

Water Resource Quality (WRQ)

Geogenic Contamination Handbook

Addressing arsenic and fluoride in drinking water

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Cover Photo:

Women collecting fluoride-treated water at the community filter in Wayo Gabriel, Ethiopia, implemented by Eawag, Oromia Self-Help Organization (OSHO) and Swiss Interchurch Aid (HEKS)

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2 Geogenic contamination

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Contamination in drinking water, both chemical and microbiological, can originate from a range of sources, most of which are anthropogenic, such as agriculture, industry or human settlements (Fig. 2.1). As the name suggests, geogenic contamination derives from geological sources. It stems from interactions between aquifer rocks and groundwater that lead to the release of substances from the aquifer rock or sediment into the water. Such interactions are always taking place – in fact, rocks and sediments largely control water chemistry – but if a particular substance is released in quantities that are high enough to have a detrimental effect on life forms, then it is termed a geogenic contaminant.

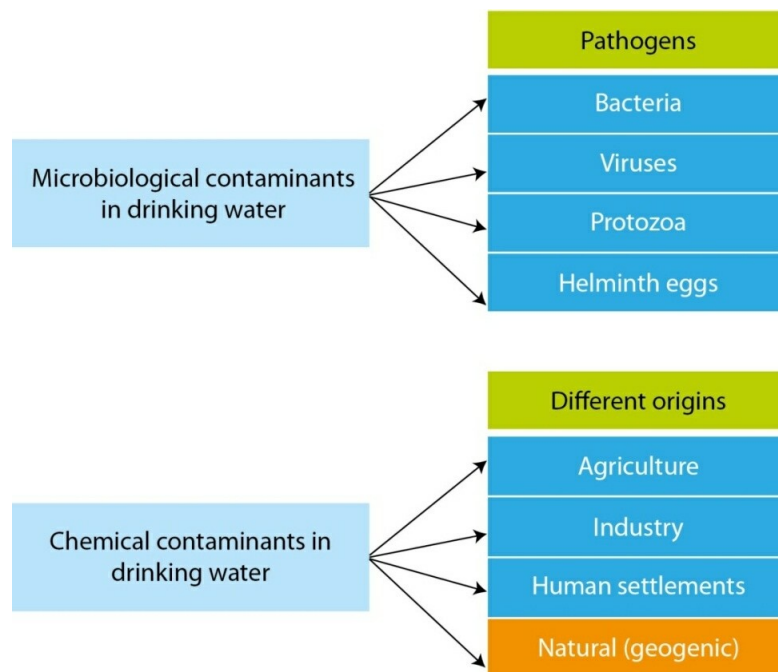


Fig. 2.1 Overview of contaminant types leading to water- and sanitation-related diseases

Only a very small number of the 98 naturally occurring elements have the potential to be geogenic contaminants. There are three critical factors:

- their concentration in rocks and sediments,
- their solubility under at least some environmental conditions and
- their presence in soluble form in concentrations that are toxic to humans.

The most common soluble ions in groundwater are sodium (Na^+), magnesium (Mg^{2+}), calcium (Ca^{2+}), chloride (Cl^-), bicarbonate (HCO_3^-) and sulphate (SO_4^{2-}). While these can make water unpalatable, they do not pose a direct threat to health.

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Contamination with dissolved iron (Fe) and manganese (Mn) can occur in groundwaters with little or no oxygen. High levels of these elements are also more of an aesthetic than a health concern, though there is increasing evidence that exposure to manganese in drinking water can cause neurological problems (e.g. [Wassermann et al., 2006](#)).

Of all inorganic groundwater contaminants, arsenic (As) and fluoride (F) clearly represent the greatest threat to human health. Many millions of people are affected worldwide. Other elements, such as selenium (as selenate), uranium (carbonated anions), boron and chromium (as chromate), can be important locally but are not as widespread as arsenic and fluoride.

