Best Practice Guide on the Control of Arsenic in Drinking Water

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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
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
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(FeAs₂), realgar (As₄S₄), orpiment (As₂S₃), niccolite (NiAs), sulphosalts (e.g. tennanite (Cu₁₃Fe₁₂As₄S₄₃; enargite (Cu₄AsS₄)), and oxides (e.g. scorodite (FeAsO₄ ⋅ 2H₂O), arsenolite (As₂O₃), pharmacosiderite (Fe₅(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 sulphosalts 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 (FeAsO$_4$ \cdot 2H$_2$O) (Dove & Rimstidt, 1985), schwertmannite (Fe$_8$O$_{16}$(OH)$_6$(SO$_4$)$_2$ \cdot nH$_2$O) Casiot et al. 2005 or jarosite (KFe$^{3+}$(OH)$_6$(SO$_4$)$_2$) (Gault et al. 2005) and particularly in the presence of iron oxidising bacteria, such as *Ferrooxidans*, 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.

\[
\text{FeAsS} (s) + 14\text{Fe}^{3+} (aq) + 10\text{H}_2\text{O} (aq) \rightarrow 14\text{Fe}^{2+} (aq) + \text{SO}_4^{2-} (aq) + \text{FeAsO}_4 \cdot 2\text{H}_2\text{O} (s) + 16\text{H}^+ (aq)
\]

\[
\text{FeAsO}_4 \cdot 2\text{H}_2\text{O} (s) \rightarrow \alpha\text{-FeOOH} (s) + \text{H}_2\text{AsO}_4^- (aq) + \text{H}^+ (aq)
\]

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):

\[
\equiv\text{FeHAsO}_4^-(s) + \text{H}_2\text{O} (aq) \rightarrow \equiv\text{FeOH} (s) + \text{HAsO}_4^2^- (aq) + \text{H}^+ (aq)
\]

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):

\[
[\text{Fe(III) reduction}]
8\text{FeO}OH (s) + 24\text{H}^+ (aq) + 8\text{e}^- (aq) \rightarrow 8\text{Fe}^{2+} (aq) + 16\text{H}_2\text{O} (aq)
\]

\[
[\text{Acetate oxidation}]
\text{CH}_3\text{COO}^- (aq) + 3\text{H}_2\text{O} (aq) \rightarrow \text{CO}_2 (g) + \text{HCO}_3^- (aq) + 8\text{H}^+ (aq) + 8\text{e}^- (aq)
\]

\[
[\text{Coupled Reaction}]
8\text{FeO}OH (s) + \text{CH}_3\text{COO}^- (aq) + 16\text{H}^+ (aq) \rightarrow 8\text{Fe}^{2+} (aq) + \text{CO}_2 (g) + \text{HCO}_3^- (aq) + 13\text{H}_2\text{O} (aq)
\]
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 deliberation 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 \( \mu \text{g}/\text{L} \) – 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 Huuhot (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.

