils and cycles during redox variations. Very high arsenic (169-178 mg/kg) is found in Fe-rich mineral plaque coating the roots of rice but in the grains of rice and wheat were found to be low in As (0.3-0.7mg/kg)[34].

The occurrence of arsenic in surface waters and ecosystems of the GBM region

Global average baseline concentrations of As in river waters lie in the region 0.1–0.8 mg l^{-1} but can range up to ca. 2 mg l^{-1}[15].. They vary according to the composition of the surface recharge, the contribution from baseflow and the bedrock lithology. There are relatively few measurements of arsenic in the GBM system in India and Bangladesh. Dissolved arsenic concentrations in the Ganges, Brahmaputra Rivers and their confluence show important seasonal variations and maximum (total of dissolved and suspended) arsenic concentrations are observed during the monsoon season (July–October). Here the arsenic is concentrated in suspended particulate (SPM) matter derived from flooding (Figure 2) and run off from agricultural lands, irrigated with arsenic rich groundwaters[35] . The high summer temperature (maximum 30^{0}C) enhances the biological activity through microbial reduction of As (V) to less particle active As (III) species and contributes to the seasonal variations in arsenic concentrations in river waters.

In sea water, arsenic occurs as arsenate (As III) with average As concentrations in open seawater usually showing little variation and typically around 1.5 μg/l[15]. Concentrations in estuarine water are more variable as a result of varying river inputs and salinity or redox gradients but are also usually low, at typically less than 4 mg/l under natural conditions. In areas with industrial pollution, concentrations may be higher. However there is a tendency for the concentration of arsenic and other metals to be removed and deposited on entering surface waters. The flocculation of Fe oxides at the freshwater-saline interface is an important consequence of increases in pH and salinity. This can lead to major decreases in the As flux to the oceans[36] .

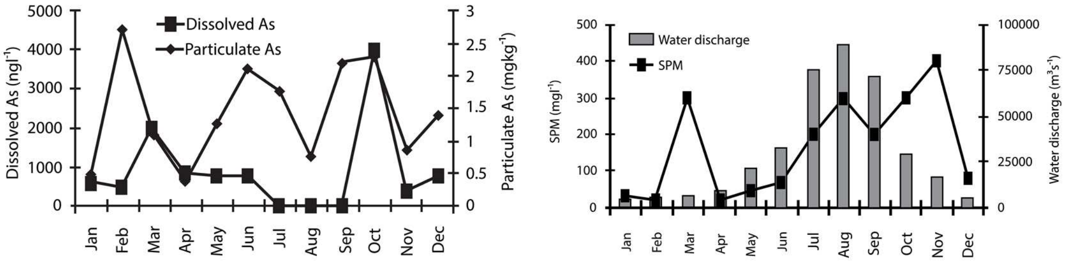

Figure 2. Water discharge (m/s), SPM concentrations (mg/l, dissolved arsenic concentrations (ng/l and particulate As concentrations (mg/kg) at the Ganges-Brahmaputra confluence Jan-Dec 2008. Redrawn after [35]

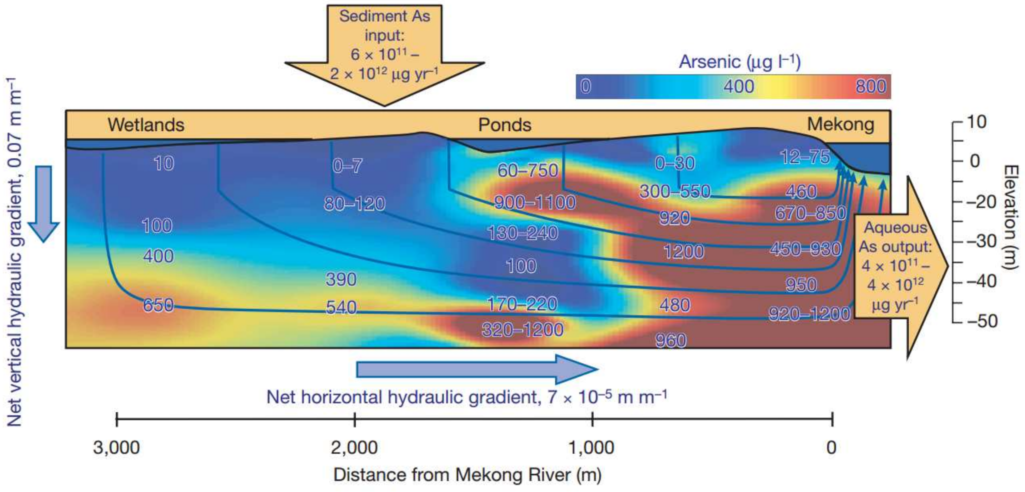

Figure 3 Groundwater flow paths and arsenic concentrations for a minimally disturbed section of the Mekong river[37]

Delta areas are subject to significant changes in surface water conditions with periods of low flow plus inundations from river flooding, widespread wetlands and marine inundation. Strong vertical seasonal gradients are likely to exist allowing natural recycling between the river and the shallow groundwater system. The likely fluxes of water and associated arsenic concentrations for the shallow (<µm) environment under minimally undisturbed conditions are shown (Fig 3) for a modelled section of the Mekong[37] .. These studies draw general attention to the risks involved for example in excessive irrigation pumping, sediment excavation, levee construction and upstream dam installations.

