British Geological Survey
NATURAL ENVIRONMENT RESEARCH COUNCIL

Water Quality Fact Sheet:

Arsenic

WaterAid

WHO provisional guideline value: 10 µg/L
National standard in most countries: 10 µg/L or 50 µg/L
Typical range in groundwater: usually <10 µg/L (but up to several thousands of µg/L)

This is one of a series of information sheets prepared for a limited number of inorganic constituents of significant health concern that are commonly found in groundwater. The sheets aim to explain the nature of the health risk, the origin and occurrence of the constituent in groundwater, the means of testing and available methods of mitigation. The purpose of the sheets is to provide guidance to WaterAid Country Office staff on targeting efforts for water-quality testing and to encourage further thinking within the organisation on water-quality issues.

Health effects

Arsenic is a trace element found at variable concentrations in the atmosphere, soils and rocks, natural waters and organisms. It is mobilised in the environment through a combination of natural processes such as weathering reactions, biological activity and volcanic emissions as well as through a range of human activities, including mining, industry and agricultural use of arsenical pesticides. Of the various sources of arsenic in the environment, drinking water poses potentially the greatest threat to human health.

Arsenic has long been recognised as a toxin and carcinogen. Long-term ingestion of high concentrations from drinking water can give rise to a number of health problems, particularly skin disorders, of which the most common are pigmentation changes (dark/light skin spots) and keratosis (warty nodules, usually on the palms and feet). A causal link has also been established between chronic ingestion of arsenic and development of a number of cancers, particularly skin, bladder and lung cancer (e.g. Smith et al., 1992; 1998). Additional arsenic-related health problems include cardiovascular disorders (hypertension, heart disease, 'blackfoot disease' and related gangrene, Raynaud's syndrome,), as well as gastrointestinal, haematological, neurological, respiratory and hepatic diseases and diabetes mellitus. Several of these symptoms have been well-documented in known groundwater arsenic problem areas, such as Bangladesh, north-east India, Taiwan, northern China, Mexico, Chile, Argentina, Thailand and parts of Burkina Faso. Some studies have shown a clear dose-response relationship for development of cancer and other diseases from chronic ingestion of high-arsenic drinking water. However, other factors such as nutritional and general health status and water chemistry (e.g. dissolved iron concentration) can also affect disease outcomes. It has been estimated that the combined lifetime cancer risk from drinking water with a concentration of 50 µg/L could be as high as 1 in 100 (NRC, 1999). However, there remains much debate over the relationship between arsenic dose and response at low intakes of 50 µg/L or less (e.g. Smith et al., 1992, 2002; Clewell et al., 1999; WHO, 2004).

A number of studies have indicated latency periods of several years before clinical symptoms of arsenic-related skin disorders and cancer become apparent. This explains in part why many of the problems in developing countries have only recently emerged despite several years of groundwater use. Many of the advanced and most serious clinical symptoms are incurable, although many of the mild early symptoms can be mitigated by supply of low-arsenic drinking water. Early detection of arsenic in drinking water and provision of acceptable alternatives is therefore important and the element warrants special monitoring in potentially vulnerable groundwaters (World Bank, 2005).

As a result of much accumulating evidence for the chronic toxicity of arsenic in drinking water, the recommended and regulatory limits of many authorities have been reduced in recent years. In 1993, the WHO guideline value for As in drinking water was provisionally reduced from 50 µg/L to 10 µg/L on health grounds. This value was maintained in the WHO (2004) guidelines. The recommended value has been set at the practical quantification limit and remains provisional. At present, most developing countries continue to use the 50 µg/L value as a national standard, largely on the grounds of analytical capability and practicalities of water treatment.

Occurrence in groundwater

Arsenic concentrations in natural waters can vary over more than four orders of magnitude. Groundwaters are particularly vulnerable to accumulation of high arsenic concentrations because of water-rock reactions and the high ratios of solid to solution in aquifers compared to surface waters. High arsenic concentrations can occur locally in surface waters (as well as groundwaters) in areas of bedrock sulphide mineralisation or mining activity, industrial contamination, or areas affected by geothermal activity. High concentrations can also occur in surface waters that are fed by high-arsenic groundwater (baseflow).