<table>
<thead>
<tr>
<th>Country</th>
<th>Continent</th>
<th>Population Exposed to Drinking Water Arsenic</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bangladesh</td>
<td>Asia</td>
<td>20,000,000  45,000,000</td>
<td>Flanagan et al. (2012); based upon Johnston (2009) exposure data</td>
</tr>
<tr>
<td>India</td>
<td>Asia</td>
<td>11,000,000  30,000,000</td>
<td>Ravenscroft et al. (2007)</td>
</tr>
<tr>
<td>USA</td>
<td>North America</td>
<td>3,000,000  30,000,000</td>
<td>Ravenscroft et al. (2007)</td>
</tr>
<tr>
<td>China</td>
<td>Asia</td>
<td>5,600,000  15,000,000</td>
<td>Ravenscroft et al. (2007)</td>
</tr>
<tr>
<td>Vietnam</td>
<td>Asia</td>
<td>1,500,000  8,000,000</td>
<td>Winkel et al. (2011) (N); Berg et al. (2007) (S) for 10 µg/L; Ravenscroft et al. (2007) for 50 µg/L</td>
</tr>
<tr>
<td>Myanmar</td>
<td>Asia</td>
<td>2,500,000  6,250,000*</td>
<td>Ravenscroft et al. (2009) Table 9.9</td>
</tr>
<tr>
<td>Pakistan</td>
<td>Asia</td>
<td>2,000,000  6,000,000</td>
<td>Ravenscroft et al. (2009); Table 5.16</td>
</tr>
<tr>
<td>Argentina</td>
<td>South America</td>
<td>1,600,000  4,000,000</td>
<td>McClintock et al. (2012)</td>
</tr>
<tr>
<td>Nepal</td>
<td>Asia</td>
<td>550,000  2,500,000</td>
<td>Ravenscroft et al. (2009); Table 5.16</td>
</tr>
<tr>
<td>Mexico</td>
<td>North America</td>
<td>450,000  2,000,000*</td>
<td>McClintock et al. (2012) for 50 µg/L; Ravenscroft et al. (2007) for 10 µg/L</td>
</tr>
<tr>
<td>Hungary</td>
<td>Europe</td>
<td>500,000  1,250,000*</td>
<td>Ravenscroft et al. (2009) Table 9.9</td>
</tr>
<tr>
<td>Peru</td>
<td>South America</td>
<td>250,000  625,000*</td>
<td>Castro de Esparza (2009)</td>
</tr>
<tr>
<td>Chile</td>
<td>South America</td>
<td>500,000  500,000</td>
<td>Castro de Esparza (2009)</td>
</tr>
<tr>
<td>Afghanistan</td>
<td>Asia</td>
<td>200,000*  500,000</td>
<td>Ravenscroft et al. (2009)</td>
</tr>
<tr>
<td>Cambodia</td>
<td>Asia</td>
<td>100,000  250,000*</td>
<td>Sampson et al. (2008)</td>
</tr>
<tr>
<td>Bolivia</td>
<td>South America</td>
<td>200,000  200,000</td>
<td>McClintock et al. (2012)</td>
</tr>
<tr>
<td>Croatia</td>
<td>Europe</td>
<td>80,000*  200,000</td>
<td>Ravenscroft et al. (2009) Table 9.9</td>
</tr>
<tr>
<td>Serbia</td>
<td>Europe</td>
<td>60,000*  200,000</td>
<td>Jovanovic et al. (2011)</td>
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<td>France</td>
<td>Europe</td>
<td>17,000  200,000</td>
<td>Ravenscroft et al. (2009) Table 9.9</td>
</tr>
<tr>
<td>Thailand</td>
<td>Asia</td>
<td>15,000  37,500*</td>
<td>Ravenscroft et al. (2009)</td>
</tr>
<tr>
<td>Ecuador</td>
<td>South America</td>
<td>3000  750*</td>
<td>McClintock et al. (2012)</td>
</tr>
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<td>Colombia</td>
<td>South America</td>
<td>3000  750*</td>
<td>McClintock et al. (2012)</td>
</tr>
<tr>
<td>Nicaragua</td>
<td>North America</td>
<td>3000  750*</td>
<td>McClintock et al. (2012)</td>
</tr>
<tr>
<td>El Salvador</td>
<td>North America</td>
<td>3000  750*</td>
<td>McClintock et al. (2012)</td>
</tr>
<tr>
<td>Honduras</td>
<td>North America</td>
<td>3000  750*</td>
<td>McClintock et al. (2012)</td>
</tr>
<tr>
<td>Guatemala</td>
<td>North America</td>
<td>3000  750*</td>
<td>McClintock et al. (2012)</td>
</tr>
<tr>
<td>Switzerland</td>
<td>Europe</td>
<td>2000*  5000</td>
<td>Ravenscroft et al. (2009)</td>
</tr>
<tr>
<td>Greece</td>
<td>Europe</td>
<td>2000*  5000</td>
<td>Ravenscroft et al. (2009)</td>
</tr>
<tr>
<td>Cameroon</td>
<td>Africa</td>
<td>1600*  4000</td>
<td>Ravenscroft et al. (2009)</td>
</tr>
</tbody>
</table>

* 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 considered more in detail in Sections 1.5 and 1.6 respectively, whilst the other exposure routes are only covered 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 of 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 $P_{450}$ 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 (Petrusevski 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 counties. 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 temperature 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 into 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 µg/kg-bw/day and 0.05 µg/kg-bw/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 µg/kg-bw/day, with the equivalent 95th percentile values being 3.16–3.38 µg/kg-bw/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, H₃AsO₃ (aq) predominates and enters rice plant cells through aquaporin water/silicic acid transport channels. Rice iAs contents vary widely between 10s and 100s µg/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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1.10 REFERENCES


Chapter 5

Sampling and analysis for monitoring arsenic in drinking water

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5.1 INTRODUCTION

Monitoring of water supplies for arsenic and associated parameters may be required for the purposes of (i) checking compliance with relevant regulations; (ii) designing locally-relevant treatment systems; (iii) checking the efficacy of treatment systems; and (iv) for better understanding of the natural and man-made controls on arsenic concentrations in a water supply. The data requirements for each of these purposes may be very different and therefore so may the nature of the associated sampling and analytical protocols that are required to be put in place to enable the monitoring data requirements to be met. Determining the most appropriate sampling and analysis protocols therefore requires an awareness of the data requirements. These protocols collectively involve (i) sampling strategy; (ii) sampling and preservation protocol; (iii) selection of analytical instrumentation; (iv) analytical and data reduction protocols; (v) total quality management protocols, including for chain-of-custody, documentation and, where appropriate, training. This chapter considers each of these in turn. See also Polya et al. (2017) for a relevant case-study.

There is an extensive literature available on methods for the sampling and analysis of water for a wide range of analytes, including arsenic. These include: BS1427:2009 (BSI, 2008) and APHA/AWWA/WEF (1999) amongst others. In this chapter, we focus on the principles of sampling and analytical protocols with a view to informing the professional: (i) in their choice, if there is one, of which protocols to follow, or – (ii) if the protocol selected is a matter not of choice but instead is determined by local or national regulation...
or guidelines and/or by resource or logistical constraints, then information to aid the assessment of the accuracy and precision of analysis and of the representativeness of the samples being obtained.