Bangladesh relies heavily on groundwater for the irrigation dry-season rice (boro) which is exposed to high arsenic with some 1360 tons of arsenic being added annually to the soils. More than 75% of the current irrigation is provided by groundwater sources, mainly pumped from the Holocene alluvial and the Pleistocene DupiTila aquifers. Under natural conditions wetlands can act as a source of groundwater recharge, recycling water back to the river on a centennial scale. However, the heavily populated delta areas at the present day are strongly affected by irrigation pumping and this increases the risk of arsenic build up[37].

The impact of seasonal monsoon flooding on these soils was studied in one area of rice paddies in central Bangladesh (Munshiganj) by Roberts et al.[38]. It was estimated that between 13-62% of the arsenic is removed by monsoon floodwaters (up to 4.6m) and that non-flooded soils are at risk of arsenic accumulation.

Arsenic in the food chain

A good number of studies have demonstrated that significant amounts of As can be ingested through food, mainly rice. However, the uptake depends on a number of factors including concentrations in irrigation water. Total intake also depends on cultural issues such as cooking practices and amount of rice taken. Rice irrigated with groundwater is generally higher in arsenic than non-groundwater sources and may be a significant dietary intake[39]. Human exposure to arsenic through rice was calculated to be equivalent to half of that from drinking water in 14% of the rice samples (using daily intake levels of 400g and 4l for rice and water, respectively, an arsenic concentration in water of 50 mg/kg and assuming equal bio-availability of arsenic in water and rice). Duxbury and Pannaulah[40] have demonstrated a halving of rice yields at soil As concentrations of around 50 mg/kg. Furthermore, significant uptake of arsenic by rice may occur in irrigated regions, as well as non-irrigated crops[41]. Processing of rice (parboiling and milling) does not appear to substantially reduce human exposure to arsenic through rice consumption.

Studies by Meharg and Rahman[33] demonstrate that there is clear variation in As speciation and concentration in rice grown in different countries. When this variation is related to dietary exposure it is evident that countries whose rice is elevated in inorganic As and who are reliant on rice as a dietary staple are most at risk.

Arsenic in groundwater of the GBM region

Although arsenic may form over 200 primary minerals associated principally with ore deposits, its geochemical distribution is diffuse and this is related, primarily with its affinity for iron[15]. Thus it is commonly found in primary and secondary minerals in the reduced form associated with pyrite and other metal sulphides ($Fe(As)S_2$) and in weathered oxidising environments associated with iron oxides. But arsenic, as mentioned above, in the GBM region is also present in other mafic minerals, still associated with iron, such as biotite and amphiboles such as hornblende transported with more common minerals to form the deltaic sediments – and which then can weather slowly as sediment diagenesis occurs. It is worth remembering that the mass of arsenic contained in the sediments is large yet groundwater concentrations of interest and concern are measured only in microgrammes per litre.

Once arrived in the delta, the various processes mentioned above, lead to the mobilisation and fixation of arsenic in the sediment pore waters and groundwater bodies. The processes take place at the scale of the pore solution with groundwater movement leading to the distribution of the solutes more widely. Thus, it is important to establish and visualise the arsenic occurrence and distribution at different scales and in three dimensions (Fig. 4) as shown by Smedley and Kinniburgh[5].

