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Review

Arsenic mobility and toxicity in South and South-east Asia – a review on biogeochemistry, health and socio-economic effects, remediation and risk predictions

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Environmental context. The presence of high arsenic concentrations in South and South-east Asian groundwater causes dramatic health issues for the local population. As a consequence, scientists, governments and agencies investigate arsenic-related health issues and arsenic origin, fate and behaviour in ground- and drinking water and have started to provide remediation and mitigation strategies. This review broadly summarises our current knowledge on arsenic biogeochemistry, health and socio-economic effects, remediation and risk predications in Asia and discusses current and future research directions.

Abstract. The dramatic situation caused by high arsenic concentrations in ground and drinking water in South and South-east Asia has been investigated and discussed by the scientific community in the past twenty years. Multifaceted and interdisciplinary research extended our understanding of the origin, distribution and effects of As in this region of the world. Scientists have joined forces with local authorities and international non-governmental organisations (NGOs) and aid agencies to provide help, education, and assistance to the millions of people exposed to As. Current research focuses on predicting the behaviour of As in the subsurface, developing strategies to remove As from drinking water and remediating As-contaminated groundwater. This introductory review of the research front '*Arsenic Biogeochemistry and Health*' gives a broad overview on the current knowledge of As biogeochemistry, exposure, health, toxicity and As-caused socioeconomic effects. Furthermore, the current research directions in predicting the presence and spreading of As in groundwater, assessing its risk and potential strategies to remove As from drinking water and to remediate contaminated environments are discussed.

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Introduction

The Agency for Toxic Substances and Disease Registry of the United States has put arsenic on top of the Priority List of Hazardous Substances for years now.[1] This is reasoned by the frequent occurrence of As in elevated concentrations in the environment and subsequently its high potential for human exposure and threat to human health.[1] Hot spots of As have been identified in the Americas, Europe, Australia and Africa,[2–5] although the most commonly known occurrence is in South and South-east Asia,[6] where it has been termed the

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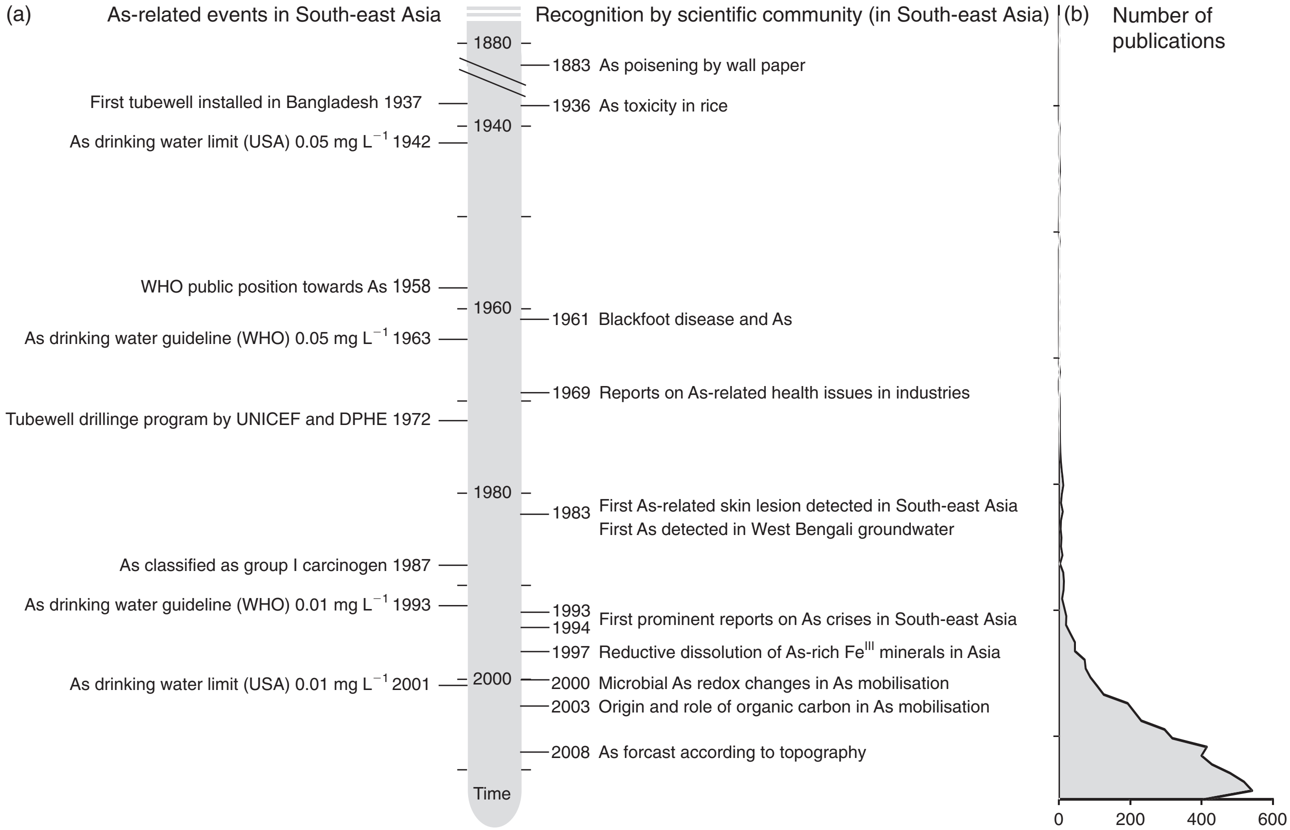

Fig. 1. Time scale of events and subsequent recognition by the scientific community related to the arsenic crises in South-east-Asia. (a) On the left side events and water drinking guidelines and governmental drinking water limits, and on the right side arsenic-related topics recognised by the scientific community are provided. (b) Number of research articles and reviews from 1883 to 2013 found in ISI Web of Knowledge using the search parameters 'arsenic + (rice or drinking water)' for topic in English.