Observed arsenic concentrations in groundwater are themselves highly variable. Most groundwaters tend to have concentrations $<10 \mu g/L$ but these may range up to several thousands of $\mu g/L$ in extreme cases. Whilst concentrations are usually low, it has been estimated that around 200 million people worldwide may be exposed to arsenic in drinking water at concentrations greater than $50 \mu g/L$. Arsenic and fluoride together are now recognised as the two most significant inorganic constituents in drinking water that pose the greatest risk to human health (WHO, 2004).

Arsenic occurs in two oxidation states in water. In anaerobic (oxygen-poor) conditions, it is dominated by the reduced form: arsenic(III) (arsenite) and in oxidising conditions by the oxidised form: arsenic(V) (arsenate). Under the oxic and near-neutral-pH conditions of most natural groundwaters, arsenic(V) tends to be strongly adsorbed to sediments and soils, particularly iron oxides, as well as aluminium and manganese oxides and clays. These are common constituents of aquifers and are the reason why most groundwaters have low arsenic concentrations. Adsorption of arsenic to iron oxides is less favourable under oxic, alkaline conditions and anaerobic conditions.

Most recognised cases of high-arsenic groundwater are naturally-derived. Although geochemical and hydrogeological conditions vary from region to region, there are a number of typical conditions under which arsenic concentrations in groundwater tend to be high:

i) oxygen-poor (anaerobic) aquifers where arsenic is dominantly present as arsenic(III). Groundwaters commonly have associated high concentrations of iron, manganese, ammonium and possibly organic carbon and low concentrations of nitrate and sulphate. Here, onset of anaerobic conditions appears to be a major factor in arsenic release, leading to desorption of arsenic from iron-oxide surfaces, together with dissolution or change in structure of the oxide minerals themselves;

ii) oxidising (aerobic) aquifers with high groundwater-pH values (>8). These are typically restricted to arid or semi-arid environments. High concentrations of arsenic in these environments are commonly associated with high concentrations of other anion- and oxyanion-forming elements such as fluoride, boron, uranium, vanadium and selenium. Many of these elements are also potentially toxic;

iii) mineralised areas containing arsenic-enriched sulphide minerals (e.g. pyrite, arsenopyrite), commonly associated with gold or other precious metals. Arsenic release occurs via oxidation (weathering) of sulphide minerals under oxic conditions. The oxidation reaction can be exacerbated by mining excavations and so arsenic problems can be severe in sulphide-rich mining areas. Some documented cases from mineralised environments have mine drainage waters with arsenic concentrations in the mg/L range. However, attenuation of arsenic by adsorption to iron oxides can reduce the impact significantly with increasing distance from the sources of contamination;

iv) some geothermal waters.

Although the precise mechanisms of arsenic release in groundwater are still debated, slow groundwater flow, either because of low hydraulic gradients (low-lying areas such as flat alluvial basins and the lower parts of deltas) or lack of active rainfall and recharge (arid areas, closed basins) appears to be an important additional factor in maintaining high dissolved arsenic concentrations. Arsenic contamination from industrial sources may also be severe locally, although such cases are comparatively rare.

Examples of anaerobic aquifers affected by arsenic include the alluvial and deltaic aquifers of Bangladesh and north-east India, alluvial and lake sediment aquifers of the Yellow River Plain of north China, the Red River delta of Vietnam, Mekong Valley of Cambodia, Indus Valley of Pakistan, Irrawaddy Delta of Burma (Myanmar), coastal Taiwan and the Great Hungarian Plain of Hungary and Romania (Figure 1).

