



Chapter 1

Arsenic in drinking water: sources & human exposure

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1.1 INTRODUCTION

Although the detrimental health impacts of chronic arsenic exposure from drinking water or beverages has been suspected for over 200 years (Martin, 1759; Neubauer, 1947; citing Egger, 1932; citing Lambe, 1809) and has been well documented for well over 100 years (Geyer, 1898; The Royal Commission on Arsenical Poisoning, 1903), it is only in the last 50 years (1964–2014) that there has been the extensive discovery of high arsenic drinking water supplies in many regions of the world. In the English language literature, reports of these include for: Taiwan (Chen & Chen, 1964), Chile (Zaldívar, 1974), northern India (Datta & Paul, 1976), Mexico (Cebrian *et al.* 1983), eastern India (Garai *et al.* 1984; Das *et al.* 1994; Chakraborti *et al.* 2009), UK (Farmer *et al.* 1989), Hungary (Varsanyi *et al.* 1991), USA (Frost *et al.* 1993), Bangladesh (Dhar *et al.* 1997), China (Sun *et al.* 1999), Vietnam (Berg *et al.* 2001), Cambodia (Polya *et al.* 2003a) and Nepal (Thanduker, 2000; Shrestha *et al.* 2003; Bhattacharya *et al.* 2003).

Notwithstanding these discoveries, particularly in Germany, Taiwan, Chile, Hungary and India, there has been an apparent widespread tardiness to recognise the importance of groundwater arsenic hazards. As late as 1999, the European Environmental Agency published an extensive report on groundwater quality and quantity in Europe (Scheidleder *et al.* 1999) that does not mention “arsenic”, presumably reflecting the paucity of relevant long-term monitoring data. Extensive drilling of what turned out subsequently to be arsenic contaminated wells in India and Bangladesh took place many years after high arsenic groundwaters and their ill-effects had been documented in Europe, South America and elsewhere in Asia. The lack of recognition of this hazard reflects in part a lack of effective distribution of local, regional and

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international scientific and technical knowledge. In part this may be because much of the early literature was not written in English – for example reports of groundwater arsenic in Argentina by Fernandez (1925) and in Germany by Geyer (1898, 1940) – however other reasons for the apparent lack of institutional awareness of the seriousness of arsenic hazard in drinking water systems must exist (at least in the English speaking world) given notable relevant English-language articles including the Royal Commission on Arsenical Poisoning (1903), Neubauer's (1947) review of arsenical cancer and numerous epidemiological papers from C.-J. Chen and his group in Taiwan. Even Rachel Carson's (1962) widely read totem of the early environmental movement, "Silent Spring", notes briefly the health risks associated with the chronic consumption of high arsenic drinking water.

Within both many regulatory institutions and the scientific community, this situation has now substantially changed. The EEA's 2013 report (Kodeš *et al.* 2013) on groundwater quality and quantity in Europe, superseding the EEA's 1999 report, highlights non-compliance of groundwater supplies with European Union drinking water standards (10 µg As/L) in 13 European countries, (albeit not Hungary, Romania and Serbia, all countries where substantial arsenic groundwater arsenic hazard has been identified). At the time of writing (mid, 2014), there were around 5000 publications matching the topic keywords of "arsenic" and "drinking water" and these have been collectively cited over 100,000 times in other publications. The 2002 review of arsenic in natural waters by Smedley and Kinniburgh (2002) is one of the most highly cited papers in the Earth Sciences literature, whilst the highly cited reviews of Mandal and Suzuki (2002), Mohan and Pittman (2007) and Smith *et al.* (2000) now provide readily available information of arsenic distribution in natural waters, arsenic removal technologies and health impacts respectively.

This chapter aims to summarise some of the now extensive literature on arsenic occurrences in drinking water supplies and, together with reviewed data on water consumption rates, provide a perspective on the absolute and relative importance of drinking water as an arsenic exposure route across the globe. For the most part, these water supplies have derived from groundwaters (Section 1.2) contaminated with geogenic arsenic (i.e. arsenic of natural origin) but there are also examples of groundwaters with high anthropogenic arsenic and of high arsenic surface water supplies (Section 1.3), with arsenic of either geogenic or anthropogenic origin. For a more detailed account than is presented in this brief chapter of the distribution of arsenic in groundwater and surface waters, the reader is referred to Matschullat (2000), Welch (2000), Mandal and Suzuki (2002), Smedley and Kinniburgh (2002), Henke (2009), Ravenscroft *et al.* (2009), Barringer and Reilly (2013) and Polya and Lawson (2015).

1.2 ARSENIC IN GROUNDWATER SOURCES

Although many groundwaters do not contain arsenic at concentrations higher than the WHO provisional guideline value of 10 µg/L, many groundwaters do – high arsenic groundwaters are not unusual and any competent or prudent operator supplying groundwater as a drinking water supply, even perhaps in medium-term emergency circumstances, should be compelled to determine and report to the potential users whether or not the arsenic concentrations in the water supply are lower than at least local regulations require.

There is an abundant literature on the main causes of high arsenic hazard in various types of groundwater and this can be used to indicate regions of the world where high arsenic hazard may be more likely – see for example compilations and reviews by, amongst others, Smedley and Kinniburgh (2002) and Ravenscroft *et al.* (2009). Recently, geostatistical models incorporating consideration of environmental parameters that may influence the genesis of high arsenic groundwaters have been developed on both a global (Amini *et al.* 2008; Winkel *et al.* 2008) and a more local/national scale (Lado *et al.* 2008; Rodriguez-Lado *et al.* 2013; Sovann & Polya, 2014).