'largest mass poisoning of a population in history'.[7] Specifically, inhabitants of the Ganges-Brahmaputra-Meghna river basin in Bangladesh and West Bengal, one of the most densely populated areas worldwide, are struck.[8,9] Owing to the humid climate of this region and unregulated waste disposal, surface water-borne pathogens triggering cholera and diarrhoea caused a high mortality rate of the population, in particular children below an age of 5 years.[10] Local and international agencies counteracted by promoting the drilling of tube wells in the early 1970s, which provided groundwater believed to be pathogen-free (Fig. 1a).[6] Consequently, millions of households followed by privately installing tube wells to have access to clean drinking water. As a direct consequence, under 5-year-old children mortality rates decreased, although recently Ferguson et al.[11] have shown that shallow tube well groundwater can also contain substantial amounts of pathogenic bacteria.

Over the years enormous amounts of groundwater were withdrawn to meet the increasing demand for drinking and irrigation water of a rising population, which engaged more and more in agriculture for a living (Fig. 2).[6,12,13] Initially it was overlooked that this freshly pumped groundwater contained high As concentrations. Because chronic As exposure takes years to show visible symptoms on the skin, the presence of As in the drinking water and its dramatic effects on the population were only recognised ten years later by a Bengali doctor (Fig. 1a).[14,15] Unfortunately, it took another ten years for this calamity to be recognised and addressed by the international science community (Fig. 1a). Since then, reports on many aspects of As in the geo-, hydro- and biosphere followed fast and in high numbers (Fig. 1b). From then onwards, other South and South-east Asian countries, including Vietnam, Pakistan, Nepal and Cambodia have been added to the list of countries with endangering As in the groundwater.[5,16,17] This list will probably continue to grow. The alarming situation in South and South-east Asia has also led to an increased interest in the occurrence of As in other parts of the world, like Mexico, Chile, Hungary and Romania, providing essential knowledge and potential help to these regions (Fig. 3).

Biogeochemical processes controlling As mobility in South and South-east Asia

Several biogeochemical processes have been identified that are believed to contribute to the mobilisation of As from sediments in the deep aquifers of South and South-east Asia (Figs 1a, 2a,b). One of the earliest and most controversially discussed mechanism of As release is the oxidative dissolution of As-containing, grey sulfidic minerals.[18–22] The abstraction of high amounts of groundwater (for irrigation and consumption) allows oxygen to enter deeper aquifers, where it abiotically oxidises, and hence dissolves As-bearing sulfidic minerals.[18–21] However, this process not only releases As, but also causes the formation of Fe^{III}, which precipitates promptly as Fe^{III} (oxyhydr)oxides at neutral pH.[23] Because Fe^{III} (oxyhydr)oxide minerals have a high affinity for As,[23–25] the mobilised As is expected to quickly sorb to and co-precipitate with the newly forming Fe minerals or sorb to existing ones.[6] Therefore the proposed oxidative dissolution of sulfidic minerals is expected not to be a