Examples of oxidising aquifers with arsenic problems include the loess aquifers of central Argentina (formed over the last few thousand years largely by wind erosion of Andean rocks), and alluvial aquifers of northern Mexico and parts of south-west USA (Figure 1).
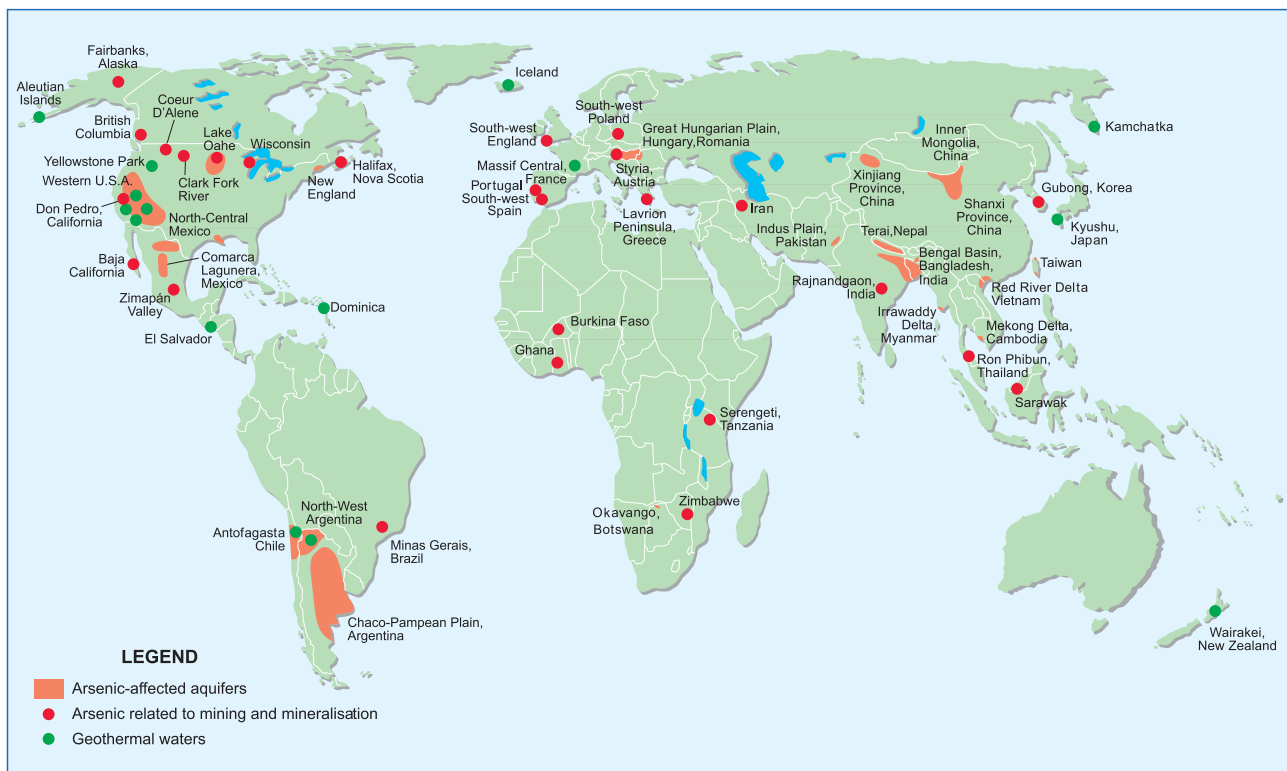
Figure 1. Distribution of documented arsenic problems in groundwaters and surface waters (>50 μg/L). Includes known occurrences of geothermal and mining-related arsenic problems (after Smedley and Kinniburgh, 2002)

Arsenic problems have been recorded in sulphide-mining and mineralised areas in many parts of the world, including many well-documented cases in the USA, Canada and Europe (Figure 1). Comparatively few have been linked directly with identifiable health problems but exceptions include the Ron Phibun area of peninsular Thailand (Williams et al., 1996), Rajnandgaon district in Madhya Pradesh, India (Chakraborti et al., 1999) and a recently documented case in Burkina Faso (Smedley et al., 2007).

Areas where potential future arsenic problems may be identified therefore include:

i)   large low-lying alluvial and deltaic basins composed of young sediments where anaerobic conditions prevail (possibilities include the Nile Basin, Egypt, lower reaches of the Niger Delta, Nigeria and the Chao Phraya Basin of Thailand);

ii)   inland basins with young sediments in arid and semi-arid areas (such as parts of northern China);

iii) sulphide-rich mineralised areas, particularly metal-and coal-mining areas (occurring in basement aquifers in for example parts of Ghana, South Africa, Zimbabwe and India);

iv)   geothermal areas (possibilities include the East African Rift of Ethiopia, Tanzania, Uganda and

Kenya, although limited arsenic data for hot springs in the Rift have revealed few samples with concentrations significantly higher than 50 μg/L).