Many groundwater systems, particularly shallow systems hosted in complex sedimentary aquifers, are highly heterogeneous. This means that high arsenic and low arsenic groundwaters may often be found in close proximity, giving rise to opportunities for well switching (van Geen *et al.* 2002). This heterogeneity also means that prediction of arsenic concentrations in yet-to-be-drilled wells may be a precarious business. Notwithstanding this, a consideration of plausible regional and local controls of groundwater arsenic concentrations may be useful in a scoping study, whilst always bearing in mind that such predictions will never be better than an accurate, reliable and representative chemical analysis/analyses of the actual groundwater to be supplied.

1.2.1 Origin of high arsenic groundwaters

High arsenic groundwaters arise as a result of a combination of all of (i) the presence of suitable arsenic-bearing source material; (ii) efficient mobilization and/or transport processes; and (iii) lack of rapid arsenic removal processes. These criteria apply to both systems in which the arsenic has a geogenic origin and those in which the arsenic has an anthropogenic source. Consideration of arsenic source materials, mobilisation processes and arsenic removal processes may therefore be helpful in assessing the likelihood or otherwise of encountering high arsenic groundwaters in a specific hydrogeological/geographical context and these are each briefly discussed below.

1.2.1.1 Arsenic-bearing source materials

Arsenic may be sourced from both naturally occurring solid materials (rocks, minerals, soils, sediments) and from anthropogenic (manufactured, synthesised) materials.

1.2.1.1.1 Arsenic in rocks, minerals, soils and sediments

Arsenic is a relatively abundant trace element in the Earth's upper crust with a mean concentration of around 5 ± 1 mg/kg (Rudnick & Gao, 2003). Although not normally classified as a geochemically incompatible element, arsenic is comparatively readily solubilised by fluids and so is commonly enriched in magmatic-hydrothermal systems, particularly those associated with (plate tectonic) subduction zones and collision zones (Borisova *et al.* 2010) – modern/relatively modern (in a geological sense) examples of such regions include the Himalayas, the Rocky Mountains and the Andes as well as geothermal areas of New Zealand, the Philippines and Japan, whilst substantial granite-associated enrichments of arsenic in areas such as south-west England, central France and Portugal reflect processes in similar environments over 300 million years ago. Accordingly, some of the highest arsenic concentrations recorded in crustal rocks are in granitoid-associated hydrothermal ore deposits (e.g. Panasqueira, Portugal – mean ore vein concentration ~8000 mg/kg (Polya, 1989); mean hydrothermally altered metasediment concentration ~200 mg/kg (Polya, 1988)).

Arsenic is also enriched by fluvio-sedimentary processes and particularly in finer-grained, relatively high specific surface area sediments rich in organic matter and/or ferric oxyhydroxides and phosphate mineral phases. Accordingly, rocks with some of the highest arsenic concentrations are coals (e.g. Guizhou Province, SW China, up to 35,000 mg/kg (Finkelman *et al.* 1999)), marine shales/mudstones (up to ~500 mg/kg (Smedley & Kinniburgh, 2002)), ironstones (e.g. Claxby Ironstone soils, Midlands of England, up to 220 mg/kg (Appleton *et al.* 2012)), glacial tills (up to ~200 mg/kg (Smedley & Kinniburgh, 2002)) and phosphorites (e.g. Hawthorn Group, Florida, up to ~70 mg/kg (Lavareva & Pichler, 2007)).

With rocks, soils and sediments, arsenic occurs in high concentrations in a relatively restricted range of minerals. The most prominent high arsenic minerals are sulphides (e.g. arsenopyrite (FeAsS), loellingite

(FeAs₂), realgar (As₄S₄), orpiment (As₂S₃), niccolite (NiAs), sulphosalts (e.g. tennantite (Cu,Fe)₁₂As₄S₁₃; enargite (Cu₃AsS₄)) and oxides (e.g. scorodite (FeAsO₄ · 2H₂O), arsenolite (As₂O₃), pharmacosiderite (Fe₃(AsO₄)₂(OH)₃ · 5H₂O)). Additionally, arsenic may occur as an important trace component, with concentrations as high as 1000s mg/kg, in pyrite and other Fe-sulfides (e.g. Lowers *et al.* 2007) and in iron–aluminium or manganese–oxyhydroxide phases (Smedley & Kinniburgh, 2002). Phosphate minerals, such as apatite and vivianite (e.g. Thinnappan *et al.* 2008), may locally be important hosts for arsenic, whilst many sulphide (e.g. Bostick & Fendorf, 2003), carbonate (e.g. Roman-Ross *et al.* 2006) and clay minerals (e.g. Pascua *et al.* 2005) are known to be able to sorb arsenic in significant quantities. Several silicate minerals can incorporate 1000s mg/kg arsenic through the substitution of AsO₄ for SiO₄ (Pascua *et al.* 2005; Charnock *et al.* 2007). Arsenic may also be sequestered by various sulphur-bearing moieties in organic matter (Langner *et al.* 2012, 2014). The sulphide phases listed above are typically found as primary ore minerals associated with modern or palaeo hydrothermal or geothermal systems, although they may also exist as secondary diagenetic minerals resulting from chemical reactions between soils/sediments/rocks and percolating groundwaters (Large *et al.* 2009). The oxide phases tend to exist as secondary minerals, often arising from the oxidation of arsenic-bearing sulphide or sulphosalt phases.

1.2.1.1.2 Anthropogenic sources of arsenic

Anthropogenic sources of arsenic are considered here to include both manufactured arsenic-bearing compounds and naturally occurring materials that become vulnerable to dissolution and/or leaching as a result of human activity.