2.1 Arsenic Occurrence

Arsenic in drinking water is a global threat to health, potentially affecting about 140 million people in at least 70 countries worldwide ([Ravenscroft et al., 2009](#)). It is considered by some researchers to have more serious health effects than any other environmental contaminant ([Smith and Steinmaus, 2009](#)).

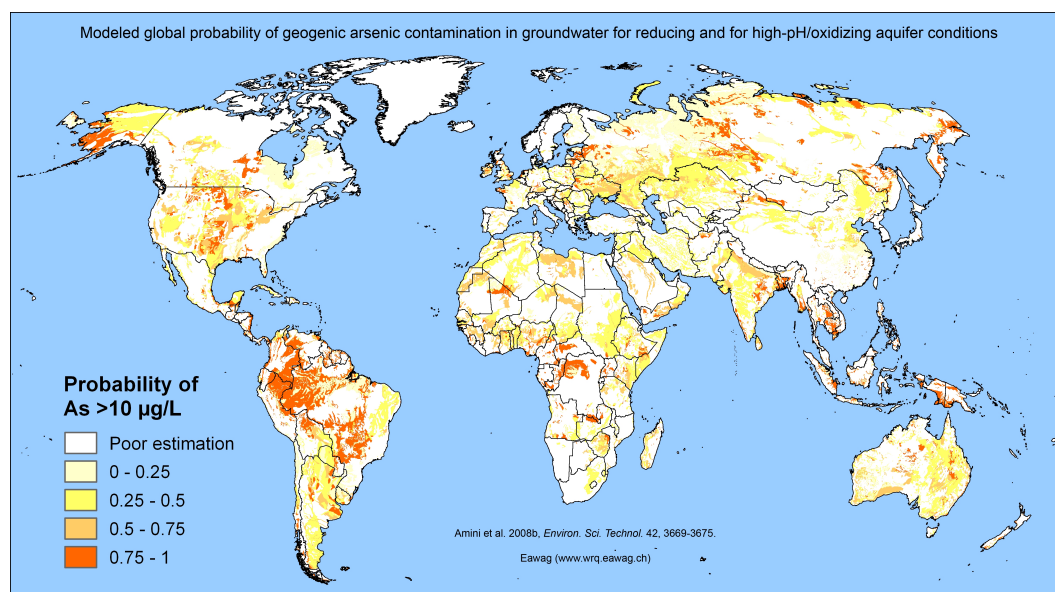


Fig. 2.2 Modelled global probability of elevated geogenic arsenic concentrations in groundwater ([Amini et al., 2008a](#))

Drinking water can contain arsenic at concentrations of up to several mg/L, most commonly as the reduced species, As(III) (arsenite), or the oxidised species, As(V) (arsenate). As(III) is uncharged (H_3AsO_3) under ambient pH conditions, and as such, is more mobile than As(V) (H_2AsO_4^- or HAsO_4^{2-}). Under most geochemical conditions, arsenic in aquifers remains tightly bound to the sediments, and concentrations of dissolved arsenic in the

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groundwater remain low. However, two geochemical conditions have been identified under which elevated concentrations of arsenic can be found in the groundwater even when solid-phase concentrations in the sediments are unremarkable: reducing conditions in young alluvial aquifers and arid, high pH oxidising conditions in rocks and/or sediments with relatively low permeability (Smedley and Kinniburgh, 2002). Figure 2.2 shows the modelled probability of the occurrence of geogenic arsenic contamination in groundwater for both of these conditions combined. In addition, geothermal contributions and sulphide oxidation in mine tailings can also lead to elevated arsenic concentrations in groundwater, but these conditions tend to be more localised and have not been included in the model.

Health effects

Arsenic causes a wide range of adverse health effects. The acute toxicity of As(III) is somewhat greater than that of As(V), but because As(V) is reduced to As(III) in the body, the two species can be considered equally toxic.

The first obvious symptoms are often skin lesions (keratosis, melanosis; Fig. 2.3), but other effects can include weakness, diarrhoea, bronchitis, vascular disease and diabetes mellitus (UNICEF/Chinese Ministry of Health, 2004).