Arsenic in water is invisible and has no taste or smell. Hence other diagnostic features of water chemistry need to be investigated to identify potential arsenic occurrences. Features of the different types of high-arsenic groundwater environment are shown in Figure 2.

Field testing for arsenic

Arsenic has not been traditionally included on lists of elements routinely tested by water-quality laboratories in developing countries and so some arsenic-rich sources likely remain to be identified. The discovery of arsenic contamination on a large scale in the Bengal Basin in particular has highlighted the need for a rapid assessment of the situation in similar aquifers world-wide. The revision of the drinking-water standards for arsenic in a number of countries has also prompted the need for inclusion of the element in routine water-quality monitoring programmes.

Aquifers with identified arsenic problems typically have a high degree of variability in concentrations, both laterally within relatively short distances (metres to kilometres), and with depth. This means

HIGH-ARSENIC GROUNDWATER PROVINCE

ENVIRONMENT

- Geothermally-influenced groundwater
- Low-temperature groundwater
  - Non-mining areas
  - Sulphide mining and mineralised areas

Low rates of flushing:
Young aquifers (Quaternary)
Low hydraulic gradients (deltas, closed basins etc)
Slow groundwater flow
Poor drainage
Low-lying terrain
Arid/semi-arid environment
Old groundwaters
High chemical spatial variability

PROCESS

Mixing/ dilution	REDUCING: Reductive desorption and dissolution (Fe oxides) Confined aquifers	OXIDISING: Desorption (Fe oxides)	Pyrite oxidation Oxidising or mildly reducing

INDICATORS

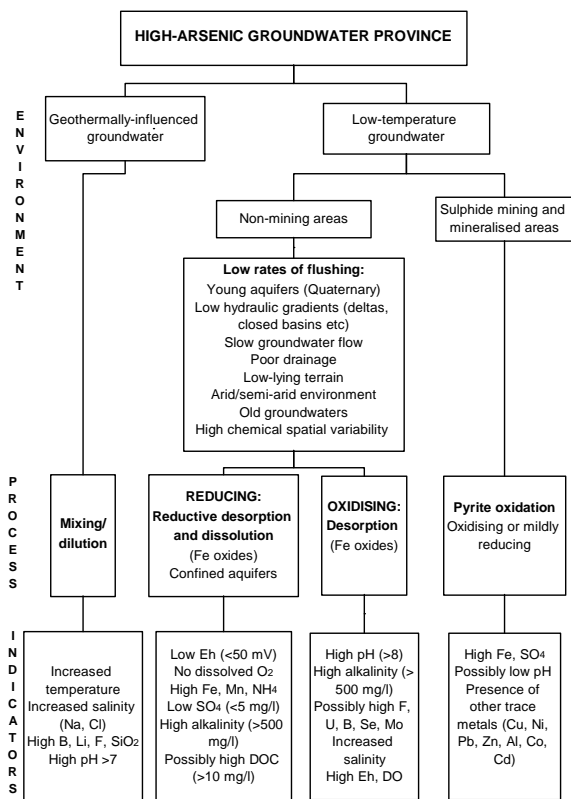| Increased temperature Increased salinity (Na, Cl) High B, Li, F, SiO_2 High pH >7	Low Eh (<50 mV) No dissolved O_2 High Fe, Mn, NH_4 Low SO_4 (<5 mg/l) High alkalinity (>500 mg/l) Possibly high DOC (>10 mg/l)	High pH (>8) High alkalinity (> 500 mg/l) Possibly high F, U, B, Se, Mo Increased salinity High Eh, DO	High Fe, SO_4 Possibly low pH Presence of other trace metals (Cu, Ni, Pb, Zn, Al, Co, Cd)

Figure 2. Flow diagram to assist identification of potential high-arsenic groundwater provinces (DOC; dissolved organic carbon, DO: dissolved oxygen, Eh: redox potential) (from Smedley and Kinniburgh, 2002)

that in vulnerable aquifers, ideally each well used for drinking water needs to be tested to ensure its fitness for use. In affected aquifers such as those of Bangladesh, this can mean large numbers of sources (several million tubewells). Laboratory analysis is preferable, but difficult on a large scale such as that necessary in Bangladesh. Field-test kits are an alternative, but need to be simple, rapid, inexpensive and reliable to use.