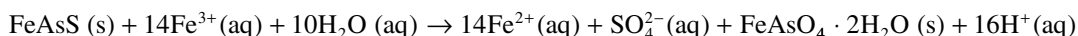
Global production of arsenic-bearing compounds has been in the order 50,000 tonnes per annum over the last 100 years with the bulk of that production arising from metalliferous mining and the mining/combustion of coal (Han, 2007). Additionally or further to its mining, arsenic bearing compounds are or have been widely used as wood preservatives (notably chromated copper arsenate (CCA)), pesticides/herbicides (e.g. arsenic trioxide, calcium arsenate, sodium arsenate, dimethylarsinic acid, disodium methanearsonate, disodium methanearsonate), growth promoters for poultry and swine (e.g. roxarsone) as well as a number of industrial (e.g. additive to certain alloys, glasses and semi-conductor components and other uses (e.g. pharmaceutical, dyes, soaps, catalysts) (IARC, 2012). Although relative contributions vary from country to country, NPI (2013) gives an idea of the range of industrial and other activities contributing to arsenic emissions to waters and their relative importance.

Groundwater (and also surface water) systems particularly vulnerable to inputs of anthropogenic arsenic therefore include: in certain mining areas, smelters, manufacturing plants for arsenical compounds, including pesticides, agricultural areas where arsenic-bearing pesticides/herbicides have been spread or growth promoters used in livestock and areas where CCA has been manufactured, used or wood treated with CCA disposed – landfill and sewage therefore also constitute potential arsenic hazard sources (Wang & Mulligan, 2006).

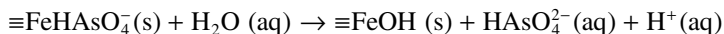
1.2.1.2 Arsenic contamination & mobilization processes

High arsenic hazard in groundwaters arises from either direct contamination of typically anthropogenic arsenic compounds or more widely through the mobilisation of arsenic, of either anthropogenic or geogenic origin, from solid phases to the aqueous (i.e. groundwater) phase. The nature of these processes depends upon the arsenic source mineral and the biogeochemical environment – some of the important combinations of these are considered below.

Oxidation of arsenic bearing sulphides, including arsenian pyrite, typically occurs in environments where such sulphides have been exposed to the atmosphere or an otherwise oxidising environment by mining or erosion or groundwater exploitation or seasonal driven changes in the water table. In acid mine drainage environments, oxidation of arsenopyrite, for example, by ferric iron, Fe^{3+} (aq), may lead initially to the formation of scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$) (Dove & Rimstidt, 1985), schwertmannite ($\text{Fe}_8\text{O}_8(\text{OH})_6(\text{SO}_4) \cdot n\text{H}_2\text{O}$) (Casiot *et al.* 2005) or jarosite ($\text{KFe}^{\text{III}}(\text{OH})_6(\text{SO}_4)_2$) (Gault *et al.* 2005) and particularly in the presence of iron oxidising bacteria, such as *Ferroxidans*, which greatly accelerate sluggish Fe^{2+} oxidation under acidic conditions (Singer & Stumm, 1970) generate acidity and high sulphate concentrations (Lengke *et al.* 2009). Subsequent dissolution of scorodite may release arsenic as arsenate (Dove & Rimstidt, 1985) however the formation of goethite ultimately contributes to the removal of arsenic from solution by sorption.



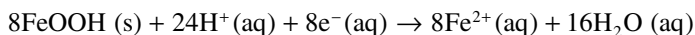
At near neutral pHs, typical of the majority of groundwaters, arsenic mobility under oxidising and slightly reducing conditions is often controlled by the sorption of arsenic onto iron-, aluminium- or manganese-bearing oxyhydroxide phases. As an oxyanion, arsenic tends to sorb more strongly to such minerals under acidic conditions, and accordingly an increase in pH at circum-neutral pH may lead to the mobilisation of arsenic by (Dixit & Hering, 2003):



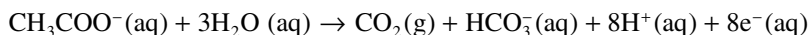
Arsenic desorption from such phases can also take place as a result of competition with other sorbing or passivating components, such as phosphate (Appelo *et al.* 2002) or silica (Swedlund & Webster, 1999).

Lastly, and perhaps most importantly in terms of the numbers of people currently impacted by groundwaters generated by this process, high arsenic groundwaters may also arise as a result of reductive dissolution of arsenic-bearing host phases (Bhattacharya *et al.* 1996, 1997; Nickson *et al.* 1998; Akai *et al.* 2004) and/or the reduction of arsenic leading to changes in the strength of sorption of arsenic to mineral phases. The process is commonly accelerated by the presence of iron reducing bacteria (Islam *et al.* 2004) which, in the absence of oxygen and other appropriate electron-acceptors in sufficient concentration, respire on Fe(III) (Lovley & Phillips, 1986) or As(V) (see Lloyd & Oremland, 2006). Such reductions are coupled to the oxidation of suitable electron donors, most commonly organic matter with reduced carbon or with a volatile fatty acid intermediate, such as lactate or acetate, as shown in the coupled equations below (after Rittman & McCarty, 2001):

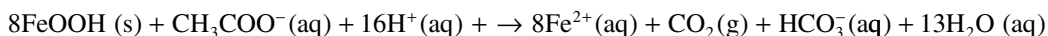
[Fe(III) reduction]



[Acetate oxidation]



[Coupled Reaction]



The required coupling of these reactions with organic matter means that the distribution and bioavailability of organic matter within aquifer sediments likely plays a major role in controlling the local mobilisation of arsenic into groundwaters. Additionally, it means that the anthropogenic addition of relatively labile reduced carbon sources may accelerate rates of arsenic mobilisation – this has been observed on short timescales upon the deliberate addition of glucose (Harvey *et al.* 2002), the amendment of soils with compost (for remediation of heavy metals) (Hartley *et al.* 2009) and where aquifers have become contaminated by hydrocarbons (Burgess & Pinto, 2005). This has led to speculation that massive groundwater abstraction in areas such as Bangladesh may lead to the ingress of relatively reactive surface-derived organic carbon into arsenic-prone aquifers and result in accelerated mobilisation of arsenic and a secular increase in groundwater arsenic hazard (Harvey *et al.* 2002). Whilst plausible, at the time of writing there was an ongoing vigorous debate in the scientific community as to the importance or otherwise of this potential process (Harvey *et al.* 2002; van Geen *et al.* 2003; Polya & Charlet, 2009; Neumann *et al.* 2010; McArthur *et al.* 2011; Lawson *et al.* 2013; Lawson *et al.* 2016).