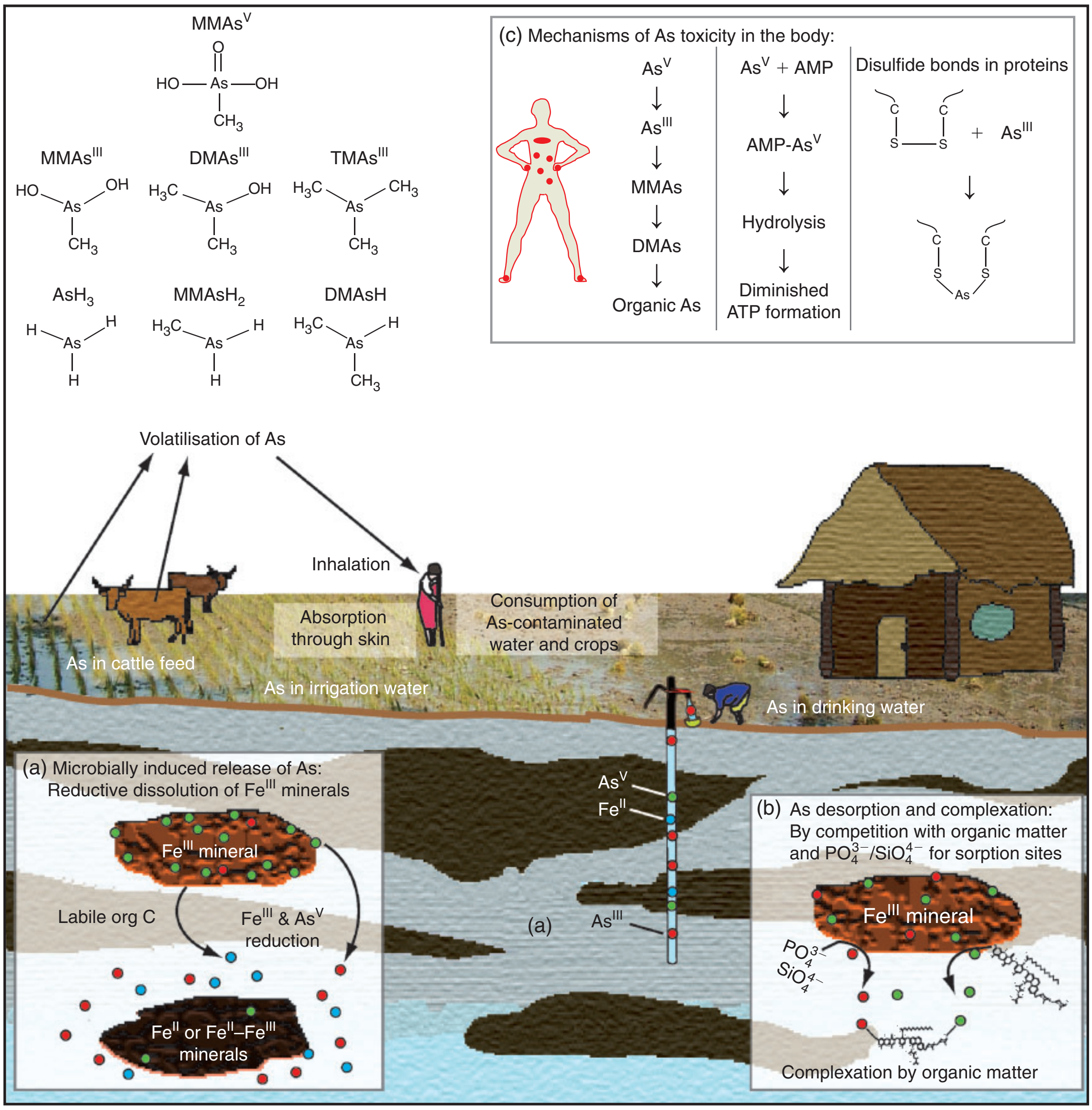

Fig. 2. Scheme summarising the cycling of arsenic (As) in the hydro-, geo-, atmos- and biosphere affecting millions of people in the highly As-contaminated regions of South-east Asia. As^{V}- and As^{III}-rich groundwater is pumped to the surface to provide pathogen-free drinking water. The water is used for drinking, irrigation of rice fields and feeding animals. Anoxic rice paddies and potentially cattle form volatile As species, such as arsines (AsH_3), monomethylated arsenic species (MMAs^{III}, MMAs^{V}, MMAsH$_2$), dimethylated As species (DMAs^{III}, DMAsH), and trimethylated arsenic species (TMAs^{III}), which are released into the atmosphere. Humans take up As by consumption of As-containing water and food, inhalation of volatile As, and absorption through skin during field work. (a): the mobilisation of As in South-east Asian aquifers is explained by the reductive dissolution of Fe^{III} minerals, which causes their dissolution to aqueous Fe^{2+} and the formation of secondary Fe^{II} and Fe$^{II/III}$ minerals. Simultaneously mineral-bound As^{V} is reduced to more mobile As^{III}. (b): In addition, the high mobility of As in Southern Asian aquifers is caused by competition of phosphate, silicic acid and organic matter with As^{III} and As^{V} for sorption sites on mineral surfaces and by the complexation of As with humics. (c): Within the body, inorganic As is transformed to organic As, As^{V} affects the energy metabolism of the body by replacing P in various metabolic processes (here an example is given for the production of adenosine diphosphate (ADP) as As^{V} binds to adenosine monophosphate (AMP) instead of phosphate. As^{III} directly affects the functional structure of proteins by binding to their disulfide groups.

main pathway of As release. Additionally, the activity of As^{III}-oxidising bacteria in these sediments would result in even more immobilised As,[26] as the forming As^{V} has a higher affinity to Fe^{III} minerals than As^{III}.[24] The presence of such As^{III}-oxidising bacteria has been verified in As-contaminated Bangladeshi and Chinese aquifers.[27,28]

In general, Fe^{III} (oxyhydr)oxides are considered as the main solids for As binding in South and South-east Asia as they are omnipresent and highly abundant in the environment,[23] and have a high capacity to bind As.[24] Nonetheless, As associated with Fe^{III} (oxyhydr)oxides can also be released by different activities of microorganisms and by abiotic processes (Fig. 2a,b). As an example, sorbed As is abiotically displaced from the surface of minerals by organic matter,[29–31] phosphate[20] or silicic acid[32–34] during competition for sorption sites (Fig. 2b). Bicarbonate[35] has been suggested as a sorption competitor as well, but its effectiveness is highly questioned.[34] Also As^{V}-reducing bacteria tackle mineral surface-bound As^{V}

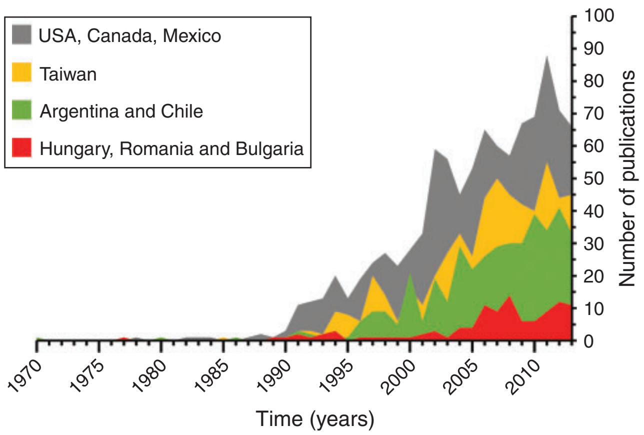

Fig. 3. Number of scientific documents on arsenic in the USA, Canada and Mexico (grey), Taiwan (yellow), Argentina and Chile (green), and Hungary, Romania and Bulgaria (red) published over the years. Number of documents found in ISI Web of Knowledge using the search parameters 'arsenic + country'.

by reducing it to As^{III},[36,37] which is considered to be more mobile (Figs 1a, 2a).[24] In contrast, Fe^{III}-reducing bacteria not only mobilise surface-bound, but also mineral-bulk-associated As (Figs 1a, 2a).[26,36,38–40] These microorganisms were suggested to dissolve Fe^{III} minerals, and hence, release the associated As.[38] Some bacteria reduce even both Fe^{III} and As^{V}.[26,37] However, reductive dissolution of Fe^{III} minerals does not always result in the mobilisation of the associated As.[41,42] Secondary Fe^{II} and mixed-valent $Fe^{II/III}$ mineral phases, for example siderite, vivianite, green rust or magnetite, form depending on the geochemistry of the environment, the rate of mineral transformation and the amount and type of initial Fe^{III} mineral. Such Fe^{II}-bearing minerals potentially re-sequester As.[22,41–49]