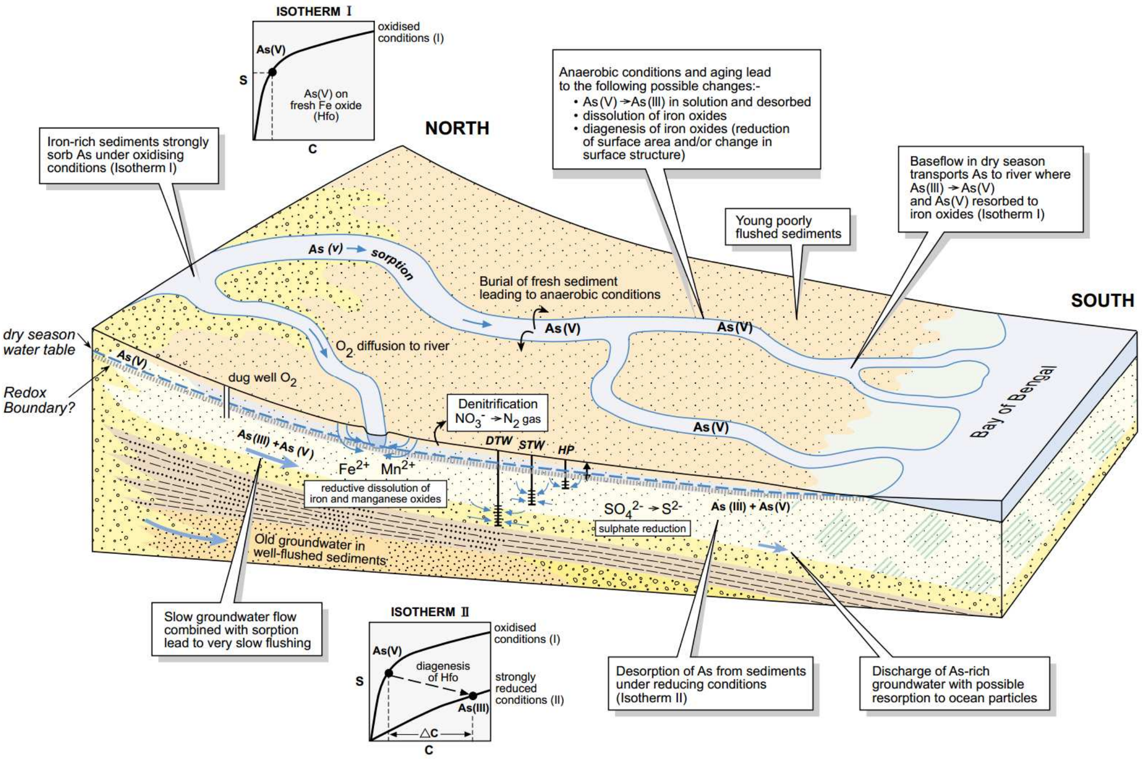

Figure 4. Schematic diagram showing the geological environment of the GBM and main geochemical processes leading to arsenic mobility (BGS and DPHE)[11].

Hydrogeological controls

The hydrogeology of Bangladesh was described in some detail by BGS and DPHE.[11],. The Quaternary system can be considered as comprising three aquifer units Table 2:

Table 2 Main aquifer units of the Quaternary delta (BGS/DPHE)[11]

	Fluvial areas	Delta areas
Upper shallow aquifer	Grey highstand braided floodplain (U Dhamrai Formation)	Grey highstand floodplain aquifer of dendritic distributary system
Lower shallow aquifer	Grey coarse grained transgressive tract/lowstand aquifer in incised channels (L Dhamrai Formation	Grey transgressive tract lowstand aquifer within incised channels
Deep aquifers	Red-brown DupiTila of the Chandina area, and Barind and Madhupur Tracts	Grey sub-150m deep aquifers composed of cyclic, vertically stacked aquifers in subsiding deltas

Groundwater flows southwards through the fluvial sediments of the northern part of the GBM system, mainly through the coarser sands and gravels of the lower shallow aquifer. As the aquifer develops towards the south the groundwater flow feeds through the stacked main channel deposits, derived from several cycles of glacio-eustatic deposition. Each of these units is a fining upwards sequence so that both horizontal and vertical permeabilities will vary within the aquifer. Within the coastal zone the shallow and deeper aquifers have been invaded by and mix with sea water and saline formation water of the subsiding delta.

Groundwater movement is strongly influenced by the incision by rivers into the stacked sedimentary sequence and also by the strong seasonal hydraulic gradients, although any fluctuation in water levels is nowadays heavily modified by irrigation pumping. The location of significant former channel deposits through the delta may also afford areas of greater transmissivity. The magnitude of the groundwater flow through the complex sedimentary sequence, flushing out porewaters and removing diagenetic products is a critical consideration in relation to the arsenic anomalies. It is considered that the low-stand sediments of the Brahmaputra valley will have been flushed at least once since their time of deposition, whilst the high-stand deposits will have only been flushed once[11].

The variations in arsenic concentrations thus clearly relate to the turnover of water in the sediments, depending in turn on the age of the sediments, aquifer hydraulic properties and the past and present groundwater flow regimes[11]. From the consideration of the hydrogeology it was concluded that high or low arsenic was likely to be found in specific locations:

Low arsenic concentrations associated with:

i) coarse sands at the base of incised channels in fluvial areas or possibly in stacked channels in delta regions
ii) relatively high hydraulic conductivity, medium porosity;
iii) high present day groundwater gradients and/or historically high gradients due to the influence of the past glacial maximum
iv) relatively rapid flushing, some 2-10ka per pore volume
v) sediments greater than 10ka years old;

High arsenic concentrations associated with:

i) areas with low recharge
ii) silts and fine sands within alluvial floodplains and delta areas leading to low groundwater flow rates
iii) areas with low groundwater gradients even at the time of the last glacial maximum
iv) areas where flushing takes 50-200 ka per pore volume even during the LGM
v) areas with low gradients at the present time leading to flushing times of 200ka
vi) regions of especially low flow eg inside river meanders, in closed basins and in dead zones of aquifers.

The hydrogeology predicts and supports the finding that the deeper aquifers should be largely free of arsenic and offer a potential mitigation for the arsenic problem. In this case pumping will induce flow vertically as well as laterally and there is still the possibility for migration of contaminants to the deeper groundwater with uncontrolled pumping. Well design, screen placement and pumping regimes need to be carefully considered.