The biogeochemistry of arsenic in shallow reducing aquifers is complex and closely coupled with the – also complex – cycling of iron, sulphur and other major crustal components. It is beyond the scope of this chapter to address these in any detail but for further information the reader is referred to BGS & DPHE (1999), Smedley and Kinniburgh (2002), Charlet and Polya (2006), Lloyd *et al.* (2006), Polya and Charlet (2009), Ravenscroft *et al.* (2009), and Polya and Lawson (2015) and references therein.

1.2.1.3 Slow arsenic removal processes

Even where there is extensive mobilization of arsenic from synthetic or natural materials in groundwaters (or surface waters), dispersion processes may lead to arsenic not reaching concentrations in potential water supplies above 10 µg/L – whether such elevated concentrations are reached depends upon the balance of rates of arsenic mobilization and arsenic removal by natural or other processes.

For example, in shallow high arsenic groundwaters in sedimentary aquifers in Bengal, the very flat topography gives rise to very low hydraulic gradients and accordingly the rates at which arsenic is flushed out of these aquifers is very low, taking place typically over 1000 or 10,000 year timescales (Smedley & Kinniburgh, 2002) – in such circumstances, the slow arsenic removal processes leads to a maintenance of relatively high arsenic concentrations in groundwater (Charlet & Polya, 2006; van Geen *et al.* 2008).

The paragenesis of secondary mineral formation within these aquifer may also impact the efficiency of arsenic removal processes – for example, Coker *et al.* (2006) note that because biogenic magnetite can more readily incorporate As(V) rather than As(III), in aquifers where reduction of Fe(III) to Fe(II) (ultimately leading to magnetite formation) takes place before reduction of As(V) to As(III), arsenic may be removed from the groundwater by secondary iron phases, whereas where As(V) to As(III) precedes reduction of Fe(III) to Fe(II), such arsenic removal is strongly inhibited.

1.2.2 Nature of high arsenic groundwaters

High arsenic groundwaters might be broadly classified into those of (i) anthropogenic origin; and those of (ii) geogenic origin. Those of anthropogenic origin may be further classified according to source – those related to acid mine drainage tend to have a distinctive water chemistry, whereas those related to contamination by pesticides, industrial chemicals and livestock growth accelerators, for example, can be highly variable in composition. High arsenic groundwaters of geogenic origin may be broadly classified (Smedley & Kinniburgh, 2002; Ravenscroft *et al.* 2009) into those made high in arsenic by (i) reductive dissolution; (ii) oxidized desorption; (iii) sulphide oxidation; and (iv) geothermal processes. There are a further number of waters for which other processes, such as evaporative concentration, are important.

High arsenic groundwaters of the reductive dissolution type (Smedley & Kinniburgh, 2002; Ravenscroft *et al.* 2009), are by far the most important in terms of number of people impacted by their use of these waters for drinking. Such aquifers are found widely across the globe but particularly in circum-Himalayan deltaic regions, such as the Bengal basin (India/Bangladesh) (Bhattacharya *et al.* 1997; BGS & DPHE, 1999), Mekong (Cambodia/Vietnam) (Polya *et al.* 2005), Red (Vietnam) (Berg *et al.* 2001) and Huhhot (China) (Smedley *et al.* 2003) river basins. These waters are typically reducing, of near neutral pH, and with relatively high Fe, Mn and HCO₃ and often relatively high in ammonia and phosphorus. Sulphate concentrations are generally low.

High arsenic groundwaters of the oxidized desorption type (Smedley & Kinniburgh, 2002; Ravenscroft *et al.* 2009), are also found extensively across the globe. Notable examples are found in Argentina (Smedley *et al.* 2002; Bundschuh *et al.* 2004; Bhattacharya *et al.* 2006; O'Reilly *et al.* 2010; Niccoli *et al.* 2012), the western USA and the Datong (Smedley *et al.* 2002; Guo & Wang, 2005) and Hetao (Guo *et al.* 2011) basins amongst other places. These waters are typically oxidising with measureable dissolved oxygen, and have alkaline pHs. Accordingly, iron and manganese concentrations are relatively low, but several other oxyanion types, such as those of sulphur, boron, molybdenum and vanadium, are commonly observed (e.g. Smedley *et al.* 2002; Niccoli *et al.* 2012).

High arsenic groundwaters of the sulphide oxidation type (Smedley & Kinniburgh, 2002; Ravenscroft *et al.* 2009) are typically associated with metallogenic provinces, such as those of the Rocky Mountains, Andes, and south-west England. These regions are commonly associated with present day or palaeo constructive or destructive tectonic plate boundaries. These groundwaters are typically very low pH, high in sulphate and often also high aluminium and other components strongly solubilised at low pHs. Additionally, sulphide oxidation may play a locally important role in mobilising arsenic in shallow aquifers where there are strong seasonal or secular variations in water table levels.

High arsenic geothermal waters (Smedley & Kinniburgh, 2002; Lord *et al.* 2012; Bundschuh & Maity, 2015) are found in the circum-Pacific rim in New Zealand, Phillipines, Japan, USA, Mexico and Chile amongst other countries, as well as further afield in Turkey, Greece, UK and Iran amongst other places. Whilst not generally used for drinking water, geothermal waters do have significant impact on waters that are so used (e.g. Waikato River, New Zealand, (Webster-Brown & Lane, 2005)). Anionically these waters are typically dominated by chloride with lesser but highly variable amounts of sulphate – a reflection of their derivation at depth and more extensive water-rock reactions involved in the genesis than for the other water types described (cf. Chabotarev, 1955).