Fig. 2.3 Skin lesions (keratosis, melanosis) indicating arsenic poisoning

The main health concerns, however, are cancers of the skin or internal organs. In particular, arsenic-related lung and bladder cancers can cause heavy mortality (Argos et al., 2010; Sohel et al., 2009). More recently, arsenic exposure has been linked to cardiac effects such as myocardial infarction (heart attacks) (Yuan et al., 2007). Cardiac risks are elevated within short exposure periods, while cancers can take decades to develop, even long after arsenic exposure has stopped (Fig. 2.4). In addition, arsenic is linked with a range of

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impacts on children, including reduced birth weight, infant mortality and impaired cognitive development (Smith and Steinmaus, 2009).

Because of the ongoing uncertainty about low-level effects and the difficulties involved in measuring arsenic concentrations below 10 µg/L or in reducing arsenic concentrations to this level, the WHO has set 10 µg/L as a provisional guideline value (WHO, 2011). Many countries have a less strict drinking-water standard of 50 µg/L. The disease burden at these levels can be considerable; Argos et al. (2010) found all-cause mortality levels to be 34% higher in a population exposed to 0.01–50 µg/L arsenic, compared to a control group with <10 µg/L exposure. Those exposed to 150 µg/L or more showed 68% higher all-cause mortality.

There is no effective medical treatment for chronic arsenicosis, except for switching to an arsenic-free drinking-water source. However, palliative care such as application of ointments to cracked skin lesions can ease suffering. Chelation therapy is effective for short-term, acute poisoning, but not for long-term exposure.

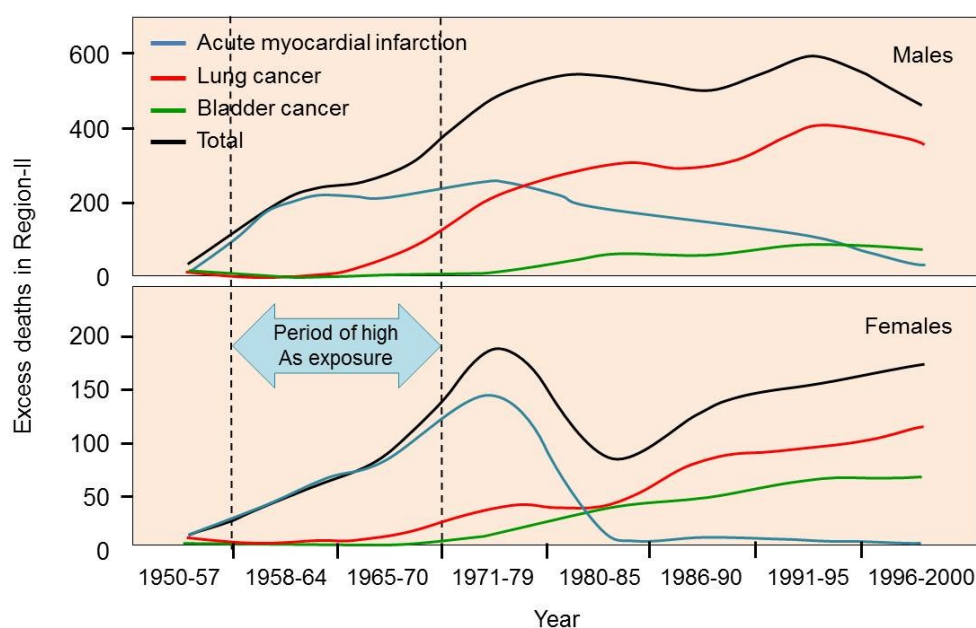


Fig. 2.4 Latency of cancer and heart disease in northern Chile. Drinking water contained approximately 800 µg/L arsenic from 1958–1971, after which an arsenic removal plant greatly reduced exposure. Source: Redrawn by Ravenscroft et al. (2009) after Yuan et al. (2007)

2.2 Fluoride Occurrence

Fluoride is the 13th most abundant element found in the Earth's crust. Its occurrence in natural waters is closely related to the abundance and solubility of fluoride-containing minerals such as fluorite (CaF_2). The fluoride concentrations of most natural waters lie below the WHO guideline value for fluoride in drinking water (1.5 mg/L, WHO, 2011). Nevertheless, elevated fluoride concentrations in groundwater are still a problem in many regions of the world (Fig. 2.5).