Arsenic occurrence and distribution

A national survey of arsenic in groundwater (BGS and DPHE 2001), using some 3,500 groundwater samples, found that 27% of samples from the Holocene shallow aquifer (<150 m depth) contained arsenic at concentrations exceeding 50 µg/l, and 46% exceeded 10 µg/l. This affected an estimated 35M people, with 57% affected by concentrations above10 µg/l. The aquifer sediments are made highly reducing by the presence of significant amounts of organic carbon in the sediments[5]. As well as high arsenic under the reducing environment the groundwaters are often enriched in Fe, Mn, HCO_3, NH_4, but concentrations of NO_3 and SO_4 are low; this indicates that denitrification and sulphate reduction are aided by the reducing environment. Methane was also detected in some groundwaters[42].

The occurrence of arsenic in groundwaters in Bangladesh is shown in Fig 5 where it is seen that arsenic concentrations exceeding drinking water limits (50µg/l) were concentrated in the south and south-east of the country. A later survey by UNICEF/DPHE[43] of 317 000 (shallow?) tube wells from the south of Bangladesh found that 66% contained arsenic above the threshold concentrations with only 10% with lower than 10 µg/l .

The problem is a little less severe in West Bengal, India but it is estimated that about 6.5 million people are drinking water with arsenic concentrations greater than 50µg/l. In India the arsenic also occurs principally in alluvial aquifers in the states of Bihar, Tripura, Uttar Pradesh, Jharkhand and Assam[44,45].

The distribution of arsenic, as described above, is quite strongly correlated with depth, which in turn relates to the age of the sediment and the aquifer properties and flow characteristics. The main depth range of the high arsenic is between 10-80m[11,28] almost entirely within the shallow aquifer (Fig 6). However there is consistent evidence that, below 150m in the lower aquifer, comprising older alluvial sediments from Holocene alluvium, concentrations of As are much reduced. Concentrations from the deep aquifer in Lakshmipur and Faridpur and Chapai Nawabganj, focal points of the BGS/DPHE survey, consistently gave low-arsenic waters and offer an alternate source of supply. Later surveys in other parts of the country demonstrated that arsenic safety is not determined by depth but by the nature of sediments occurring at a particular depth.

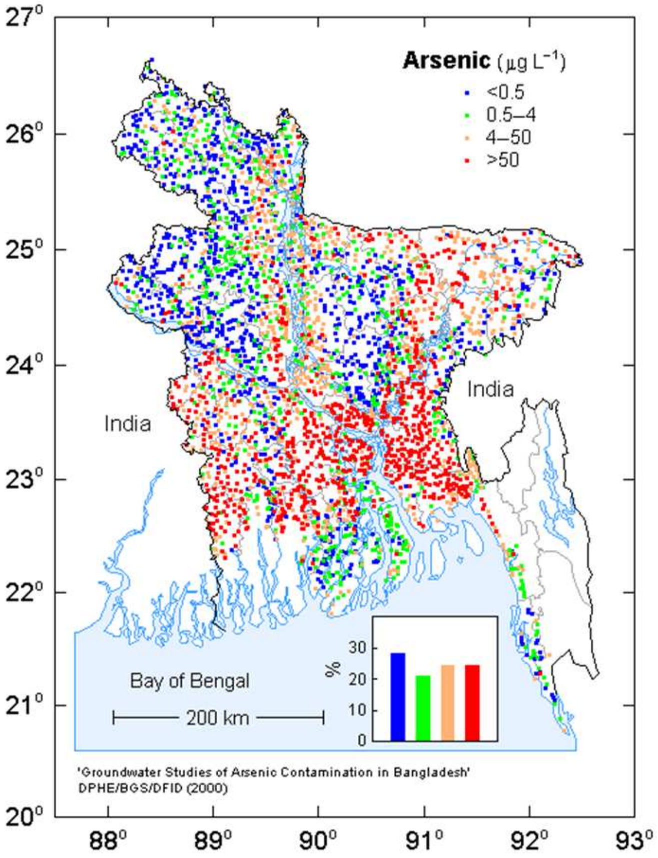

Figure 5. Arsenic concentrations in groundwaters in Bangladesh showing high (>50 mg/l) concentrations in red associated with the delta of the GBM river system[11].

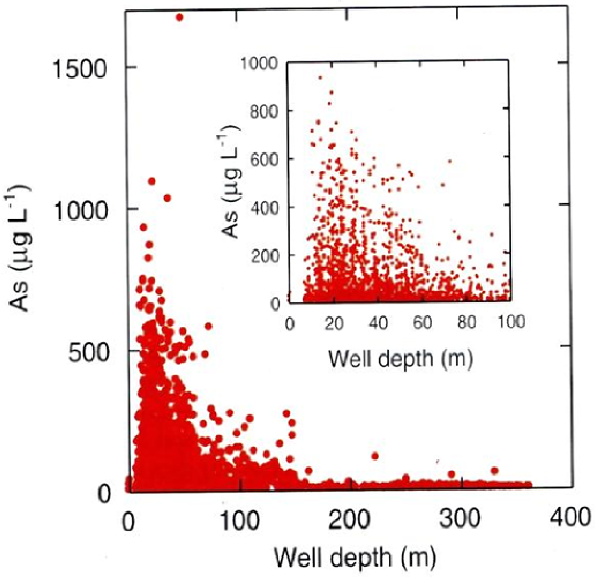

Figure 6. Arsenic concentrations in relation to tube well depth showing the predominance of high arsenic between 10-60m depth and the widespread low arsenic abundance in groundwaters below 150m

Dug wells to a few metres depth also often have low arsenic. The UNICEF/DPHE survey found that only 11% of the shallow dug wells had arsenic concentrations above 50µg/l. However these wells are prone to microbiological contamination, the very problem that the tube well programmes of the 1980s sought to resolve.