Support for the importance of microbially mediated cycling of As and Fe comes from a combination of 16S rRNA gene sequencing approaches of Asian aquifer sediments and from sediment microcosms. The presence of dissimilatory Fe^{III}- and As^{V}-respiring bacteria including the genera *Geobacter*, *Bacillus*, *Sulfurospirillum* and *Chrysiogenes*, has been demonstrated in many different As-bearing aquifers in South and South-east Asia.[39,40,50,51] Further evidence for supporting the role of metal-reducing bacteria for the mobilisation of As comes from incubations of As-containing sediments from South and South-east Asia, in which the natural microbial communities were shifted towards known metal-reducing bacteria.[39,50,52] In the past years, researchers have tried to elucidate whether microbial metal reduction is actually responsible for the mass mobilisation of As we observe in the Asian aquifers, and which microbial process, As^{V} or Fe^{III} reduction, contributes to a larger extent. Experimental approaches (column *v.* batch experiments, artificial *v.* sediment microcosm, etc.) and the combination of parameters (identity of Fe mineral, microbial strain, buffer, As and Fe concentrations and ratios, competitive sorbents, etc.) were diverse, leading to enormous amounts of collected data. For example, Weber et al.[53] have looked at aqueous and solid phase Fe and As geochemistry and have shown that total microbial Fe^{III} and As^{V} reduction are very closely related to each other (see also article by Rizoulis and colleagues in this research front). Hence, there is growing evidence suggesting that although sorption competition plays an important role for controlling As mobility, metal reduction is a main trigger for the release of As in these systems and that both As^{V} and Fe^{III} reduction contribute to the mobilisation of As depending on the geochemistry of the environment.

A pre-requisite for microbial metal reduction to proceed in these aquifers is the presence of an electron donor such as organic carbon (Figs 1a, 2a).[46,54] Labile natural organic matter resides in organic rich peat lenses,[2,55] but can also freshly enter As-bearing aquifers along water percolation pathways from surface waters,[56,57] or migrate as naturally occurring petroleum.[58] Another important source of labile organic carbon is cell-derived organic matter,[49,59–62] which was shown to associate with Fe^{III} minerals, when they were produced by Fe^{II}-oxidising bacteria.[60]

The amount, availability and quality of organic carbon determine the extent and rate of metal reduction. As labile organic carbon is the main driver of microbial metal reduction in these aquifers, research has focussed strongly on the origin, (re-)distribution and quality of the organic carbon present. However, organic carbon not only influences the release of As from Fe minerals by functioning as an electron donor. Organic material (humic substances) can also form mobile complexes of As^{V} and As^{III},[29,30,63–65] and also form ternary complexes of As–Fe^{III}–organic matter.[63,66] Hence, humic substances stabilise As and Fe^{III} and are therefore very relevant under reducing environmental conditions. These binary or ternary complexes prevent or at least retard a re-sequestration of the released As by soil particles or newly precipitating mineral phases (Fig. 2a).[49,67,68] However, binding of As to natural organic matter does not necessarily increase As mobility. Particulate organic matter also binds As and thereby immobilises it[69–71]; especially under the reducing conditions of peatlands and the fossil peat layers in South and South-east Asia this is of importance and often acts as a sink for As.

Different pathways of As exposure for people living in As-contaminated Asian river plains

Rural inhabitants of the Bengal basin depend almost exclusively on tube well water (Fig. 2), of which they drink ~3–6 L per person per day.[72,73] Unfortunately 46 % of the shallow tube wells (less than 150 m in depth) bear As concentrations exceeding the World Health Organizational (WHO) drinking water guideline of 10 $\mu g\ L^{-1}$ based on numbers collected in 1998–99 (see Fig. 1a for the development of drinking water quality guidelines and agency limits),[13] indicating that many people in this region are widely exposed to toxic As. In addition, South and Southern Asia is one of the most active agricultural areas of the world, and also relies on As-laden tube well water for irrigation (Fig. 2).[6,74] Through irrigation of paddy soils with As-rich groundwater from the tube wells, As may be enriched in the soils over the years.[75] The regular flooding of paddy soils with monsoonal rains may counteract the enrichment of As in many agriculturally used areas in Bangladesh, although this will probably not prevent the enrichment of As in the soils.[76] The presence of As in paddy fields is especially consequential for the locally produced staple food rice,[77] which has been shown by loss of rice growth yield with increasing As soil concentrations in field studies in Bangladesh by Panaullah et al.[78] Even though commercially available rice grown all over the world was shown to contain As, rice from Bangladesh and China hold larger fractions of the more toxic, inorganic As species.[79] Farmers, in particular, are heavily exposed to As, as their rice-based subsistence diet relies on locally grown rice.[79] In fact, it has been discussed that As-bearing rice can substantially contribute to the intake of As by villagers in addition to drinking water.[80,81] Local people consume ~0.42 kg of dry weight rice per day, meaning that between 13.4–525 μg of As is ingested daily, depending on the type of rice, the growth conditions and the As content of the soil the rice was grown in.[82] Cooking rice in As-laden well water showed that most substances present in the cooking water, including dissolved As are non-selectively absorbed by the rice grains,[83,84] suggesting that an even higher amount of As is consumed. Based on studies with swine as model organisms and in vitro studies, it was concluded that the bioavailability of inorganic As in the gut is almost 100 %,[82,83] and one can expect that also in humans most of the consumed As actually enters the body's blood circulation.[79] He and Zheng[85] have actually conducted an arsenic bioaccessibility study with rice and could demonstrate that most As entered the body, but was also efficiently excreted through urination. Meharg et al.[79] have modelled the actual risk of the Asian population of getting cancer from consuming As and showed that the upper cancer risk goal targets of the WHO (1 in 100 000) and US Environmental Protection Agency (EPA) (1 in 10 000) are exceeded.