5.2 DATA REQUIREMENTS

5.2.1 Overall aims of monitoring

Project data requirements are informed by the types of questions required to be answered (Table 5.1). For example, assessing the seasonal controls on arsenic concentration in drinking water or the long-term effectiveness of arsenic removal treatment technologies requires sampling over a period of time, whilst assessing the homogeneity with respect to arsenic of a groundwater drinking source may require sampling of wells screened at various depths and spread over a particular area. The sampling density, both in temporal and spatial dimensions, depends in part on the variability of the water being sampled and on the pre-determined levels of confidence required for any decision made on the basis of the data obtained. Since often such variability is not known in advance of sampling and analysis, sampling design may need to rely on expert judgement, conditional design protocols or be iteratively updated.

Table 5.1 Typical questions informing data requirements for arsenic-in-water sampling and monitoring.

<table>
<thead>
<tr>
<th>Question</th>
</tr>
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<tbody>
<tr>
<td>Does the arsenic concentration in the drinking water exceed a regulatory value?</td>
</tr>
<tr>
<td>Is the arsenic concentration significantly higher than background values?</td>
</tr>
<tr>
<td>Is the arsenic concentration likely to lead to an unacceptable health risk?</td>
</tr>
<tr>
<td>Is arsenic concentration too high for recommended operational limits of a treatment technology?</td>
</tr>
<tr>
<td>Has the arsenic concentration changed significantly (i) since last year? (ii) since last week? (iii) since a new treatment technology was put in place?</td>
</tr>
<tr>
<td>Is the effectiveness of arsenic by a water treatment technology degrading with time?</td>
</tr>
<tr>
<td>Does the arsenic concentration change on a cyclic (e.g. seasonal, diurnal) basis?</td>
</tr>
<tr>
<td>Are arsenic concentrations consistent with a particular biogeochemical hypothesis?</td>
</tr>
</tbody>
</table>

5.2.2 Representativeness

Sampling and monitoring protocols need to ensure that a sample is sufficiently representative of the water supply being investigated. In particular, the protocols should be designed to ensure that all of the following are considered if required: (i) differences between dissolved aqueous species, colloidal species, arsenic associated with suspended particulates; (ii) unrepresentative first-taken samples e.g. waters lying in pipes or boreholes; (iii) preservation/contamination during sampling; (iv) preservation/contamination during storage prior to analysis; (v) seasonal, diurnal, other cyclic changes and secular and other non-cyclic changes in composition on various timescales.

5.2.2.1 Speciation

In drinking waters, arsenic may occur (i) as various dissolved species; (ii) in colloids; (iii) or associated with suspended particulates. The most common dissolved forms are inorganic arsenic species; as As(III) these forms are typically charge-neutral at acidic, neutral and slightly alkaline pHs; as As(V) these forms are typically negatively charged for all but extremely acidic waters (Figure 5.1). Arsenic may also occur, in waters with high nutrient loadings and hence high levels of biological activity, or in waters contaminated
by pesticides or herbicides, as various methylated forms (Bednar et al. 2002; Wallschlager & London, 2008). Even where the concentrations of methylated forms are low, determination of these species may be important to inform understanding of biogeochemical processes in which they act as intermediary species (Maguffin et al. 2015). In alkaline waters where there is sufficiently high dissolved sulphide, arsenic may also occur predominately as thioarsenates or thioarsenites – recognition of these species may be important because they are often not preserved well by commonly used sampling and preservation protocols, notably acidification, and this may lead to underestimation of total arsenic in such waters (Planer-Friedrich et al. 2007; Suess et al. 2011). Colloidal arsenic concentrations are generally low except in waters that are high in organics and/or iron – peat-land derived waters are a notable example (Rothwell et al. 2007). A significant fraction of arsenic may also be associated with suspended particulates, especially when the loading of such particulates is high – environments where this may be significant include areas of high physical weathering, resulting from climate and/or anthropogenic activities, such as mining (Schäfer & Blanc, 2007) – in most waters, however, the difference between total arsenic and total dissolved arsenic is relatively small.

![Eh vs pH arsenic species predominance diagram at 25°C/1 bar showing the predominance fields of As(V) and As(III) species and the stability fields for the arsenic sulphide minerals, orpiment and realgar. ∑As = 10⁻⁶ molal; ∑S = 10⁻⁴ molal. Calculated using Geochemists Workbench® Professional Version 11.0.2.](image)

**Figure 5.1** Eh vs pH arsenic species predominance diagram at 25°C/1 bar showing the predominance fields of As(V) and As(III) species and the stability fields for the arsenic sulphide minerals, orpiment and realgar. ∑As = 10⁻⁶ molal; ∑S = 10⁻⁴ molal. Calculated using Geochemists Workbench® Professional Version 11.0.2.

### 5.2.2.2 Spatial and temporal variations

The first water samples taken from taps, pipes or boreholes may not be representative of the bulk water supplied for a variety of reasons including: (i) in boreholes, particularly those with iron-based casings, the water standing in the borehole itself may be considerably different from that in the aquifer, especially with regard to components and chemical species whose concentrations depend upon the state of oxygenation of the water; (ii) in piped systems that have not recently been used, turning on a tap may result in flakes of deposits built up on the interior of the pipe to be flushed out upon initial sampling.
Similarly, in surface waters, the bulk composition of the river, pond or lake, may be significantly different from that at the boundaries of the water body – notably the surface layer, the bottom or even near the sides of the water body.