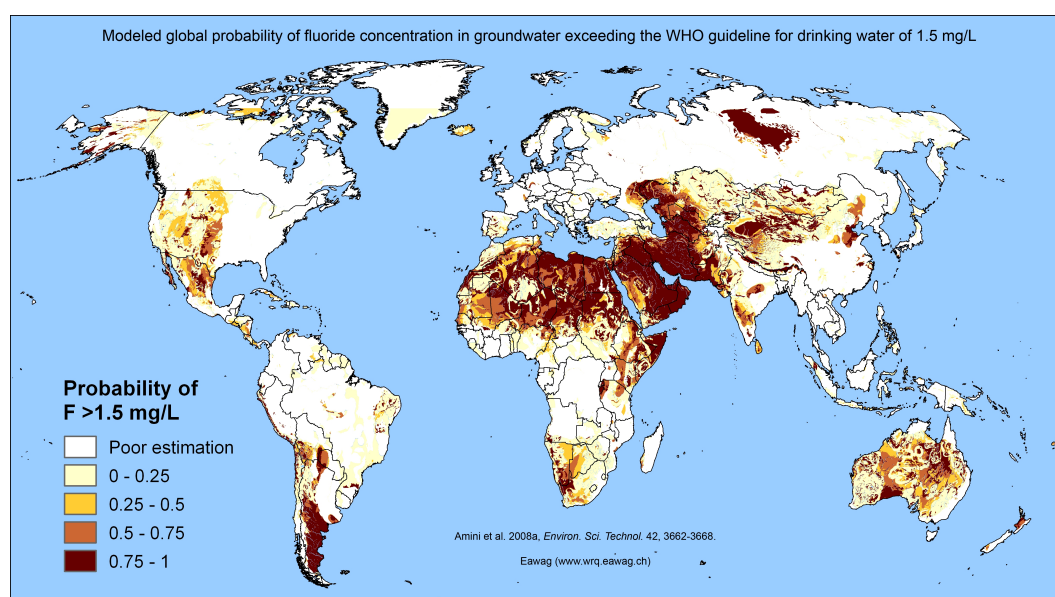


Fig. 2.5 Modelled probability of fluoride concentrations in groundwater exceeding 1.5 mg/L (Amini et al., 2008b)

High geogenic fluoride concentrations in groundwater (>1.5 mg/L) are associated with a variety of geological and climatic conditions:

- Granitic basements
- Arid climates
- Alkaline volcanic rocks

Granitic basement aquifers containing a relatively large proportion of high-fluoride minerals, such as micas, apatites or amphiboles, can yield groundwaters with elevated dissolved fluoride concentrations (e.g. in India, Sri Lanka). High fluoride concentrations can also be found in arid climates, where groundwater infiltration and flow rates are slow, and prolonged water-rock reaction times promote leaching of fluoride. Some of the highest fluoride concentrations are found in alkaline volcanic regions, such as the East African Rift Valley, where high-fluoride hyper alkaline volcanic rocks are present and fluoride is furthermore added to groundwater via high-fluoride geothermal solutions (Edmunds and Smedley, 2005).

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Low calcium concentrations can also lead to high fluoride concentrations in water, as fluoride is not removed from solution by the precipitation of CaF_2 . Such conditions are found, for example, in alkaline groundwaters whose chemistry is dominated by sodium bicarbonate. Also, groundwater associated with granitic rocks tends to contain little calcium.