Most of the current popular field-test kits (e.g. from Hach, Merck, Wagtech) are based on modifications of the 'Gutzeit' method, which involves the reduction of arsenite and arsenate by zinc or more commonly sodium borohydride to arsine gas. This produces a stain on mercuric bromide paper. Reliability and sensitivity have traditionally been major limitations of these kits, although there have been major improvements in recent years (e.g. van Geen et al., 2005). Some recent evaluations have nonetheless highlighted reliability problems with field-test kits (Rahman et al., 2002; Sankararamakrishnan et al., 2008).

Most manufacturers claim that test kits are sensitive to 10 μg/L. In practice, detection of the yellow stain on mercuric bromide filter paper at such concentrations can be difficult, especially to the untrained eye. A digital readout of the arsenic concentration offers some advantages. Stringent quality control of analyses using field-test kits needs to be carried out by laboratory cross-checking (Jakariya et al., 2007).

Remediation techniques and supply of low-arsenic drinking water

A number of solutions to the arsenic problems of vulnerable aquifers have been suggested for different situations. The only clear conclusion is that no single solution is appropriate for all problems.

Identification of safe tubewells

In areas where groundwater-arsenic problems may be suspected but data are lacking, a randomised reconnaissance survey of selected tubewells is required to identify the scale of the potential problem.

In areas with recognised arsenic problems such as Bangladesh and north-east India, safe tubewells are being identified by rigorous water testing (laboratory and field tests) of sources used for drinking, as well as periodic monitoring to ensure long-term safety. Even in severely contaminated areas, not all wells within a given aquifer are contaminated (greater than the national standard concentration). Hence groundwater need not be abandoned completely without further evaluation. In a survey of some 5 million tubewells tested nationally in Bangladesh for arsenic by field-test kits, the Bangladesh Arsenic Mitigation and Water Supply Program (BAMWSP, 2005) showed that around 30% had arsenic concentrations above 50 μg/L. There is also the possibility of selective use of contaminated sources (for washing etc). However, in some areas, a high percentage of tubewells may be contaminated and alternatives therefore need to be found. Well switching has been relatively common practice in Bangladesh as a means of reducing arsenic intake (Johnston and Sarkeri, 2007).

Groundwater treatment

The most commonly used methods of treatment of high-arsenic waters at community and municipal level are by the addition of coagulants such as alum or ferric chloride. Alum is readily available in most countries but the presence of high concentrations of residual aluminium and sulphate in treated waters represents a drawback. The method is less efficient above pH 7.5. Alum has been promoted for domestic use in Bangladesh using a two-bucket (alum, potassium permanganate and sand) system. Potassium permanganate is added to the reducing waters to oxidise arsenite to arsenate to facilitate removal. Adsorption of arsenic to the manganese oxide produced also occurs. Activated alumina is

also used in some areas to remove arsenic by adsorption, though this is expensive and not so suitable for many developing countries. Both alum and activated alumina are also commonly used to remove fluoride (see *Fluoride* Fact Sheet).

Treatment of groundwater in arsenic-affected areas of Asia is also being tried at household level using pots with various adsorption media (e.g. sand, gravel, clay, brick chips) with varying success. The 'three-kolshi' method (e.g. Munir et al., 2001) has been used for example in many households in Bangladesh and is popular. The system is inexpensive and simple to operate but has been prone to breakage and bacterial contamination and produces relatively small volumes. Passive sedimentation (leaving water to stand in a container overnight) has also been tried in some high-iron areas. The efficacy of co-precipitation of arsenic with iron oxide in this approach depends significantly on iron concentrations and iron:arsenic ratios. However, field testing of household treatment methods in Bangladesh found significant increases in bacterial contamination using passive sedimentation in particular (Jones and Uddin, 2000). Indeed, all village-scale treatment methods require considerable care to avoid bacterial contamination.