1.2.3 Distribution of high arsenic groundwaters

A rough picture of the known or predicted global distribution of high arsenic groundwaters can be discerned from Table 1.1. More detailed accounts of the distribution or predicted occurrences may be found for the USA (Focazio, 1999), China (Rodriguez-Lado *et al.* 2013), Cambodia (Sovann & Polya, 2014), south-east Asia (Winkel *et al.* 2008) whilst maps of known global occurrences, including maps for each continent, are provided by Brunt *et al.* (2004) and Ravenscroft *et al.* (2009) and of predicted occurrences by Amini *et al.* (2008).

Particularly in sedimentary aquifers, arsenic distribution may be highly heterogeneous, so the mapping of an area as being of high predicted mean arsenic, or high probability of high arsenic or as a known occurrence does not necessarily mean that a well drill in that area would encounter high arsenic waters. Equally, the converse is true, high arsenic concentrations may be found in areas not so mapped. Amongst others, both Sovann and Polya (2014) and Yang *et al.* (2014) provide estimates for their models of what effectively are type I and type II misclassification errors and, whilst the specific values clearly do not

Table 1.1 Populations exposed to drinking water arsenic at concentrations greater than 10 µg/L or 50 µg/L. Generally refers to peak exposure from known occurrences unless otherwise indicated. Lack of an entry does not indicate the lack of arsenic groundwater hazard. Data quality varies from substantially. Hazard may vary substantially within countries.

Country	Continent	Population Exposed to Drinking Water Arsenic		Reference
		>50 µg/L	>10 µg/L	
Bangladesh	Asia	20,000,000	45,000,000	Flanagan <i>et al.</i> (2012); based upon Johnston (2009) exposure data
India	Asia	11,000,000	30,000,000	Ravenscroft <i>et al.</i> (2007)
USA	North America	3,000,000	30,000,000	Ravenscroft <i>et al.</i> (2007)
China	Asia	5,600,000	15,000,000	Ravenscroft <i>et al.</i> (2007)
Vietnam	Asia	1,500,000	8,000,000	Winkel <i>et al.</i> (2011) (N); Berg <i>et al.</i> (2007) (S) for 10 µg/L; Ravenscroft <i>et al.</i> (2007) for 50 µg/L
Myanmar	Asia	2,500,000	6,250,000*	Ravenscroft <i>et al.</i> (2009) Table 9.9
Pakistan	Asia	2,000,000	6,000,000	Ravenscroft <i>et al.</i> (2009); Table 5.16
Argentina	South America	1,600,000	4,000,000	McClintock <i>et al.</i> (2012)
Nepal	Asia	550,000	2,500,000	Ravenscroft <i>et al.</i> (2009); Table 5.16
Mexico	North America	450,000	2,000,000*	McClintock <i>et al.</i> (2012) for 50 µg/L; Ravenscroft <i>et al.</i> (2007) for 10 µg/L
Hungary	Europe	500,000	1,250,000*	Ravenscroft <i>et al.</i> (2009) Table 9.9
Peru	South America	250,000	625,000*	Castro de Esparza (2009)
Chile	South America	500,000	500,000	Castro de Esparza (2009)
Afghanistan	Asia	200,000*	500,000	Ravenscroft <i>et al.</i> (2009)
Cambodia	Asia	100,000	250,000*	Sampson <i>et al.</i> (2008)
Bolivia	South America	200,000	200,000	McClintock <i>et al.</i> (2012)
Croatia	Europe	80,000*	200,000	Ravenscroft <i>et al.</i> (2009) Table 9.9
Serbia	Europe	60,000*	200,000	Jovanovic <i>et al.</i> (2011)
France	Europe	17,000	200,000	Ravenscroft <i>et al.</i> (2009) Table 9.9
Thailand	Asia	15,000	37,500*	Ravenscroft <i>et al.</i> (2009)
Ecuador	South America	3000	7500*	McClintock <i>et al.</i> (2012)
Colombia	South America	3000	7500*	McClintock <i>et al.</i> (2012)
Nicaragua	North America	3000	7500*	McClintock <i>et al.</i> (2012)
El Salvador	North America	3000	7500*	McClintock <i>et al.</i> (2012)
Honduras	North America	3000	7500*	McClintock <i>et al.</i> (2012)
Guatemala	North America	3000	7500*	McClintock <i>et al.</i> (2012)
Switzerland	Europe	2000*	5000	Ravenscroft <i>et al.</i> (2009)
Greece	Europe	2000*	5000	Ravenscroft <i>et al.</i> (2009)
Cameroon	Africa	1600*	4000	Ravenscroft <i>et al.</i> (2009)

* Indicates estimated from 10 µg/L or 50 µg/L datum as appropriate.

apply to other models and areas, they do give an indication of the scale of possible misclassification errors. Whilst all of these observation-based and model-based distributions are useful for scoping studies, decisions regarding the utilisation of a particular well for drinking water should be based on actual reliable measurement(s) of arsenic concentration.

1.3 ARSENIC IN SURFACE WATER SOURCES

Arsenic in most surface waters tends to be low, mostly considerably lower than 10 µg/L. However, there are notable exceptions, particularly in geothermal areas, highly evaporated inland lakes, upland peat-dominated catchments, surface waters fed by high arsenic groundwaters and in anthropogenically contaminated waters. As with anthropogenically polluted groundwater systems, anthropogenic sources of arsenic in surface water systems include use and disposal of inorganic arsenic, municipal waste sites, industrial waste sites, mining and/or smelting and the sites in which there has been the manufacture and/or use of arsenic-based wood preservatives, herbicides or pesticides (Welch *et al.* 2000). In both systems with arsenic of geogenic origin and those with arsenic of anthropogenic origin, concentrations may vary on a cyclic seasonal or diurnal basis (e.g. Kuhn & Sigg, 1993; Rowland *et al.* 2011; Ullrich *et al.* 2013) or – not only but particularly where there are anthropogenic inputs—on an irregular or secular basis (e.g. Gault *et al.* 2003a).