Health effects

Fluoride has beneficial effects on teeth at low concentrations, but excessive exposure to fluoride can have a number of adverse effects, such as dental and skeletal fluorosis, the severity of which depends on the level and duration of exposure (Gazzano et al., 2010). Worldwide, an estimated 200 million people are at risk of fluorosis. However, incomplete data make precise quantification of the global health burden of fluorosis impossible (Fewtrell, 2006).

The ingestion of moderate amounts of fluoride, including that from drinking water, can lead to structural strengthening of tooth enamel and a lower rate of dental caries. The greatest decline is seen when drinking-water fluoride concentrations lie between 0.7 and 1.2 mg/L (Oszvath, 2009). This has led to the widespread fluoridation of drinking water in countries such as the USA and to the use of fluoridated toothpaste.



Fig. 2.6 Examples of dental and skeletal fluorosis

Childhood exposure to fluoride concentrations in drinking water that exceed the WHO guideline limit of 1.5 mg/L can lead to dental fluorosis (Fig. 2.6), a condition characterised by the mottling and pitting of teeth. Dental fluorosis occurs in young children as the tooth enamel is developing (NRC, 2006). Fluoride ingestion after about the age of 8, when adult teeth have been formed (even if they have not yet erupted), will not lead to dental fluorosis.

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Adults with dental fluorosis must therefore have been exposed to high fluoride concentrations in their early childhood. Symptoms of mild dental fluorosis are the appearance of white striations or patches on the tooth enamel, while yellow and brown staining, pitting and chipping of the tooth enamel are symptoms of more severe fluorosis. Dental mottling is permanent, though some cosmetic treatment (bleaching, abrasion) can remove some of the visible stains.

Prolonged exposure to high fluoride concentrations over several years increases the risk of developing crippling skeletal fluorosis. This condition is characterised by pain and stiffness in the backbone and joints, accompanied by increased bone density (osteosclerosis). In its later stages, crippling deformities of the spine and joints arise, together with neurological defects, muscle wasting and paralysis (Oszvath, 2009). Studies on occupational and endemic fluorosis have shown that the extent of the symptoms is related to the duration and level of exposure and that skeletal fluorosis is at least partially reversible over a number of years. (e.g. Grandjean, 1982; Krishnamachari, 1986; Susheela and Bhatnagar, 2000). In addition to these more obvious symptoms, there are others grouped under the term “non-skeletal fluorosis”. Non-skeletal fluorosis includes a reported decrease in cognitive capacity (measured by IQ tests), lethargy, an impaired ability to concentrate and possibly even the onset of dementia (USRC, 2006). Whether these effects could be due to enzymatic changes or impaired function of the thyroid gland is unclear. Fluoride may also disturb the endocrine system, acting as an inhibitor of secretions from the parathyroid glands, which regulate extracellular calcium and phosphate concentrations. Possible effects on the gastrointestinal, renal, hepatic and immune systems have also been reported (USRC, 2006). There has been difficulty in proving observed health effects (in scientific studies) to be the result of elevated fluoride intake, and more rigorous epidemiological studies have been recommended.

The WHO guideline value of 1.5 mg/L might not be suitable for hot, arid areas where people have a higher daily water intake (Brouwer et al., 1988). The recommended maximal daily fluoride intake for children younger than 8 years (to prevent dental and skeletal fluorosis) is 0.1 mg/day per kg of body weight (SCSEDRI, 1997, Table 3.3). For adults, a daily intake of 14 mg leads to an excess risk of adverse skeletal fluorosis, and there is evidence for increased risk of an effect on the skeleton at an intake of 6 mg/day (Fawell et al., 2006). Not only drinking water, but also cooking water and fluoride contained in food products can contribute considerably to a person’s daily fluoride uptake (Malde et al., 2011). A review of fluoride and nutrition is presented in Chapter 3. Skeletal effects in fluorotic areas may vary in severity depending not only on the daily fluoride uptake, but also on the intake of other essential nutrients important for bone formation, such as calcium, zinc, iron and magnesium. Deficient nutrition will therefore increase the risk of bone deformation when excess fluoride is consumed (Chakma et al., 2000).

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