Field workers are additionally exposed to As during work in the field, as they often stand barefooted for hours in flooded paddies (Fig. 2). However, As absorption through the skin is considered a minor pathway of As uptake into the body.[86] In contrast, the inhalation of atmospheric As could contribute substantially to the overall uptake of As into the body,[87] especially in industrial areas with a high output of atmospheric As[88] and burning of As-bearing straw present in dried cow dung.[89] Also field workers in South and Southern Asia are exposed to atmospheric As when working in rice paddies (Fig. 2). Volatile methylated As species mainly originate from the methylating activity of microorganisms in the paddy soil (Fig. 2).[90] Mobile or mineral-bound As^{V} is microbially reduced in the soil to As^{III},[36] which in turn is oxidatively methylated to monomethyl As^{V} ($MMAs^{V}$) by the oxidative transfer of a methyl group from *S*-adenosyl-L-methionine (SAM).[91,92] Methylated As^{V} species are subsequently reduced to methylated As^{III} species like monomethyl As^{III} ($MMAs^{III}$) and again oxidatively methylated leading to the formation of dimethylated ($DMAs^{V}$ and reduction to $DMAs^{III}$) and trimethylated As species ($TMAs^{V}$ and reduction to $TMAs^{III}$) in the soil, which are all volatile except $DMAs^{V}$ and $TMAs^{V}$.[92] According to Mestrot et al.,[93] the release of arsines from soil contributes up to 2.6 % to the global input of atmospheric As. Further on, rice plants are known to take up inorganic and methylated As species,[90] and even release $TMAs^{III}$ to a minor extent into the atmosphere.[94] A third, possibly very minor origin of methylated As species in the atmosphere are cattle (Fig. 2). In South and South-east Asia, cattle roam on rice paddies and feed on As-enriched paddy water and feed straw.[95] The ingested As is potentially accumulated in the meat,[95] but could theoretically also be released as volatile organo-As species together with methane, which cattle are known to produce during digestion.[96]

Chronic and acute cellular arsenic toxicity in microorganisms, animals and plants

Arsenic, once in the body, is known to evoke several cellular responses depending on the As concentrations leading to acute or chronic toxic effects. After ingestion, a large fraction of the As is excreted in the urine within hours and days.[18,85,97] The amount of excreted As depends on the type of consumed food, As species present and the health status of a person, although it is widely accepted that most of the excreted As is released in the form of organic derivatives.[98] Some organically bound As such as arsenobetaine is often just passed through the body unchanged.[99] Additional minor portions of the ingested As are relieved through faeces, hair, nails, skin and lungs (Fig. 2c).[73,97] In the circulatory system of the body, ~96 % of the inorganic As is bound to plasma components of the blood, where it is transported throughout the body.[73] DMAs were also reported to bind to red blood cells, reducing the ability to bind oxygen.[97] Longterm As presence in the blood causes gangrened blood vessels, as evidenced by the blackfoot disease in Taiwan,[100] and As accumulation and excretion through the skin causes the known skin manifestations generally referred to as arsenicosis.[97] Body organs absorb As derivatives, which results in cancer of the lungs, skin, intestine, kidneys and bladder.[73] Owing to the sufficient evidence of As carcinogenicity in humans, As is classified as a group 1 carcinogen.[101] At least a doubling of the lifetime mortality risk from cancer in Bangladesh was estimated because of As in drinking water,[102,103] as well as increased infant mortality.[104] Intellectual and motor functions were described to decrease in children.[105,106] Cardiovascular diseases are common.[107] A potential role of As in the development of type-2 diabetes has been suggested and is currently under closer investigation.[108,109]

In terms of acute toxicity of As, it is generally known that organic and inorganic As^{III}-bearing species are more toxic than As^{V}-containing derivatives.[110,111] Acute toxicity in different animals is determined by the lethal death of 50 % of the test subjects (LD_{50}). For human adults a dose of 1–3 mg of inorganic As per kg bodyweight can result in death.[112] For chronic exposure of As the level of toxicity of the different As compounds is under debate.[97,113] It is often believed that the body methylates inorganic As for detoxification.[98] Methylation of the inorganic As species occurs in the liver, where methyltransferase enzymes transfer methyl groups from SAM using the essential co-factor glutathione (GSH) (Fig. 2c).[97] However, As^{III}-containing compounds also bind to the sulfhydryl groups of GSH, decreasing its performance.[114] One of the main pathways of As^{III} toxicity is the binding to sulfhydryl groups in proteins, forming a dihydrolipoylarsenite chelate, which disrupts the 3-D structure of proteins and enzymes (Fig. 2c).[97] That means that essential enzymes functioning in energy generation, DNA repair, etc. are impaired. In contrast As^{V}, being a structural homologue of phosphate, can directly compete with phosphate and for example disrupt oxidative phosphorylation[97] and glycolysis[110] (Fig. 2c). In these processes As^{V} binds to adenosine monophosphate (AMP), adenosine diphosphate (ADP) or for example glyceraldehyde 3-phosphate instead of P (phosphate), respectively producing AMP-As^{V}, ADP-As^{V} or 1-arseno-3-phosphoglycerate (Fig. 2c).[110,115] These compounds are highly unstable and hydrolyse spontaneously, a process called arsenolysis.[97,115] Hence, the production of the metabolic energy carrier ATP is impaired by As^{V} replacing P on the substrate and mitochondrial level.[110] Additionally, As^{V} could also replace phosphorus in DNA,[116] although the existence of such an As-containing DNA molecule has been questioned recently.[117–121] Furthermore, $MMAs^{V}$ and As^{V} were shown to structurally perturb cell membranes.[122]

To summarise, different inorganic and organic compounds of As disrupt main, energy, structural and reproducing functions of cells in animals and plants. Many different symptoms of chronic As poisoning have been observed worldwide. Which symptoms develop depends on the kind of exposure, concentration and uptake of different As species and the person's dietary and health status.