Irrespective of these issues, representative samples need to be collected recognising possible or likely cyclic, irregular or secular changes in arsenic concentration as well as spatial variations in concentration. Seasonal variations in arsenic concentrations in lakes and rivers (McLaren & Kim, 1995; Masson et al. 2006) are well known, and have also been observed in shallow groundwater systems (Polizzotto et al. 2008). Diurnal cycles of arsenic concentrations have been noted in geothermal waters (Farnfield et al. 2012; Ullrich et al. 2013), upland catchments in the UK (Rowland et al. 2011) and rivers draining mining areas (Barringer et al. 2008). In eutrophic lakes, seasonally dependent redox processes can also lead to abrupt discontinuities in the spatial distribution of arsenic concentrations (e.g. Kuhn & Sigg, 1993).

5.2.2.3 Contamination during sampling

Contamination of surface water samples may arise from the process of sampling itself – for example by an operator who has entered a water body upstream of the sampling point or who has disturbed fine-grained sediments or deposits at the bottom of a shallow river or pond. Contamination may also arise from inadequately washed or chosen sampling equipment, in situ measuring equipment or other equipment.

5.2.2.4 Preservation

Any removal of water samples from their ambient environment may create the potential for homogeneous reactions changing solute speciation, including that of arsenic, and heterogeneous reactions, such as degassing of CO$_2$ (g) or precipitation of Fe-O-H or Fe-S phases, all of which may result – if adequate steps are not taken – in subsequent analyses under-representing arsenic solute concentrations. Preservation steps required may vary from water-type to water-type – for example, high bicarbonate groundwaters may typically require larger amounts of added acid to achieve a target pH of less than 2, and where high bicarbonate concentrations are anticipated (or even if they are not) prudent practice would be to test, on representative disposal samples, whether or not the target pH for preservation is achieved by the protocol utilised and to amend the protocol accordingly.

5.2.3 Data & data quality objectives (DQOs)

Data and data quality objectives (DQOs) include field site related parameters, a list of analytes (including arsenic) to be determined and chemical measurement performance characteristics. These should be informed by the relevant project aims.

5.2.3.1 Field site related parameters

A site conceptual model may be helpful in determining relevant field site related parameters (Yeskis & Zavala, 2002). For example, the nature and connectivity of surface and sub-surface water bodies, land use and its distribution, distribution of anthropogenic and other inputs, climatic and other geographic controls, including river stage, rainfall, humidity and temperature – may all be relevant parameters to a useful site specific conceptual model.

5.2.3.2 Analytes

In addition to arsenic, other analytes may be required to be determined for a project. Over and above those that might be required, for example, by regulatory or contractual drivers, some of the example analytes
below may be of utility in better understanding sources and controls on arsenic concentrations in source
waters, for quality assurance or for assessing risk:

(i) Arsenic speciation, notably of inorganic As(III) and As(V), and – where contamination of a water
supply is suspected, of methylated arsenicals, monomethylarsenic(III) and monomethylarsonic(V)
acids, dimethylarsenic(III) and dimethylarsenonic ~ (V) acids, TMAO; and in reduced high
sulphur waters, thioarsenites and thioarsenates
(ii) Fe, Mn, Al, PO₄, DOC, HCO₃, CO₃, pH, Eh, dissolved oxygen, turbidity, suspended solids – are
all parameters that may influence the mobility/solubility of arsenic in water or the efficacy of
preservation methods or the suitability of various remediation technologies aimed at removing
arsenic to below regulatory or other standards
(iii) Na, K, Ca, Mg, HCO₃, Cl, SO₄ – are parameters that collectively typically account for most of the
ions in natural waters and accordingly analysis of which can be collectively used to obtain a charge
balance, which may in turn be used for quality assurance purposes; additionally measurement of
electrical conductivity may be helpful in this regard
(iv) Thermally tolerant coliforms, E. coli or other microbiological parameters – particularly where the
purpose of a project is to calculate overall water supply associated health risks

5.2.3.3 DQOs – required chemical measurement performance characteristics

It is important to have an awareness of the specifications required of a meaningful chemical analysis – this
is irrespective of whether the analysis is carried out in-house or by an external sub-contractor. Awareness
of these Data Quality Objectives (DQOs), both the parameters and their target values, for the relevant
project can be of critical value in informing the selection of appropriate analytical instrumentation
and methods, and may also contribute to more cost-effective analyses being procured. Table 5.2 lists
commonly used chemical measurement performance characteristics and typical values that might be
required in a routine monitoring of drinking water supplies. It is worth emphasising, however, that the
actual values required for a given monitoring project should depend upon the project aims and consequent
data requirements.

The values of precision (Table 5.2) are commonly achieved in routine analysis of arsenic in drinking
water, although it is worth noting that the analytical precision is generally dependent upon concentration,
particularly for low concentrations below or just above the method detection limit. The difference in
typical values for repeatability and reproducibility reflects that replicate analysis of the samples on the
same day, by the same operator by the same method generally reveals a better (i.e. numerically smaller)
precision than replicate analysis involving different methods and laboratories and so may, on its own,
give an overestimation of the quality of a chemical analysis.