Unpolluted rain water and snow typically contains less than 1 µg/L arsenic, although Crecelius (1975) reports as much as 16 µg/L arsenic in rainwater polluted by smelters and Dousova *et al.* (2007) report as much as 70 µg/L arsenic in ice accretions impacted by industrial airborne emissions. Cuoco *et al.* (2013) observed concentrations as high as nearly 7 µg/L in rainwater impacted by volcanic plume emissions.

Most unpolluted rivers contain less than 4 µg/L arsenic, although concentrations of 10s, 100s or even 1000s of µg/L of arsenic have been recorded in rivers impacted by geogenic arsenic from acid rock drainage (Routh *et al.* 2007) or geothermal areas (Li *et al.* 2014) or anthropogenic arsenic from mining (Gault *et al.* 2005), smelting or other industrial effluent (Gault *et al.* 2003b; Smedley & Kinniburgh, 2002), geothermal plants (Robinson *et al.* 1995; Polya *et al.* 2003b; Pascua *et al.* 2005), or from run-off from pesticide-treated agricultural areas (Törnqvist *et al.* 2011). Additionally, arsenic concentrations of around 10 µg/L have been observed in upland peat-dominated catchments (Rothwell *et al.* 2009) particularly in waters with high humic acid concentrations (Buschmann *et al.* 2006; Neal *et al.* 2010) reflecting the potential for peats to accumulate significant concentrations of arsenic (McArthur *et al.* 2001) from both geogenic and, often more importantly, anthropogenic sources (Nieminen *et al.* 2000; Küttner *et al.* 2014) and the abilities of Fe(III)-oxide phases (Langner *et al.* 2014) and organic sulphur (Langner *et al.* 2012) to sequester arsenic.

Unpolluted lake waters typically contain less than 2 µg/L arsenic, although lake waters subject to natural evaporative concentration (e.g. Mono Lake, California) may contain 10,000s of µg/L of arsenic (Oremland & Stolz, 2003) and 100s µg/L arsenic have been recorded (Freeman *et al.* 1986) in the geothermally-impacted Lake Ohakuri in New Zealand. Arsenic in polluted lakes may commonly considerably exceed 10 or even 50 µg/L (e.g. Mystic Lakes of the Lake Aberjona watershed, Aurillio *et al.* (1994).

Seawater typically contains less than 2 µg/L arsenic (Andreae, 1979).

1.4 GLOBAL EXPOSURE SCENARIO

1.4.1 Exposure routes

Human exposure to chemicals in the environment may take place through a variety of routes – these include: (i) ingestion of water and other fluids; (ii) ingestion of food; (iii) ingestion of soil; (iv) inhalation

of gas and particulates; and through (v) dermal contact. Other than in relatively restricted environments, such as occupational settings, or to restricted sub-populations, human exposure to arsenic is predominately through ingestion of water and other fluids and through ingestion of food, particularly rice and seafood, as a result of arsenic concentrations in the uncooked foodstuff and/or introduction of arsenic through the cooking process. Much of the arsenic ingested from seafood has been thought to be relatively non-toxic compared to the inorganic arsenicals typically predominating in water supplies. Accordingly, and also because the focus of this volume is on drinking water, exposure through drinking water and the food chain are covered in more detail in Sections 1.5 and 1.6 respectively, whilst the other exposure routes are only considered briefly below.

1.4.2 Exposure and bioavailability

The chemical form of a chemical component, including that of arsenic, may be critical in determining the extent to which it is taken up by the body. Therefore, particularly in the development of unbiased risk assessment models, it is important to distinguish between “exposure” and “bioavailability” and have knowledge of how chemical speciation impacts on the relationship between these two parameters. “Bioavailability” is defined here, following Ng *et al.* (2010) and NRC (2003) as “the amount of a contaminant that is absorbed into the body following skin contact, ingestion or inhalation” and differs from “Exposure” which is widely calculated on the conservative basis that a chemical is 100% bioavailable. However, bioavailability is normally lower to varying degrees than exposure largely because of (i) the inefficiency of passage of the chemical across physiological membranes, such as the skin or gut lumen; and (ii) in the case of an ingestion route, the solubility of the chemical in the gastrointestinal tract. The proportion of an ingested chemical contaminant that is solubilised in the gut is often referred to as the “Bioaccessibility” (e.g. Ng *et al.* 2010; Cave *et al.* 2013). “Bioavailability” may be determined through the measurement various biological endpoints, such as concentration in blood, urine, faeces, adipose tissue (Ng *et al.* 2010), hair or nails (Gault *et al.* 2008; Button *et al.* 2009) or various other biomonitoring markers, for example DNA adduct formation or P₄₅₀ monooxygenase induction (Ng *et al.* 2010).