Health and socio-economic effects of the As crises in South and South-east Asia

According to a survey performed by the British Geological Survey (BGS) and the Department of Public Health Engineering (DPHE) in Bangladesh,[13] over 92 million people in Bangladesh alone are exposed to drinking water with elevated As concentrations. However, the number of people affected by As in the US, Mexico, Argentina, Chile, Bolivia, Hungary and Romania should not be underestimated. Comprehensive information on the number of As-affected people can be viewed in Ravenscroft et al.[5] The problems caused by As in the groundwater of South and South-east Asia are far-reaching and multifaceted. The most widely known effect is health issues (Fig. 2c).

The presence of As in irrigation and drinking water in South and South-east Asia also causes severe socio-economic problems.[4] The social acceptance of people showing visual signs of arsenicosis often decreases,[123] as non-infected villagers unknowingly suspect leprosy and avoid the person.[18] If only one person in a marriage is affected, that person is often divorced and, sometimes including the children, sent back to the families.[14,18] Wedding arrangements are cancelled or no matrimonial agreement can be made for affected sons and daughters.[14] People with obvious skin lesions are not offered jobs,[18] or are asked to leave.[123] Often affected individuals only dare leaving the house at night. In particular, people with a lower income and subsequently higher dietary deficiencies are more often struck by arsenicosis,[124] decreasing the chances of a better life for these people even more.[123]

The production of food in terms of yield and quality are also notably impaired in South and South-east Asia.[125,126] In Bangladesh, ~4 million hectares of the agriculturally used land is under irrigation, of which 3 million hectares are watered with tube well water.[125] Bangladeshi soils contain background contents of 4–8 mg As per kilogram, although these levels can increase substantially in areas, where As-contaminated water is used for irrigation.[127–130] Agricultural products, especially the mainly grown crop rice, accumulate a lot of As in the edible parts.[95] Constant As exposure to rice plants results in a decreased growth yield, grain number and size.[75,127,131–133] In fact, the uptake of too much As by rice would completely inhibit grain formation, which is known as straighthead disease.[134] Khan et al.[133] have shown that irrigating paddy soils with As-containing irrigation water leads to a higher bioavailability of As in these soils, and hence, to a lower biomass of the rice. A loss in rice yield would negatively affect agricultural sustainability, national economies and the food security and nutritional status of the farmers,[84,126,127,133,134] as rice accounts for 76 % of their average calorie intake.[135] However, as Asian rice is exported worldwide, the health of people from other parts of the world could also be negatively affected.[84]

Strategies for remediation and removal of arsenic from drinking water and soils

Some Asian governments have responded to the alarming situation caused by As in their countries. In Bangladesh for example, the Ministry of Local Government, Rural Development (LGRD) and Cooperatives of the Government formed a Ground Water Task Force (GWTF) in 2001, which recommends on legal and administrative issues, screening and monitoring of tube wells, mapping of aquifers, managing ground water and propose research initiatives (A. Zahid, Water Development Board, Dhaka, pers. comm., 2013). A 'National Policy for Arsenic Mitigation' was enacted in 2004,[136] which advised the regular testing of tube well water for As content.[137] Henceforth, villagers were advised to share 'safe wells' with low As in the pumped water, which were labelled by green paint.[137] The sharing of tube wells and ensuring safe water has actually worked well in the past, although on an insufficient scale.[137] However, the enormous challenge for a government to test these wells regularly has been recognised and alternative monitoring programs such as supporting private companies to test the water and using field kits has been suggested.[137] Furthermore, the installation of deep aquifer community wells has been implemented in order to provide safe drinking water as well.[137] Water pumped from these sources also require regular monitoring for As.[137]

The 'National Policy for Arsenic Mitigation Act' also promoted the use of safe water giving priority to surface water over groundwater sources.[138] The GWTF advised not to drill new tube wells in As-affected areas as long as other alternatives, that is, surface water treatments, dug wells, pond sand filters, rain water harvesting, etc., are available (A. Zahid, pers. comm., 2013). However, many Bangladeshi were rarely willing to switch from tube well water to home-treated surface and pond water as they doubted the quality of the water.[138] This doubt seemed justified[139] and partially self-inflicted as sewage and industrial outputs almost uncontrollably enter surface water bodies and the household filters (e.g. Sono filters[140]) used to treat water were often not taken care of correctly by the owners.[138,141]

Local researchers and social workers responsible for educating the local population work closely together with international NGOs and international research institutes in order to inform villagers about As, to understand the below-ground fluxes of As and to develop and establish cost-efficient water cleaning technologies. Unfortunately the geochemical parameters of the As-affected aquifers in the different South and South-east Asian countries vary drastically, making it difficult to provide a widely applicable technology to remove As from drinking water.[142] The aquifers of the Red River delta in North Vietnam, for example, contain a lot of aqueous Fe^{2+} besides As.[56,143] There, the villagers have employed household sand filters in their backyards that are filled with sand from the Red River (Fig. 4).[143] The aqueous Fe^{2+} present in the freshly pumped anoxic water is oxidised as soon as it enters the filter and the precipitating Fe^{III} (oxyhydr)oxides bind and remove As from the water very efficiently.[143] Besides these household sand filters being very efficient and a low cost option to remove As from groundwater, they are often in use for years without reaching the maximum capacity of As uptake. Now researchers are investigating the hydrogeochemical, microbiological and mineralogical mechanisms leading to the high efficiency of As removal by these filters (see article by Andreas Voegelin in this research front). The presence and effect of As- and Fe-metabolising bacteria in these filters is investigated to understand the filter's efficiency to remove As and the potential of pathogenic bacteria to develop in the filter systems and threaten the health of the users is determined (A. Kappler, pers. comm., regarding current work in progress).

