

Arsenic Contamination of Ground Water: Disastrous Consequences in Bangladesh

Bangladesh is currently confronted with what is probably the largest case of mass poisoning in the history of humankind. About one third of her 125 million inhabitants are being slowly poisoned by drinking water that contains arsenic. The consequences have already affected tens of thousands: skin discoloration, ulcers, and cancer of the skin, lungs and intestines. Experts both in Bangladesh and at the World Health Organization (WHO) suspect that nearly 20 million people are, to a greater or lesser extent, already suffering from arsenic poisoning. If non-polluted drinking water supplies are not restored soon, arsenic poisoning might soon be the most frequent cause of death in Bangladesh. EAWAG scientists are presently concentrating on the development of a simple solar arsenic-removal-procedure (SORAS).

In Bangladesh, more than 90% of the population now drinks ground water. Previously, their drinking water supplies came from rivers and lakes, which continuously caused epidemics of cholera and diarrhea. The transition to drinking ground water, which started about 30 years ago, was quite rapid since it only took one day for a few workers to drive steel piping through the soft sediments to depths from 5 to 50 meters; the ground water was then simply pumped by hand to the surface. During the so-called "drinking water decade" (1980–1990) supported by the WHO and UNICEF, about three million ground water boreholes were sunk throughout Bangladesh. This drastically reduced the waterborne-disease epidemics, but the current arsenic crisis overshadows that success. The first cases of arsenic poisoning reportedly occurred between 1987 and 1992 in northeastern Bangladesh. Almost no official attention was paid to the problem until various organizations insisted and an international conference was held in Dhaka in 1998.

Arsenic Contamination – a Worldwide Problem

Ground water used for drinking is contaminated by arsenic in many parts of the world (Fig. 1). In some cases, this situation is attributable to human causes such as mining, fungicides, pesticides, and timber preservatives. Mostly, however, the cause is natural

arsenic which occurs in the subterranean strata.

Arsenic can be dissolved in water-bearing sediments through biogeochemical processes, thus polluting ground water, springs and rivers. While the arsenic content in the Pacific Ocean is only 1.5 µg/liter, it varies in lakes and rivers from less than 1 µg/l up to several thousand µg/l. For humans 150–300 mg of arsenite (As_2O_3) are deadly, but it is not as easy to determine the chronic poisoning dose based on daily intake in

food and water. This depends on numerous factors such as the nutrition, general health care, age, sex and genetic preconditions.

The maximum limit currently set for arsenic content in drinking water is 50 µg/l in most countries, including Switzerland, but in many parts of the world this limit is exceeded. Based on epidemiological studies, the WHO recommends setting a lower limit of 10 µg/l, so that many regions now must be regarded as problematic. Arsenic concentrations of 10–50 µg/l are found in Switzerland, for example in Astano (TI), as well as in Alsace and many other parts of Europe. According to the latest findings, arsenic is one of the most problematic water contaminants worldwide.

Arsenic in surface water occurs in two states of oxidation:

- in the trivalent form As(III), mainly as arsenite (up to pH 7 as H_3AsO_3)
- in the pentavalent form As(V), mainly as arsenate (from pH 7 as $\text{H}_2\text{AsO}_4^-/\text{HASO}_4^{2-}$).

There are also numerous organic arsenic compounds formed by microbial activity and by metabolic processes in humans and animals.