Use of long-term LODs can help to provide a more robust approach in addition to long-term QC charts
to define instrumental trends in performance characteristics. Laboratory proficiency testing schemes (e.g.
Aquacheck) provide another level of defining analytical precision and accuracy for a variety of matrices
(e.g. clean, waste water) through scoring against a true ‘spike’ value and in a blind comparison with other
peer laboratories. Proficiency schemes can provide an additional layer of confidence in the precision and
accuracy of analyses.

The typical values for maximum total dissolved solids (TDS) in a sample are based on the lower limit of
unacceptable tasting drinking water (WHO, 1996), although under some circumstances analysis at higher
concentrations might be required.
Table 5.2 List of commonly used chemical measurement performance characteristics and typical values that might be required for routine monitoring of a drinking water supply. See glossary for definitions.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Explanation</th>
<th>Typical Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Detection limit (DL)</td>
<td>The minimum concentration at which the presence of an analyte can be determined to a specified degree of confidence</td>
<td>0.05 µg/L (99%)</td>
</tr>
<tr>
<td>Limit of quantification (LOQ)</td>
<td>The minimum concentration at which the concentration of an analyte can be quantified to a specified degree of confidence</td>
<td>0.10 µg/L (99.5%)</td>
</tr>
<tr>
<td>Precision – repeatability</td>
<td>The dispersion of repeat measurements of an analyte in a sample by the same method and by the same operator on the same day.</td>
<td>±1% @ 10 µg/L</td>
</tr>
<tr>
<td>Precision – reproducibility</td>
<td>The dispersion of repeat measurements of an analyte in a sample by different methods and different laboratories/operators.</td>
<td>±2% @ 10 µg/L</td>
</tr>
<tr>
<td>Accuracy/Bias</td>
<td>The difference between a measured concentration of an analyte and the true concentration</td>
<td>&lt;5%</td>
</tr>
<tr>
<td>Concentration range</td>
<td>The range between the expected minimum and maximum concentrations of the analyte in a set of samples</td>
<td>0.1–1000 µg/L</td>
</tr>
<tr>
<td>Matrix &amp; impacts on sensitivity &amp; selectivity</td>
<td>The matrix refers to chemicals present in a sample other than the analyte – these may include H₂O as the solvent, major ions such as HCO₃⁻, CO₃²⁻, Cl⁻, SO₄²⁻, Ca²⁺, Mg²⁺, Na⁺ and K⁺ or other chemical moieties.</td>
<td>1200 µg/L &lt;10%</td>
</tr>
<tr>
<td></td>
<td>Sensitivity refers to instrumental response for a given concentration of an analyte</td>
<td>&lt;10%</td>
</tr>
<tr>
<td></td>
<td>Selectivity refers to a uniqueness of an instrumental response to a particular analyte.</td>
<td>&lt;10%</td>
</tr>
</tbody>
</table>

5.3 SAMPLING STRATEGIES/DESIGN

In many, indeed in perhaps most applications, the purpose of analysing drinking water samples for arsenic requires that the samples obtained are representative of some suitably defined water body – whether that be groundwater, surface water, water in specific stage of a treatment plant, water in a supply pipe or water at the point of use. Although its importance is often overlooked, good sampling is often critical to obtaining meaningful chemical analyses – conversely poor, unrepresentative sampling can, under some circumstances, render even the most accurate and precise analyses next to useless or potentially highly misleading.

“Good” sampling is defined by Gy (1995) as sampling that results in unbiased samples representative of a batch of material that cannot “be submitted to analysis in totality” and further requires that such sampling is “probabilistic”, meaning that “all the constitutive elements of a batch [of, say, a water body, for example] [have] a [known] non-zero probability of being selected to make up a sample”. In contrast “poor” sampling, often the result of a strategy to obtain samples from the most accessible points in the cheapest manner possible, is non-probabilistic and consequently non-representative and associated with (sometimes
Simplifying and analysis for monitoring arsenic in drinking water

high) sampling errors with non-zero means. Gy (1995) further describes sampling as “the most dangerous quality destroyer” – its importance should not be underestimated. USGS (2006) states “field personnel must take steps to ensure that … samples collected will be representative of the aqueous system being investigated. [Representative samples are] delineated by the objectives and scope of the study.”

Geostatistics may be of utility in identifying deficiencies in sampling regimes as well as indicating the scale of spatial heterogeneity (de Gruyter, 2006; Webster & Lark, 2013). Temporal heterogeneities should also be addressed, as appropriate, in designing a sampling strategy. Good sample design will accordingly take into account possible regular diurnal, weekly or seasonal variations and more irregular variations due to precipitation events and anthropogenic events, such as discharges of effluent (Gault et al. 2003).

5.4 SAMPLING/PRESERVATION PROTOCOLS

Suitable sampling and preservation of water samples are required to ensure that samples are neither unacceptably contaminated nor unacceptably altered prior to analysis.