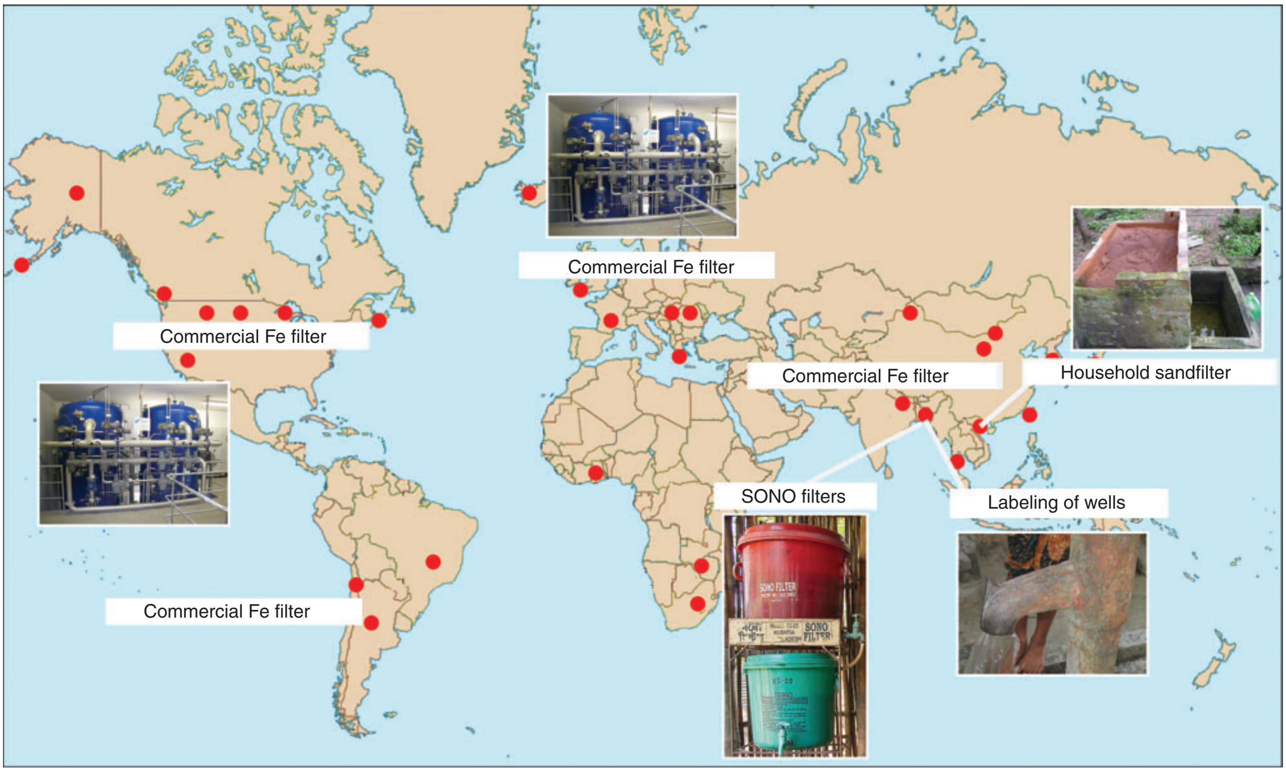

Fig. 4. Arsenic-bearing areas worldwide (red dots) and the respective main technology used in these regions to provide drinking water with As concentrations below 10 μg L^{-1}.

Many other ground water aquifers in South and South-east Asia do not, unfortunately, contain aqueous Fe^{2+} at such high concentrations, making this Fe^{II}-dependent household sand filter system used in Vietnam not applicable for other regions.[142] Many commercially available As filter systems are based on the ability of highly porous Fe^{III} (oxyhydr)oxides to bind As (Fig. 4).[67,144] Other commercially available filter systems work with, for example, activated carbon, silicates or titanium oxides (see also articles by Zaccheo and colleagues and Hug and colleagues in this research front).[145] Such filter systems are in use worldwide and are often part of the municipal cleaning water facilities (GEH Wasserchemie (a drinking water filter producing company), Germany, pers. comm.), but are too expensive to be purchased by the villagers. Many different kinds of As removal technologies including ion exchangers, membrane filters, activated aluminium, coagulation and lime softening were tried to be successfully implemented in As-affected countries. Because these technologies require sophisticated technical systems, they are not appropriate for household use in developing countries and could not be manifested on a broad scale. Filters with a manufactured composite iron matrix, so called Sono filters, consist of Fe, charcoal, sand and brick and were shown to successfully remove As from water[140] and were recommended for use throughout Bangladesh by the government (Fig. 4).[123] These filters are probably implemented most widely in Bangladesh at the moment, although not as successfully as initially hoped because of unaffordability by the very poor and low sustainability.[141]

Arsenic in ground water bodies could also be directly immobilised in the subsurface instead of being removed later after the water has been pumped and contains As. Spiking groundwater aquifers with nitrate leading to nitrate-dependent Fe^{II} oxidation and Fe^{III} mineral precipitation or with sulfate in combination with organics leading to sulfate reduction and sulfide mineral precipitation was suggested as a potential strategy to immobilise As,[61,146–149] although only nitrate seemed feasible as an agent reducing aqueous As concentrations below the WHO recommended drinking water guideline of 10 μg L^{-1}.[61,146]

However, the consequences of spiking groundwater aquifers with nitrate should be considered with great care. Nitrate could also lead to the mobilisation of other toxic compounds such as manganese,[146] lead to an undesirable eutrophication of these aquifers over time, and can potentially stimulate the formation of the greenhouse gas N_2O.[150] Additionally, nitrate is potentially harmful for human health when ingested through drinking water.