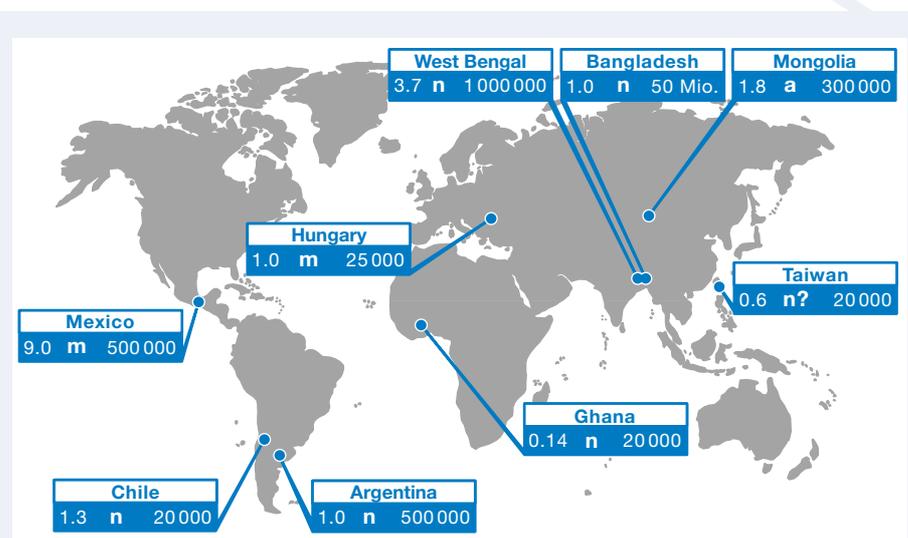


Fig. 1 Regions with high arsenic concentrations. On the left in each box is the maximum detected arsenic concentration in mg/l. The suffix indicates the type of source (n = natural, m = mining, a = agriculture). The number on the right shows how many people are affected.

Chemical transformations and the properties of various arsenic compounds determine not only the transport and distribution of arsenic in the environment, but also the most effective ways of reducing its content in drinking water. Figure 2 shows how transport and erosion processes since the last Ice Age might have brought arsenic into the Bangladeshi ground water, according to generally accepted hypotheses. The primary sources of arsenic are ores such as arsenopyrite (FeAsS) found in the Himalayas. They are oxidized in the atmosphere, or by water containing oxygen, to release As(III) , Fe(II) and sulfate. In the presence of oxygen at neutral pH values, Fe(II) is oxidized within a few minutes or hours to $\text{Fe(III)(hydr)oxides}$. Within days, As(III) is also oxidized to As(V) . $\text{H}_2\text{AsO}_4^-/\text{HAsO}_4^{2-}$ adsorbs to $\text{Fe(III)(hydr)oxides}$, with which it is deposited in sediments, while the sulfate is washed out. Since As(V) in $\text{Fe(III)(hydr)oxide}$ is practically insoluble, it does not pollute water. The Bangladesh flood plain contains a great deal of organic material, however, which provides nutrition for microorganisms. When all available oxygen has been consumed, the microorganisms set about to reduce the $\text{Fe(III)(hydr)oxides}$, whereby the Fe(II) and As(V) are released and then reduced to As(III) . These processes explain the ground water composition: anoxic, 200–400 mg/l HCO_3^- , 0–20 mg/l Fe(II) , 0–2000 $\mu\text{g/l}$ As(III) and As(V) , <3 mg/l sulfate. The iron and arsenic content are usually correlated.

Removing Arsenic

To remove arsenic, the As(III) release process must be reversed. This is done in industrial plants by oxidizing As(III) with chlorine, hypochlorite, ozone or other oxidizing agents which results in the formation of As(V) ; Fe(II)- , Fe(III)- or Al(III)- salts are additionally used as flocculation agents. As(V) adsorbs strongly into the Fe(III)- or Al(III)- hydroxides, with which it is then precipitated and removed. In industrialized nations, it is possible to reduce the As -content to

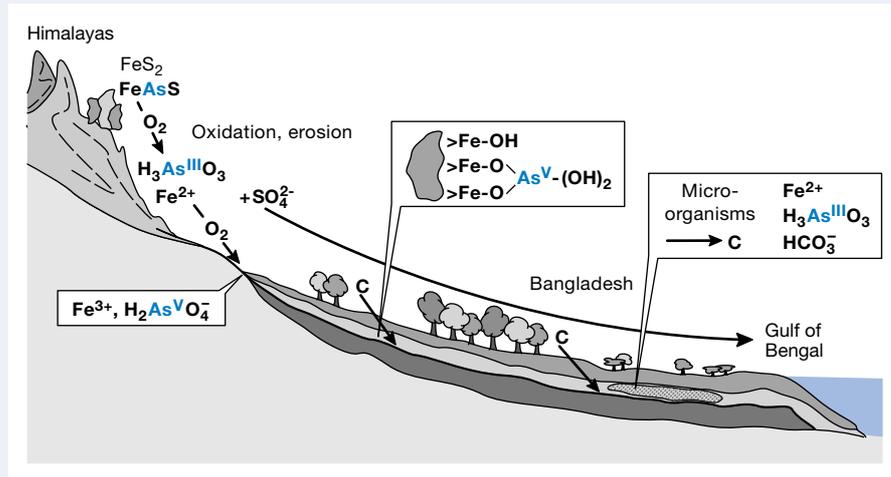


Fig. 2 Natural sources and distribution of arsenic in Bangladesh.