Guidance on suitable sampling protocols are provided by, amongst others, USGS (2006) and Johnson (2008), and should include consideration of contamination of water samples by (i) operators; (ii) sampling media or reagents; (iii) non-target waters; (iv) the atmosphere. Operator contamination may be reduced by clean handling techniques and ensuring that the operator and/or associated measuring devices are downstream of the sample being collected. Washing out pre-cleaned sampling media with the water to be sampled is a widely used protocol, whilst the use of field blanks is essential to check whether or not sampling devices and or storage vessels contribute to sample contamination. For surface water sampling, samples should not be taken close to effluent discharge, transport infrastructure, water surface or turbid basal flow zones (unless that is the target sample to be taken). The use of flow cells are extremely useful in (i) ensuring that measuring devices do not contaminate the collected sample; (ii) permitting parameters such as pH, Eh, electrical conductivity and/or D.O. to be monitored to aid the collection of uncontaminated samples; and (iii) where oxygen poor waters are being sampled, aiding the preservation of redox sensitive analytes, including arsenic, during sample storage.

Preservation issues include: (i) precipitation of (hydrated) oxides or iron and other transition metals; (ii) microbiological activity; (iii) abiotic oxidation of As(III); and (iv) UV-induced photo-oxidation (Polya et al. 2003). Effective preservation protocols are designed to address these issues and notably variably include: (i) filtering through 0.45 μm (or smaller pore diameter, e.g. 0.10 μm) cellulose nitrate filters, if appropriate after the use of a 1 or 2 μm pre-filter; (ii) acidification to a target pH of around 2 with AnalR or equivalent grade hydrochloric acid; (iii) storage in a refrigerator (but not a freezer under some circumstances); and (iv) storage in the dark. Addition of a bacteriocide (Scudlark & Johnson, 1982) or additions of complexing agent such as EDTA (Gallagher et al. 2000) have also been used to preserve arsenic or arsenic speciation. Ultimately, these techniques may not be 100% effective in preserving analytes, so an important further protocol to maximise sample preservation is to analyse collected samples as promptly as possible. Further discussion of preservation techniques may be found in APHA/AWWA/WEF (1999), Polya et al. (2003), Gault et al. (2005), USGS (2006) and Johnson et al. (2008) amongst others.

5.5 ANALYTICAL METHODS

Total arsenic and arsenic speciation (Francesconi & Keunhelt, 2004) are routinely measured by a variety of methods, involving a variety of analytical techniques involving ICP-MS, ICP-AES, HG-AAS or field based separations and techniques, and a variety of data reduction protocols.

The criteria for selecting the most appropriate methods include both logistical and technical criteria. Logistical criteria include convenience, availability, turnaround time, cost and documentation/reporting.
standards. Technical criteria include precision, accuracy, detection limits, limits of quantification, sensitivity, selectivity and traceability. The relative weighting given to each of these criteria will depend upon project constraints and the purpose of the analyses.

Notwithstanding the relative technical merits of various methods, analyses undertaken as part of project to test/demonstrate regulatory compliance (WHO, 2011a; WHO, 2011b) or as otherwise contractually required may be required to be performed by certain approved methods (cf. APHE/AWWA/WEF, 1999) or under methods validated under an appropriate national accreditation body.

5.5.1 Analytical instrumentation

5.5.1.1 Total arsenic

Total arsenic may be determined in waters using a wide variety of instruments, with ICP-MS, ICP-AES, HG-AAS amongst the most widely used. The main consideration for the selection of the methodology besides available resources, must consider the sensitivity and ability to measure arsenic at concentrations below guideline concentrations and ability to provide accurate analyses despite the presence of matrix components that may inhibit analytical performance. An alternative approach was reported by Dominguez-Gonzalez et al. (2014) who was able to achieve a detection limit of 2.5 µg/L for visible spectrometry using functionalised gold nanoparticles. Field kits widely used for total arsenic determinations include the Merckoquant®, HACH®, Wagtech® Digital Arsenator test kits (UNICEF, 2010). The use of such field kits is particularly indicated where rapid on-site measurements are required and where the precision requirements are not tight and where there are logistical difficulties, including ensuring appropriate preservation, in transporting samples to fixed laboratories and returning data to the field. The reliability of such kits has been evaluated by van Geen et al. (2005) amongst others whilst Mukherjee et al. (2005) comments on human factors that may impact this.

5.5.1.2 Arsenic speciation

With nearly 1000 original articles on arsenic speciation analysis (Tyson, 2013), hyphenated techniques are established as the preferred methods for arsenic speciation due to their reproducibility of results, short analysis times and development of advanced instrumentation, capable of measuring more than 20 arsenic compounds (Akter et al. 2005; Ronkart et al. 2007). However, not all laboratories have the necessary infrastructure, such as a stable power supply, abundant supply of argon or resources to support consumables and associated reagents. Field kits for arsenic speciation facilitate measurements that can be robust, inexpensive and can in some cases provide real-time analyses for a fast response to remediation (Gupta et al. 2012). Some field methods can reduce the need for preservation reagents in the field to prevent oxidation of As(III) to As(V), as required for return of samples to laboratory based hyphenated techniques (Meng et al. 2001; Kumar & Riyazuddin, 2010; O’Reilly et al. 2010; Sugar et al. 2013). Field kits can be used on-site by field workers who do not have extensive training and therefore present an affordable approach for arsenic speciation. Significant efforts have been reported in the scientific literature in recent years to improve the robustness, sensitivity and prevent transformation of As(III) and As(V). A range of technologies, including: colorimetry, ion-exchange solid phase exchange (SPE) cartridges, voltammetry (Dozortsev, 2017; this volume) and biosensors (Siegfried, 2017; this volume) have been employed.