Elevated As concentrations in contaminated surface environments, such as rice paddies, could be removed with plants such as hyacinths or the brake fern *Pteris vittata*.[145,151] In fact, using plants to remove toxic compounds from water – a process called phytofiltration – seems to be a promising strategy.[152] However, the remediation of agricultural soils is also of concern in order to provide high quality rice with low As contents. Different irrigation schemes such as growing rice on non-flooded, oxic soils were shown to be successful for decreasing the accumulation of As in rice,[130,153–155] but led to an increased uptake of other toxic metals such as cadmium.[156] Hence, phytoremediation could actually be useful for the sanitation of As-bearing paddy soils. However, this biological remediation technology is often limited by the plants growth performance (biomass growth and amount), its ability to access metals beyond its rhizosphere and metals strongly bound to soil particles.[157] The activity of microorganisms in the soil could actually support the metal-extracting activity of hyperaccumulating plants.[157] Plant-growth promoting bacteria were shown to increase the root radial zone to access contaminants further away.[157] Also mineral solubilising bacteria, such as Fe^{III}-reducing bacteria, could mobilise mineral-associated metals.[158] Such mobilised metals could be kept mobile by chelator-excreting microorganisms, and eventually be taken up by plants when they move into the rhizosphere.[157] Combing the activity of Fe^{III}-reducing bacteria in flooded rice paddies with the hyperaccumulating activity of a suitable plant such as *P. vittata* might be worth investigating in the future.

Risk prediction of arsenic contamination

In many surveys and studies, groundwater As concentrations were found to decrease with increasing tube well depths.[13,72,159,160] These deeper aquifers were often tapped with so called deep tube wells to provide As-free drinking water to the population. However, it was shown that As concentrations vary over time in the same aquifer, and hence, tube wells with previously no detected As could suddenly contain As and pose a threat to the population.[55] These changing As contents in the aquifers are often imposed by strongly fluctuating water tables caused by, for example, extensive abstraction of water for agricultural or municipal use.[6,161] Hence, monitoring and constant analysis of the As output by individual wells was suggested,[159] followed through[136] and switching to known uncontaminated wells was advised.[162] Chakraborti et al.[72] argued that the uncontrolled and careless installation of even deeper tube wells into supposably uncontaminated aquifers and unrestrained withdrawal of irrigation ground water without effective agricultural management results in further spreading of the As in other aquifers and an increased risk to the population. In fact, in the National Policy for As mitigation Act of 2004 it is stated that the Bangladeshi Government was reluctant to tap deeper aquifers, because of cross-contamination of As from shallow to deep aquifers (A. Zahid, pers. comm., 2013).[136] However, the Bangladeshi population was often not willing to accept treated surface water for providing drinking water, so more and more deep tube wells were used for providing water for domestic use only, and not for broad-scale purposes like irrigation or municipal functioning. The installation of these deep tube wells actually brought a short-term relief of As exposure to the villagers,[163] although higher As contents in these deep aquifers have recently been reported in the Bengal delta.[164–166] From these measurements it remained unknown whether these elevated As concentrations were caused by natural sources or anthropogenic input. Badly installed and constructed wells can cause cross-contamination by aquifers from above.[163] However, there is only limited evidence for a large scale contamination of deeper aquifers with As over time.[167,168] In Vietnam it was shown that lateral As migration from an As-laden Holocene aquifer (younger) infected an As-free Pleistocene aquifer (older) 150 m away due to excessive groundwater abstraction.[169] Our current understanding of As cross-contamination between aquifers shows that regular monitoring and assessment of well water is absolutely essential for the South and South-east Asian population to be provided with water acceptable for drinking.

Large-scale predictions on the presence, distribution and fluxes of As in the underground[17,170–174] could be used in support of well testing (view article by Kocer and colleagues in this research front). Lado et al.[171] used geological and hydrogeochemical proxies to predict safe and unsafe areas with respect to geogenic groundwater As contamination throughout China, where no data of As in the underground was available. Previously it has already been noted that areas bearing elevated As concentrations coincide with a low relief topography that gently rises to the west and east of valleys in Cambodia.[173] These features correlate with the boundary of sediments originating from the Holocene, which are known to contain As.[173] Lado et al.[171] have identified the following parameters as the most important proxies: Holocene sediments, soil salinity, fine subsoil texture, topographic wetness index and the density of rivers to correlate positively with high As concentrations, whereas slope, distance to rivers and gravity are negatively correlated. Even though the authors suggest that their model should be verified with field data first, such an approach could be taken as a first proxy to estimate a potential risk of As exposure to a population in various parts of the world.[171] As more and more countries have been identified in the past 20 years to bear elevated As concentrations in their groundwater,[175,176] predicting the presence of As in groundwater and its potential risk to the population is of importance. Now that we have reached a deeper understanding of the processes leading to the release of As observed in South and South-east Asia, the challenges of future research are to identify As-bearing aquifers as early as possible, preferably before drilling new tube wells, to monitor and to predict As fluxes in the underground and to provide well functioning and cost-effective cleaning water technologies that are widely accepted by the inhabitants of this region.

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