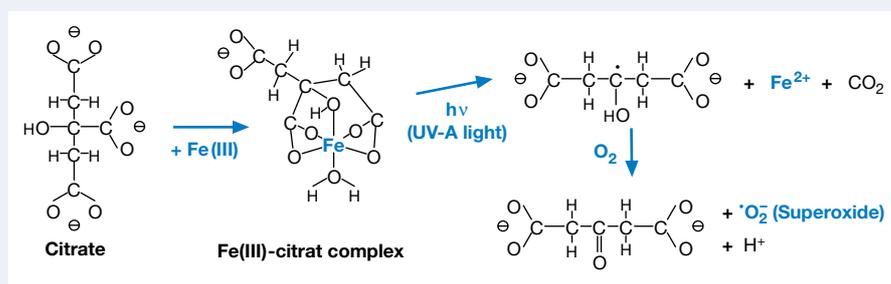


Fig. 3 Photochemical generation of oxidizing oxygen species with absorption of UV-A light by Fe(III) complexes.

<10 $\mu\text{g/l}$, thereby eliminating all health risks. For financial reasons, and due to the completely decentralized drinking water supply system, large industrial decontamination plants are not possible in Bangladesh. Instead, technologies are required with which small communities and villages can decontaminate their own drinking water at the lowest possible cost. Most of the arsenic-polluted wells in Bangladesh contain sufficient iron for successful decontamination. The As(III) must first be oxidized as completely as possible, and afterwards the As(V) adsorbed to the $\text{Fe(III)(hydr)oxide}$ can be removed by flocculation and precipitation or by filtration.

Purification by Sunlight

Some years ago, an Australian team patented a process for the photochemical oxidation of As(III) in strongly acidic mining effluents. However, this process is not suitable for the Bangladeshi ground water, which is neutral (pH 7). Organic ligands, especially polycarbonic acids, are known to form photoactive complexes with Fe(III) . Earlier EAWAG studies on the photochemical reduction of toxic chromium(VI) to the far less toxic Cr(III) demonstrated that citrate, which is found in numerous fruits, is very active

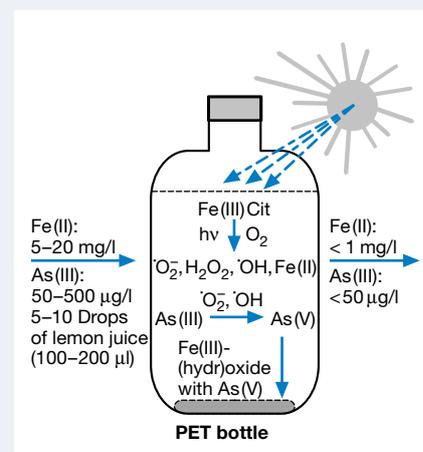


Fig. 4 Solar oxidation and arsenic removal in PET bottles.

even at pH 7. Figure 3 shows the formation of Fe(III)-citrate complexes and the photochemical generation of oxidizing oxygen species such as superoxide (O_2^-). Along the same lines as the successful SODIS water disinfection process, a small team of EAWAG chemists and engineers started development work last year on a practical method for removing arsenic from drinking water in Bangladesh. The new SORAS process (Solar Oxidation and Removal of Arsenic, Fig. 4) is amazingly simple. Citrate or lemon juice is added to the

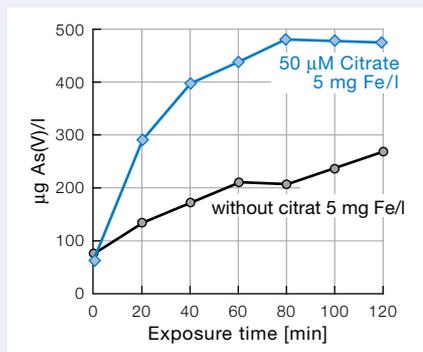


Fig. 5
Acceleration of As(III) oxidation by citrate at pH 7.

water, which is transferred into PET bottles and left in the sun for some hours. The bottles are then placed upright and left overnight, after which the purified water is either decanted from the precipitated Fe(III)-(hydr)oxide particles or passed through textile filters.

In order to reproduce Bangladeshi conditions in the laboratory, synthetic ground water was used that contained known concentrations of Ca, Mg, HCO₃, As, Fe as well as silicate, phosphate and dissolved organic carbon. Adding 500 µg/l As(III) and 5 mg/l Fe(II) to the air-saturated water creates a situation similar to that of anoxic ground water saturated with air by shaking for one or two minutes. Once 50 µM citrate or 3–6 drops of lemon juice per liter have been added, the water is poured into PET bottles and exposed to UV-A lamps (ca. 80 mW/m²). In the presence of citrate, the As(III) is quickly oxidized to As(V), as shown in Figure 5. Another advantage of adding citrate is that the Fe(III) in the treated water flocculates rapidly and is easily removed by precipitation.