1.5 EXPOSURE THROUGH DRINKING WATER

1.5.1 Global distribution of exposure to high arsenic (>10 µg/L) drinking water

Drinking water is the dominant contributor in areas where groundwater (and sometimes surface waters) with elevated arsenic concentrations are utilized as the main drinking water supply (e.g. Mondal *et al.* 2010; WHO, 2011). Such is the case in many south and south-east Asian countries (Ng *et al.* 2003), with the most notable occurrences to date being those of West Bengal (India) and Bangladesh, where estimates reach 100 million people at risk of consuming drinking water with concentrations exceeding the WHO provisional guide value of 10 µg As/L (Chakraborti *et al.* 2009; Chakraborti *et al.* 2010). The impact in Bangladesh alone is so severe that epidemiologist Allan Smith from the University of California, Berkeley has described it “the largest mass poisoning of a population in history”, worse than both the 1984 Bhopal industrial poison gas tragedy and the Chernobyl nuclear plant disaster in 1986 (Smith *et al.* 2000). Flanagan *et al.* (2012) estimate over 40,000 arsenic attributable excess deaths per annum for Bangladesh, based on exposure data from Johnston (2009) and the epidemiological data of Sohel *et al.* (2009). Although the problem is most recognised in these developing Asian countries, As exposure through drinking water is a global issue, with concentrations of >10 µg As/L being found in water supplies in countries on all continents (Petruševski *et al.* 2007). Table 1.1 shows a recently updated sketch of the global extent of high

arsenic drinking water together with estimates of the population exposed for each country known to be significantly affected.

High drinking exposures to arsenic are largely in regions of world where there is a significant reliance on groundwater for drinking water. In Bangladesh, for example, exposure results largely from the installation of tube wells tapping into naturally As-rich aquifers. This was increasingly carried out from the 1970s as a measure to counter the high occurrence of diarrheal diseases resulting in part from the consumption of bacterially contaminated standing surface waters (Smith *et al.* 2000). Whilst the most extensive exposures are currently in developing countries, there are also notable exposures in developed countries. For example, in the USA approximately 15% of the population rely on private water supplies (PWS) for drinking water (Steinmaus *et al.* 2005), whilst the figure is much higher in some states, e.g. 40% in New Hampshire, Maine and Vermont (Peters *et al.* 1999). Across the USA, Focazio *et al.* (1999) estimated around 8% of water supply systems exceeded 10 µg As/L and Welch *et al.* (2000) estimated around 10% of sampled US groundwaters to have arsenic concentrations above 10 µg As/L. Again, this figure is higher in some states, for example, 20–30% for wells surveyed in New England (Ayotte *et al.* 2006; Ayotte *et al.* 2017).

1.5.2 Drinking water intake rates

Quantifying water consumption, expressed as an (Water) “Intake Rate” (IR) is pivotal to quantitatively assessing exposure to arsenic from drinking water. It is also helpful to assessing arsenic-attributable health risks from contaminated well water (Watanabe *et al.* 2004) (although this may also be determined by epidemiological studies; e.g. Argos *et al.* (2010)). In many cases, regulatory bodies such as the USEPA and WHO have used a notional fixed “typical” IR of 2 L/day for 60 kg adults in order to estimate exposures and arsenic-attributable health risks and this figure has been widely adopted by many groups (Hossain *et al.* 2013). This has been developed at a whole population level in countries in the Global North in largely temperate or cool climatic zones (e.g. USA, Canada, northern Europe) but the many factors modifying IR are highly variable by region. Age, gender, body weight, occupation and more importantly climate are all important considerations. Assuming a default value in a country of the Global South (e.g. Bangladesh, Cambodia, Myanmar) with a warmer climate, and many of whose population partakes in more outdoor physical labour, could likely underestimate total As exposure from drinking water. Global water consumption data are sparse for developing regions but several studies have addressed the issue (e.g. Hossain *et al.* (2013), Milton *et al.* (2006), Watanabe *et al.* (2004)). Patterns of global water consumption highlight the differences in consumption between the USA and Canada and the developing region of South East Asia. The warmer climates of Bangladesh, India, Cambodia, Vietnam and Taiwan result in higher rates of consumption, in some cases reaching 6 L/day in rural communities prone to physical outdoor labour (Watanabe *et al.* 2004). This raises the concern that in zones where population exposure is already highest, the problem may be exacerbated by higher rates of As ingestion due to the higher bodily demands of fluid for people living in these environments.

Even in countries of the Global North, drinking water intake rates may differ substantially from the 2 L/person/day. Notably, Mons *et al.* (2007) review estimates of cold tap water consumption in several countries of the Global North, notably The Netherlands, Great Britain, Germany and Australia – they found mean daily consumptions varying from 0.1 to 1.55 L/person/day, identified the Poisson distribution to best fit the distribution of water consumption rates and emphasized the importance of using country specific data for evaluation of risk associated with water consumption. For the USA, the USEPA (2011) has provided such detailed exposure factors, tabulating mean and 95th percentile drinking water ingestion rates and drinking water ingestion rates/kg-bw for 13 different age classes for children and adults, as well as noting the different consumption rates for both pregnant women and for lactating women.

Lastly, although the use of more accurate consumption data may lead to more accurate exposure and health risk assessment, such assessment needs to take in account the model intake rates actually used by epidemiological studies. If, for example, such studies are based on an erroneous drinking water consumption rate of 2 L/person/day, risk assessments incorporating a more accurate datum, say 1 L/person/day, could erroneously underestimate health risks unless the epidemiological data themselves were suitably adjusted.

Several studies also found variation between males and females and age groups, where studied, also showed significant differences. In a study in Bangladesh (Khan *et al.* 2009) adult average IR was reported at 2.88 L/day in contrast to a child (≤ 13 years) IR of 1.41 L/day. Similarly, in West Bengal, IRs for adults and children (≤ 11 years) were found to be 3.5 and 2 L/day respectively (Chowdhury *et al.* 2001). Findings were similar in a more recent West Bengal study group with adult and child (≤ 15 years) IRs of 3.49 and 2.14 L/day respectively, and – values with respect to relative to bodyweight of around 71 ml/kg-bw/day and 87 ml/kg-bw/day for adults and children respectively. Differences have also been observed between rural and urban populations, again most likely as a result of manual labour associated with rural lifestyles. Average consumption in a rural Bangladeshi population was found to be 3.1 L/day in comparison to 2.75 L/day in an urban population (Watanabe *et al.* 2004). The findings of this study in particular have relevance beyond Bangladesh due to, as previously mentioned, the significant number of people in rural areas rely on PWS in developed countries. Factors such as occupation and time spent outdoors, for example in agricultural work, should all be taken into consideration when performing exposure and risk calculations during risk analyses.