It is widely accepted that the reducing conditions in the aquifer involve reduction of As(V) to As(III) with resultant changes in sorption behaviour. The process of reductive dissolution and reductive adsorption of arsenic are the main processes leading to the increase in dissolved arsenic concentrations[2,5]. The mobilisation of arsenic is still not fully understood however and involves a complex sequence of diagenetic reactions as outlined above. These reactions may also involve microbial, which are favoured by the presence of organic matter in the young sediments and dissolved in the groundwater. The organic matter is preserved under reducing conditions in the rapidly forming sediments and is both reactive and assimilable for microbially-mediated reactions. This is a natural biogeochemical process and any anthropogenic origin of organic matter has been largely rejected[32,46].

Groundwater radiocarbon age was determined on samples from piezometers drilled at the three aquifers at research sites (Special Study Areas or SSA's) in Chapai Nawabganj, Lakshmipur and Faridpur[11] From 10-40m depth the groundwater had values of 83% modern carbon (pmc) indicating modern water no more than several decades, some of these waters also containing tritium. Groundwater from 150m (Faridpur) with 51% pmc indicated an age (based on geochemical modelling) of 2000 yr. Deep groundwater from Lakshmpur had values of 28pmc indicating ages in the range 2000-12000 yrs. Using modelling studies and environmental tracers (^{3}H, ^{3}He/^{3}H, ∂^{18}O), Klump et al.[32] have also shown that modern water is found to a depth of 25m and likely to have been influenced hydrodynamically by pumping. However, the major zones of As enrichment lie below the depth of the modern water, supporting the hypothesis of enrichment from natural diagenetic processes.

Thus, it is clear that the hydraulic gradients, transmissivity and extent of flushing of the aquifer have been important in concentrating and then distributing the arsenic rich waters away from the sedimentary zones undergoing active diagenetic processes. Borehole drilling in recent decades has intercepted a layered aquifer and has undoubtedly affected flow patterns with intensive pumping for irrigation. Pumping can influence the water chemistry by removing arsenic from zones of enrichment, but also, depending on the vertical permeabilities, drawing down arsenic-rich water from overlying horizons (say below 20m). Modelling studies have shown the importance of careful abstraction regimes and that it is unlikely the low-arsenic groundwater at depth would be disturbed by hand-pumps. The irrigation from the shallow aquifer (with higher concentrations of arsenic) would also provide an effective hydraulic barrier[47].

In the original survey of the arsenic problem[11] a wide range of inorganic constituents were also screened from the whole region and especially from SSA samples to assess any natural anomalies that could present problems for drinking water and other usage. By far the major problem was arsenic-related but for example some 35% of samples also exceeded the WHO guideline value (0.5mg/l) for manganese. Wells in western Bangladesh tend to be high in Mn but relatively lower in As, but the reverse is true in southern Bangladesh; there is currently no apparent explanation for this.. Only 2% of the deeper groundwater sampled in the national survey had Mn exceeding 0.5 mg/l).

It is notable that due to the strongly reducing nature of all but the shallow aquifer, nitrate is absent (or has been reduced to values below detection by natural remediation). In the shallow (mainly aerobic) aquifer, the presence of nitrate can mainly be used as an indicator of anthropogenic contamination and recently recharged water.

National surveys of arsenic

Statistical analysis was used to calculate the percentage of the population at that time who were exposed to arsenic at various concentrations[11]. However, in the coastal areas mostly deep wells were sampled where shallow water is brackish and not suitable for drinking. The survey produced the National Map of As distribution in shallow groundwater and was subsequently used for designing the Bangladesh Arsenic Mitigation Water Supply Project[48]; 29% of the sampled shallow wells and 2% of the deep wells exceeded the 50 µg/l limit for drinking water.

The percentage of wells exceeding 50 µg/l in 462 upazilas (administrative area) of the country combining the results of the BAMWSP national screening and UNICEF/DPHE screening in arsenic non-affected upazilas are shown in Figure 7. This consolidates the wells survey distribution maps of the previous BGS/DPHE studies.

The Government of Bangladesh estimated the number of people exposed to 50 µ/l level as 29.3 M as shown in Table 3. Of these, more than 10 M people have been identified in 8511 villages in 191 upazilas of 51 districts where tube wells have As above 50 µg/l as shown in Table 3. About 13 000 suspected arsenicosis patients have been reported from these villages.