Disposal of arsenic-rich sludge generated from the removal process is a cause of potential concern. Some studies have concluded that release of arsenic from sludge to the environment should be negligible (Eriksen-Hamel and Zinia, 2001), albeit dependent on local pH and redox conditions. Incorporation of sludge as a component in bricks or cement has been tested as a means of stabilisation.

In oxidising aquifers with high pHs, arsenic is often not the only water-quality problem. Water treatment may also require salinity reduction alongside removal of other problem elements such as fluoride, boron, uranium, vanadium and selenium. Where possible, reverse osmosis is commonly carried out to remove these constituents, but the method is expensive and not suitable for village-level treatment in poor communities.

Alternative tubewell siting

In Bangladesh and West Bengal, groundwater from an older aquifer at greater depth (>150 m) usually has low arsenic concentrations and in some places has been developed as an alternative source of drinking-water supply (van Geen et al., 2007). Many concerns have been raised over the long-term sustainability of the deeper resource with increased development, although a recent modelling investigation concluded that supplies should be sustainable if the deep aquifer is used only for

domestic (small-scale) supply (Michael and Voss, 2008).

The great spatial variability in arsenic concentrations in shallow boreholes in the Bengal Basin and elsewhere also offers some possibilities for alternative siting. Potential for alternative tubewell siting, either laterally or with depth therefore arises in some vulnerable aquifers. However, lateral and depth variations in arsenic concentrations are not universally predictable in different aquifers. For example, the occurrence of low-arsenic groundwaters at depth in parts of Bangladesh and West Bengal is specific to the region and cannot be used as a rule of thumb elsewhere. This approach requires a detailed knowledge of the hydrogeological and geochemical conditions of the local aquifers. Provision of deeper tubewells involves significant extra cost. The current extent of understanding of spatial variations on a local scale probably does not allow accurate prediction of the locations of low-arsenic groundwater sources spatially.

Use of protected hand-dug wells in reducing aquifers

In reducing (anaerobic) aquifers, it has often been found that shallow hand-dug wells have low arsenic concentrations whilst tubewells only a few metres deeper have much higher concentrations. The difference is likely due to maintenance of aerobic conditions in the open well and also to regular flushing of the shallowest parts of the aquifer, close to the water table, by inputs of recent rainwater. Low arsenic concentrations are typical of hand-dug wells in many arsenic-affected aquifers of Asia, although concentrations less than 10 µg/L cannot always be guaranteed. Problems can arise with bacterial contamination of the water in the well and adequate sanitary protection is required. UNICEF, for example, has developed a sanitary well system with a well cover, hand pump and chlorination pot for this purpose. Hand-dug wells may also not be suitable in all areas because of large fluctuations in water levels which could mean loss of supplies during dry periods.

Rainwater harvesting

In areas with sufficient rainfall, collection and storage of rainwater for potable use may be possible, at least seasonally. The method involves collection of rainwater either from roofs or with sheets of plastic and storage in large cement tanks, some underground. Once in the tank, rainwater can be stored safely without bacterial contamination for several months. Rainwater harvesting has been practised for a long time in many coastal areas, island communities and other areas where aquifers are saline. It has also been tried in arsenic-affected areas, for example Bangladesh.

Surface water usually has low arsenic concentrations (generally much less than 10 µg/L) but may suffer from serious bacterial contamination and can cause severe health problems if not treated. Use of pond sand filters is being tried to remove bacteria in some areas. These usually involve filtration of surface water through a sand- and gravel-filled tank. Such filters are being installed for example by UNICEF in parts of Bangladesh. The filters are generally effective, provided they are periodically cleaned. However, in Bangladesh the common use of ponds for aquaculture compromises their use for potable supply because of chemical contamination.

On a larger scale, urban piped-water supplies distributing treated river water have been installed in some arsenic-affected areas (e.g. West Bengal). This is expensive and not suitable for many large, dispersed and rural communities in developing countries.

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