1.6 EXPOSURE THROUGH THE FOOD CHAIN

An assessment of exposure to inorganic arsenic (iAs) from drinking water might prudently also consider how exposure from other dietary sources adds to the overall exposure – in particular, it is noted that cases could arise where daily arsenic exposure from drinking water alone might be less than recommended (e.g. EFSA, 2009; JECFA, 2010; EFSA, 2014) values, yet the combined exposure from both drinking water and other dietary sources may exceed these values. Accordingly, arsenic exposure from non-drinking-water dietary sources is briefly considered here.

Non-water dietary sources are the predominant source of exposure to iAs for most of the world's population. Seafood and rice constitute dietary sources that warrant further comment here, however it is recognized that – for the most part – seafood, although often high in total arsenic, is typically low in iAs ($< 0.1\%$, Ruttens *et al.* (2012)), and, for those not on a high rice diet, there are a broad range of dietary sources. Xue *et al.* (2010), for example, based on food consumption and food arsenic concentration data from the National Health and Nutrition Examination Survey (NHANES), report the major dietary contributors to iAs exposure for the general U.S. population to be vegetables (24%), fruit juices & fruits (18%), rice (17%), beer & wine (12%), and flour, corn & wheat (11%), with the mean total and iAs intakes from food for the U.S. population estimated to be 0.38 $\mu\text{g}/\text{kg-bw}/\text{day}$ and 0.05 $\mu\text{g}/\text{kg-bw}/\text{day}$, respectively. In Europe, the pattern is similar (EFSA, 2009), with “cereal grains and cereal based products, food for special dietary uses, bottled water, coffee, beer, rice grains & rice based products, fish and vegetables contributing to [overall] arsenic exposure” (FAO/WHO, 2011), with the median total arsenic intake for the European population estimated to be 0.94–1.22 $\mu\text{g}/\text{kg-bw}/\text{day}$, with the equivalent 95th percentile values being 3.16–3.38 $\mu\text{g}/\text{kg-bw}/\text{day}$. The recognition of the impact of relatively high inorganic arsenic uptake has now led to changes to European regulation of inorganic arsenic in rice (EC, 2015).

Rice consumption determines a major proportion of the difference between the mean and 95th total arsenic intake values reported by EFSA (2009) – whilst rice forms only around 4% of the European diet, for over 3,000,000,000 people around the world, rice is the dominant source of calories, and in many cases,

also of iAs. Of the carbohydrate staples, rice is particularly susceptible to taking up high concentrations of inorganic arsenic, largely as a result of its widespread cultivation in flooded paddy fields, which create reducing conditions under which the neutral As(III) species, H_3AsO_3 (aq) predominates and enters rice plant cells through aquaporin water/silicic acid transport channels. Rice iAs contents vary widely between 10s and 100s $\mu\text{g}/\text{kg-dw}$ and several percent of rice consumed globally contains greater than 180 μg iAs/kg-dw, a concentration above which Banerjee *et al.* (2013) have observed elevated micronuclei frequency in urothelial cells in a West Bengal (India) cohort consuming rice as a staple (~500 g/day).

1.7 IMPORTANCE OF NON-ARSENIC PARAMETERS

Whilst this chapter has focussed on arsenic distribution in source waters for water supply systems, it is worth noting that measureable parameters other than arsenic may also be of considerable importance when assessing the utility of a source water, assessing overall risks associated with a water supply, evaluating remediation options for other considerations in the preparation of an effective water safety plan. For example, it is noted that:

- (i) The effectiveness of some remediation options for high arsenic waters have been shown to be strongly impacted by the presence of other constituents, notably suspended particulates, organic matter, iron and phosphate (cf. Chiew *et al.* 2009).
- (ii) It has been speculated that the presence of other constituents may modify dose-response relationships in those chronically exposed to high arsenic drinking water (cf. Tseng, 2002; Ting *et al.* 2010 & references therein). An example relates to “blackfoot disease” – a disease characterised by “progressive discolouration of the skin extending from the toes gradually upward toward the ankles ... and ... numbness ... before the development of gangrene [and in some cases] spontaneous amputation” (Tseng *et al.* 2002). “Blackfoot disease” in Taiwan was thought by some to be the result of combined high humic and arsenic concentrations in drinking water (see Tseng *et al.* 2002) although the direct (Lu *et al.* 1990) or confounding role of humic substances in the etiology of “blackfoot disease” is questioned (Tseng *et al.* 2005) or largely discredited by others (Engel *et al.* 1994).
- (iii) Particularly in developing rural areas, questions have been raised and there has been considerable discussion over the possible substitution of water-borne pathogen attributable health risks for water-borne arsenic attributable health risks when improved arsenic-remediated water supply options are put in place (Esrey *et al.* 1996; Howard *et al.* 2003, 2007; Clasen *et al.* 2003, 2004; Lokuge *et al.* 2004; Van Geen *et al.* 2011; Mondal *et al.* 2014) – accordingly analysis of arsenic-impacted water supplies for microbiological quality may also be indicated.

1.8 CONCLUSIONS

Arsenic is a widespread trace constituent of groundwaters in many parts of the world, with well over 100,000,000 people exposed to this hazard through consumption as drinking water: this has given rise to devastating health impacts. Understanding the distribution of arsenic in groundwaters and remediating those used as drinking or cooking waters therefore represent endeavours of great importance.

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