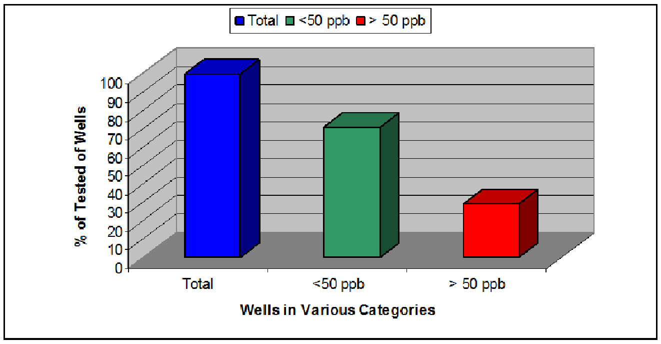

Figure 7. Summary of DPHE/BGS National Hydrochemical Survey Arsenic Analysis of 3534 wells. British Geological Survey: Keyworth.

Table 3: People exposed to 50 µg/l or more arsenic in drinking water[48]

Modes of water supply	Population coverage (millions)	% tube wells contaminated with As>50µg/l	Population exposed to As>50µg/l (millions)
Piped water supply	13.10	7.2	0.94
Manually operated Deep Tube wells	8.20	1	0.08
Manually operated Shallow Tube wells	103.00	27.4	28.2
Dug wells	1.30	0	0
PSF, VSST, SST, RWH etc	1.50	0	0
Others	2.15	0	0
TOTAL	129.25	35.6	29.24

Arsenic and socio-economic issues

Estimates of the economic impact of poor health arising from arsenic in groundwater in Bangladesh suggest that the cost of inaction is extremely high. .The Gross Domestic Product (GDP) output lost due to illness and people becoming unable to work is estimated to be US$23 billion[49] while the cost of treating arsenic-related diseases is estimated to be much lower at US$0.6 billion for a constant discount rate of 10% over a 50-year period. This suggests that while the costs to the health care system are large, the costs to the economy due to loss in productivity are at least an order of magnitude greater.

People with lesions from arsenic poisoning still suffer social stigma in Bangladesh, although the situation has improved. Ten years ago, many people believed arsenic poisoning was contagious or a curse. Parents were reluctant to let their children play with children suffering arsenic poisoning. Arsenicosis patients were shunned within their villages. For women, the situation was worse and still remains an issue. In Bangladesh, a woman's attractiveness is often associated with the pale complexion. This makes it harder, in some cases impossible, for single women suffering from arsenic poisoning to marry. Once married, women face the risk of divorce if they develop arsenicosis skin lesions. This can be a dire situation in Bangladesh's male-dominated society, where unmarried women are more vulnerable to poverty and social exclusion[43]

The discovery of wide spread arsenic contamination in tube wells, installed initially to provide bacterially safe water presents a double challenge: to ensure that the health gains on diarrhoea would not be lost while also reducing the health impact of arsenic. The challenges are both technical and social-economic. In certain arsenic-affected areas there are few if any affordable safe water options for rural households with average income. Many alternatives are safer, but less convenient or more costly than arsenic-contaminated shallow tube wells. Solutions such as rainwater harvesting have shown low social acceptability. It is not rare to still see people drinking arsenic contaminated water from red painted tube wells. It is hard to compete with the low-cost easily maintained and convenient shallow tube wells when it comes to water supply to rural households.

Arsenic mitigation and management

The first substantive overview of the response to the arsenic emergency was provided by the World Health Organisation[50]. Arsenic removal is generally expensive and technically difficult and solutions can pose their own health risks; the reduction of standards from 50 µg/l to 10 µg/l leads to a sharp escalation of costs. Whatever national standards are, it is of key importance that priority be given to measures that reduce the absolute intake of arsenic as much as possible, even if the standard is not met immediately. From lessons learned worldwide, communities must be fully committed to take an appropriate level of managerial and financial responsibility for the construction, operation and maintenance of any mitigation system. The government's role lies in developing national plans of action, and ensuring that mitigation efforts by external support agencies and civil society organisations are implemented in a coordinated fashion. For a problem as complex as arsenic contamination the Government also works with academic and research institutions to improve the understanding of the causes, extent and impact of arsenic contamination. Substitution of arsenic free water such as rainwater (with adequate storage and treatment) presents one possible option.

The understanding of the occurrence of arsenic is sufficient to direct national strategies for lowering exposure[51]. Field kits were used in the very extensive 1999 campaign to test tube wells in the most affected portions of the country. Some 1.4M tube wells that did not meet the local standard for arsenic in drinking water of 50 µg/lwere painted red. Another 3.5M wells with up to 50 µg per litre arsenic were painted green[48]. Such testing did not however reduce the rate of private well installations; sadly, most tubewells that were installed after the national testing campaign remained untested by time of the study.