5.5.1.2.1 Colorimetry and UV-Visible spectrophotometry

Hu et al. (2012) employed a colorimetric method for field arsenic speciation in groundwater using KMnO₄ and CH₄N₂S as effective As(III) oxidant and As(V) reductant, respectively, in the formation of a
molybdenum blue complexes enabling the differentiation of As(III) and As(V), with a detection limit of 8 µg/L. A cloud point extraction method provided a limit of detection of 1.14 µg/L with a preconcentration of 65 following complexation of As(V) with acridine orange as a fluorescence cationic dye and subsequent analyses using UV-Visible spectrophotometry (Gurkan et al. 2015).

5.5.1.2.2 Ion exchange – solid phase extraction (SPE)
One of the earlier field-based methods for separating As(V) and As(III) using ion exchange cartridges was developed by Ficklin (1983) but suffered from the lack of separation of organo-arsenicals from As(V). An improved system, involving a resin based cation exchange cartridge and anion exchange cartridge connected in series, was developed by Le et al. (2000) and enabled the separation of As(III), As(V), MA and DMA from water samples. Ion exchange resins offer the advantage of being low cost, portable, easy to use, without the need for reagents in the field. Considerations for the employment of SPEs in the field should include the influence of competitor ions and extreme pH, such as found in acid mine drainage waters (Impelleteri 2004). Watts et al. (2010) reported the impact on MA recoveries in slightly saline water samples or in the presence of elevated phosphate or sulphate. However, cation and anion exchange SPE cartridges were employed successfully for ground and surface waters from Argentina for the four arsenic species (O’Reilly et al. 2010) and in Hungarian well waters for inorganic arsenic species (Sugar et al. 2013). These methods provide the advantage of a pre-concentration enabling the measurement of lower concentrations (sub-µg/L) of arsenic species (Issa et al. 2010; Issa et al. 2011), but also a limited need for reagents to modify the water samples, simply requiring a preconditioning of the ion exchange cartridges and elution with weak acids. Many reported techniques described in reviews by Clough et al. (2012) and Chen et al. (2014) used a different approach. For example, Rahman et al. (2011) used SPE’s and differences in pH to affect quantitative separation of As(III), As(V), MA and DMA, firstly buffering the sample to pH 5, then passing it through a TE-01 column retaining As(V) and MA, effluent adjusted to pH 9 and loaded onto an AS-01 column which retained As(III) and eluted DMA. As(V) and MA were eluted together, pH adjusted into two portions at pH 5 and 8 and washed separately into separate AN-01 columns and selectively eluted, whilst As(III) was eluted with weak nitric acid. Overall, this approach provides arsenic speciation where expensive laboratory methods are not available, but does need careful logistical considerations for use in the field. Ideally no reagents should be required in the field, with a minimum of effort to precondition the SPE cartridges, preferably in advance with stability of SPEs sufficient over a number of weeks to enable return of the cartridges to the laboratory for simple elution of the arsenic species. Strong Based anion exchange (SBAE) and hydrate iron oxide particles integrated HY resin possess high adsorption capacities toward arsenic species in elevated concentrations i.e. more than 370 µg g⁻¹ for As(V) in SBAE resin, more than 4150 µg g⁻¹ of As(III) and 3500 µg g⁻¹ of As(V) for the HY resin (Issa et al. 2010). Doker et al. (2013) employed a relatively straightforward technique using PHEMA microbeads in a micro-pipette tip to selectively adsorb As(III) in snow samples, with As(V) calculated by the difference between total As and As(III).

5.5.1.2.3 Biosensors
Biosensors (e.g. Pfeiffer et al. 2015; Siegfried, 2017) are devices that use a biological recognition element to detect a specific analyte, which then converts this response into a quantitative output signal in the form of luminescence, fluorescence or an electrical current or potential. Molecular recognition features: enzymes that recognise substrates, receptors their ligands or nucleic acids their complimentary strands. This process is highly specific and sensitive, but can be fragile, which is a critical design feature for a biosensor robustness
(French et al. 2012). Merulla et al. (2013) reviewed bioreporter and biosensor assays capable of determining As(III) at 10–50 μg/L and below. Arsenite sensitive electrochemical biochips using bacterial (E. coli) resistance to As(III), providing detection limits of 0.8 μg/L in tap water. Ezeh et al. (2013) employed As(III) specific chemodosimeters, which incorporate a coumarin fluorescent reporter coupled with an As-reactive benzothiazoline functional group, to yield a highly fluorescent coumarin-6 dye with detection limits of 0.23 μg/L. Male et al. (2007) reported the development of a bionsensor for arsenite using arsenite oxidase and multiwalled carbon nanotube-modified electrodes. This approach is specific for As(III) with a detection limit of 1 μg/L. Solid phase biosensors using a GFP-tagged ArsR protein and fluorescence detection have been developed for the measurement of As(III) in tap and mineral water with detection limits of 5 μg/L for field use, but with analysis times of 15 to 30 minutes (Siddiki et al. 2011). There is a disadvantage to these methods as they do not measure As(V), so cannot be used across a complete pH/Eh range, leaving large swathes of water supplies across the world that cannot provide reliable As data, unless additional total As measurements are undertaken to calculate As(V) concentrations by subtraction. A number of biosensors have been developed based on whole cell or cell-free (DNA, protein) based biosensors. Optimisation of detection limits, specificity and response times are required. The advent of aptamer-targeted technology provides the potential for target specific biosensors (Chen & Rosen, 2014; Kaur et al. 2015).