Optimization for Practical Use

Comparison of the laboratory tests with field trials in Bangladesh (Fig. 6) indicate significant differences in the results. At pH values of 6.5 to 8.0, the arsenic removal efficiency in the laboratory was 80–90%, while removal efficiencies in the field varied widely. There is a possibility that phosphate (0–2 mg/l) and silicate (up to 70 mg/l) in the Bangladeshi ground water may have influenced the arsenic removal, but this was not confirmed in the laboratory where neither phosphate nor silicate had a large effect on photo-oxidation. Although these ions compete with the adsorption of arsenate in Fe(III)(hydr)oxides, the removal of As(V) in the presence of 5 mg/l Fe was only slightly affected.

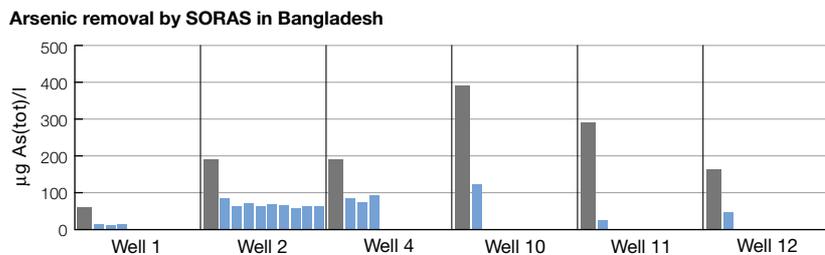
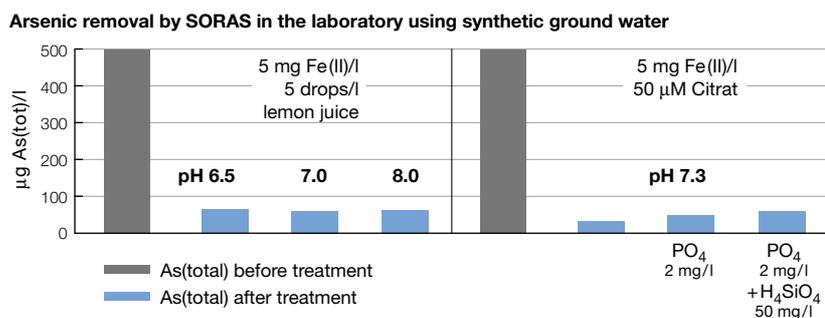


Fig. 6
Arsenic removal rates in laboratory tests and field trials.

It may be possible to optimize the SORAS process by adding citrate at different times to allow for dark periods before exposure to sunlight, by changing the exposure period, or by repeatedly adding citrate. The reasons for these various possibilities is that during the aeration and exposure of the ground water to sunlight, several reactions take place both in parallel and in sequence. Even in the dark, Fe(II) is oxidized within 10 to 60 minutes to numerous Fe(III) species, as shown by the turbidity and brown coloration [formation of Fe(III)(hydr)oxides]. The composition of the water changes continuously during this time. Both in the dark, and even more so in sunlight, many oxidation and reduction reactions are possible. Based on a complete list of reactions, the system could be numerically simulated and optimized by computer methods; but this is presently only possible to a limited extent due to the large number of reaction constants that are still unknown.

Research Needed for Optimized Technology

Reactions greatly involving iron and manganese oxidations and reductions affect the distribution of contaminants and hence the quality of ground water. If the relevant reactions are known, the water quality can be improved by appropriate measures, both before and during drinking water extraction. By injecting oxygen into the sediments around boreholes, for example, the iron and manganese content in water can be reduced, and possibly the arsenic content as

well. Solar treatment methods have great potential for disinfecting drinking water and for removing inorganic and organic pollutants.

The development of appropriate technologies depends, however, on a detailed knowledge of the basic reactions involved in complex technical processes. While simple technologies must be used in developing countries, well-equipped laboratories in the industrialized world are needed to acquire the necessary knowledge. In the long term, high-capacity water treatment plants will have to be installed in developing countries, at least in heavily urbanized regions. This will, of course, necessarily depend on know-how and teamwork with the industrialized nations.



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Information on the arsenic crisis in Bangladesh:
<http://bicn.com/acic> (West Bengal and Bangladesh arsenic crisis information center).

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