More than half of the population of Bangladesh remains at risk from arsenic exposure. To reach a greater fraction of the population several actions have been proposed[52]: (i) stimulate vastly the periodic monitoring of water quality, no matter what the mitigation option, (ii) encourage rather than discourage the wise use of deep aquifers that are low in arsenic, and (iii) include the newly demonstrated effects of arsenic on the mental development of children in information campaigns[53]

The Government of Bangladesh adopted a National Arsenic Policy and Mitigation Action Plan in 2004 for providing arsenic safe water to all the exposed population, to provide medical care for those who have visible symptoms of arsenicosis and also to investigate the issue of arsenic in agriculture. The policy demonstrates the political will in recognising the severity of the problem and needs for its mitigation. The mitigation action plan provides guidelines for implementation of projects in order to reduce arsenic exposure by use of surface water, rain water and deep groundwater. Surface water was given higher priority as the source of arsenic safe water; deep groundwater was considered as the source where no other options were available. This created some problems in arsenic mitigation as availability and quality of surface water were major constraints. Eventually groundwater, more specifically deep groundwater, has become the prime source of safe water.

Various mitigation options had been installed by 2005 by the Government of Bangladesh and NGOs to provide As-safe water in the areas where more than 50 µg/l As had been detected. A large number of arsenic removal technologies were introduced in the country using various different methods. However, the government took an initiative to verify the technology and issue certificates before they could be used. Accordingly five household and one community level arsenic removal technologies were given an approval certificate. Due to various management and technological issues the overall contribution of the removal technologies to arsenic mitigation is insignificant. Thousands of removal units have been distributed under various projects but very few were found operational and has not been adopted as a sustainable option.

DPHE/APSU[54]) conducted a national survey to identify the number of options installed by various government and non-government programs. A large number of agencies installed some 107 000 safe water options based on surface water, rain and groundwater; 70% of the mitigation by that time had been provided by low arsenic deep tube wells, followed by 12.5% rain water. In a more recent study, Ravenscroft et al[55] compiled the number of safe water options installed for As mitigation in Bangladesh. Deep tube wells provided 84.4% followed by shallow tube wells (5.1%) and dug wells (4.9%). Therefore, low arsenic groundwater accounted for more than 94% of safe water options followed by 3.2% by rainwater and 1.4% by surface water (PSF). The contribution of arsenic removal technologies was insignificant.

Thus, vast effort was made in the first decade of the arsenic crisis into technologies for arsenic removal with numerous scientific publications on the subject. The experience has been that, whilst these technologies are capable of removing As to a safe level in a majority of cases, maintenance is a major issue and performance falls significantly as soon as project support is withdrawn from communities. However, there is a better future for community-based units rather than household based solutions. Although these technologies were proposed as a means for emergency response, the certification procedure took too long a time for the effective use of the removal technologies. It is very unlikely that household removal technologies will be widely used in the future as a safe water option in the country.

The conclusions from the BGS/DPHE studies[11], that deep tube wells offer a safe source of low or arsenic-free water have now been more widely corroborated. As a result over 200 000 deep wells had been installed by DPHE by 2007. Rural piped water supplies have been evolving as a source of safe water, both in and outside the arsenic affected areas of the country[55] .

A risk assessment of various arsenic mitigation options was carried out to understand the relative health risk, risk management potential and social acceptability of the widely used technology options including DTW (deep tube well), DW (dug well), PSF (surface water) and RWH (rain water harvesting)[54]. The study included 36 DWs, 36 DTWs, 42 PSFs and 42 RWHs randomly selected from 26 clusters. A quantitative health risk model was developed which showed that there was significant health risk substitution for DWs and PSFs with respect to pathogens. There was much lower risk substitution in DTWs and RWHSs in relation to either pathogens or other chemicals. DTWs had the highest aggregate water safety followed by RWHSs, while disease burdens from DWs and PSFs were unacceptably high. The disease burden increased significantly for the DWs and PSFs in the wet season with greater deterioration of microbiological water quality.

A map of the mitigation situation and technologies in use for number of upazilas was produced[56] under the GOB-UNICEF project based on criteria such as depth to water table, arsenic concentration, salinity and presence of the deep aquifer (Figure 8). It should be noted that, other than deep tube wells, no other option can be prescribed as a solution for the entire country. Deep tube wells also have some limitations in certain parts of the country. The local geology, and hydrogeology need to be accurately determined as well as decisions about alternative technology. In addition, the overriding issue of providing safe water rather than just arsenic-safe water should get due importance in introducing new/alternative options. The relative risks of various arsenic-safe water sources need to be assessed in order to avoid inadvertent risk substitution.

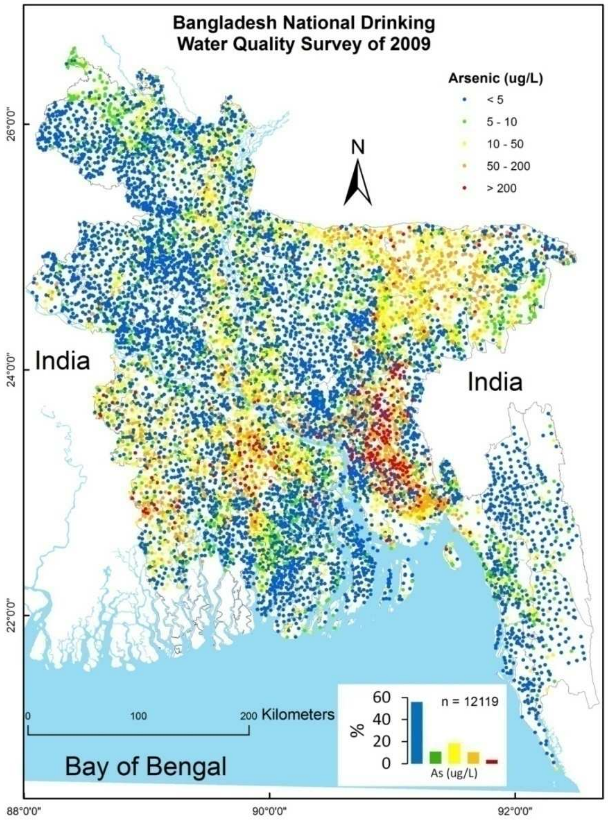

Figure 8. Situation regarding arsenic at household water as of 2009 based on 12119 samples. Note the widespread occurrences of arsenic in certain parts of the delta region. (Source: BBS/UNICEF, 2009: Bangladesh national drinking water quality survey of 2009 accessed at *http://www.unicef.org/bangladesh/knowledgecentre_6868.htm)*

A visual comparison of the arsenic contamination maps of 2009 and 2005 (not shown) indicates that there have been some changes for the worse in the degree of contamination in some areas. It is worth noting that more upazillas were studied in 2009 and also the reorganisation of administrative boundaries by government since 2005 has also impacted the distribution pattern of arsenic contamination and the affected population.

While comparing the patient numbers of 2009 with those of 2005 it is noted that the latter were collected from the BAMWSP data[48] of 2004 while the 2009 patient data was collected from DG Health sources. The BAMWSP data came from various uncoordinated sources while the DG Health data records patients who were medically treated by qualified professionals. In the comparison it can be seen that that the 2005 position paper in 2004 records 38,118 patients for 270 upazilas[48], and 12853 patients for 191 upazilas. The 2009 study recorded 37,015 patients for 301 upazilas most of which were also covered in 2005 study. A good indicator of the trend in patient number distribution is the patient-population ratio; although the patient numbers have increased the percentage compared to the total population is on a positive declining pattern.

A similar trend can be visually interpreted from the arsenicosis patient map for both 2005 and 2009. Another table produced in the 2005 report showed a list of 41 unions where the number of arsenic patients exceeded 100 per 10,000 population. A similar calculations done in the 2009 study showed that 26 unions fell in the same category.

Comparison was also made between arsenic mitigation situations of 2009 with that of 2005. Over this period there has been a significant increase (1245%) which has helped improve the mitigation situation. In 2005 38% of the total households within the study area had safe water coverage. In comparison 54% of the population had safe water coverage in 2009. This also could be the likely reason for reduction of patient percentage in 2009.

Summary and Conclusions

The arsenic problem in Bangladesh is first of all a natural phenomenon related to geology. It has become exacerbated by rapid development through abstraction of groundwater as a resource upon which millions of people have become dependent. .Arsenic may therefore be added to the list of stress factors affecting health, livelihoods and the ecosystem of the delta region. It is found that the immediate coastal region of Bangladesh with very young sediments sometimes only a few hundred years old, is relatively unaffected and that the persistent problem of high arsenic commences some 50km inland where potable water supplies are derived from established older sediments tapped by tube wells in excess of 30m depth. In these areas the main water quality problem is salinity caused by flooding and also saline intrusion caused by excessive pumping.

Nevertheless a large number of people are still exposed to arsenic at levels above the acceptable limit, mostly in the southern deltaic part of the country away from the coast. Significant efforts at mitigation have been undertaken but these do not match the severity and magnitude of the problem. This is despite the adoption of a National Policy for Arsenic Mitigation in 2004.

Various options have been introduced for providing arsenic safe water ranging from household removal technologies targeting small groups to piped water supplies targeting up to 1000 people. As of 2009 deep tube wells provided 84.4% followed by shallow tube wells (5.1%) and dug wells (4.9%). Therefore, low arsenic groundwater accounted for more than 94% of safe water options followed by 3.2% by rainwater and 1.4% by surface water (PSF). The contribution of arsenic removal technologies was insignificant.

More than 40,000 patients in 2009 had been registered with government hospitals and were under government arsenic healthcare coverage; but it is widely believed the actual number of affected people is larger. The number of deaths linked to arsenicosis is widely predicted to increase over the coming years. The impact of arsenic in irrigated agriculture is a matter of serious concern but not yet well understood. However, this has been considered as another major issue and more work is needed. .Arsenic can have significant impacts on economic growth and livelihood of the people of the country. More focussed mitigation actions are needed to provide safe water to the population still exposed to arsenic above the drinking water limits.

The freshwater in rural Bangladesh provides an essential ecosystem service, sustaining people and their livelihoods. This is at the core of the ESPA Deltas project and thus arsenic is a key concern of National and local government.

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†European and US EPA regulations implement the current recommended WHO guideline for As in drinking water (10µg /l). Bangladesh like several other countries continue to use the pre-1993 WHO standard, partly due to difficulties in testing as well as difficulties in compliance.

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