5.5.2 Analytical & data reduction protocols

5.5.2.1 Control samples & standards

Control samples and standards are necessary to assure the quality of analysis and sample preparation. Although often determined by a laboratory carrying out the analyses, the nature and number of these may also form part of the analytical criteria specified to a laboratory (see Table 5.3). Reporting the outcomes of the analysis of control samples and standards may be critical to better enable a reader to judge data quality.

5.5.2.2 Order of Analysis – randomisation

Randomisation of presentation of samples for analysis is recommended to minimise systematic biases arising, for example, from any drift in sensitivity over the course of an analytical session or of carry-over effects.

5.5.2.3 Data reduction – calibration models

Reduction of instrumental responses to analyses is typically done through the use of model calibration curves (Table 5.4). Such curves are most commonly first order linear, but other models are used from time to time – these include first order linear forced through zero (generally not recommended, but worth being aware of as a bias-introducing model), and second and higher order linear and error weighted (generally recommended) (Table 5.5) models. Several commonly used models may give rise analytical bias particularly for samples in concentration ranges that either lie outside the concentration ranges of the calibration standards or at very low concentrations. The appropriateness of calibration models should be checked by (i) inspecting residuals as a function of concentration – any significant association found indicates that the calibration model is biased, the extent to which this requires consideration of a different calibration models depends upon project requirements; (ii) determining the association between analytical precision and concentration – a heteroscedastic distribution of such precisions indicates that a weighted calibration model should be considered; and (iii) comparing sample concentrations with the range of concentrations for the calibration standards – the reliability of calibration models much above the highest calibration standard concentration is suspect, particularly for polynomial calibration models.
Table 5.3 List of commonly used control samples and standards. Numbers required for each type will depend upon project including, where appropriate, regulatory or contractual, requirements.

<table>
<thead>
<tr>
<th>Sample/Standard Type</th>
<th>Purpose</th>
<th>Typical Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Replicate samples</td>
<td>Estimate sampling error</td>
<td>One set of replicates per 10 to 30 samples.</td>
</tr>
<tr>
<td>Sample repeats</td>
<td>Estimate repeatability of measurement</td>
<td>One set of replicates per 10 to 30 samples.</td>
</tr>
<tr>
<td>Blank</td>
<td>Facilitate calculation of detection limit and limit of quantification.</td>
<td>One per 10 to 20 samples. Minimum 3 per set of samples.</td>
</tr>
<tr>
<td>Procedural blank</td>
<td>Estimate contamination arising from sample processing.</td>
<td>Minimum 3 per set of samples.</td>
</tr>
<tr>
<td>Calibration Standards</td>
<td>To determine the instrumental response to analyte.</td>
<td>Minimum 5 to 7 different standards, analysed at least 3 times each. Concentrations should range from 0 to somewhat above the highest expected sample concentration. Mean concentration of the calibration standards should be in a concentration range where the highest analytical precision is required.</td>
</tr>
<tr>
<td>Internal standard</td>
<td>To correct for irregular instrumental responses</td>
<td>Typically µg/L concentrations of Ge (or other trace if Ge is of analytical interest) added to all samples and standards. The concentration is typically determined after an assessment of instrument sensitivity.</td>
</tr>
<tr>
<td>Spiked (with a range of amounts of arsenic) samples</td>
<td>To determine and correct for matrix effects</td>
<td>Indicated where matrix of calibration standards and samples differ significantly and where matrix effects are suspected; recommended 5 different additions per selected sample; numbers of samples selected for spiking strongly dependent upon project requirements and budget.</td>
</tr>
<tr>
<td>Certified Reference Materials (CRMs)</td>
<td>To ensure accuracy of analyses and traceability</td>
<td>At least one CRM analysed in triplicate per sample set; further CRMs as required depending upon range of arsenic concentrations and matrix compositions.</td>
</tr>
</tbody>
</table>
**Table 5.4** Commonly used calibration curve models, together with the equations to calculate concentrations from signals for samples, using the calibration curve models.

<table>
<thead>
<tr>
<th>Model</th>
<th>Equation of Calibration Curve</th>
<th>Equation to Calculate Concentration from Signal</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>First order linear; forced through zero</td>
<td>$y = bx$</td>
<td>$x = y/b$</td>
<td>Simple; may result in bias, if the best calibration curve is not 1st order linear or if the signal errors are not homoscedastic</td>
</tr>
<tr>
<td>First order linear;</td>
<td>$y = bx + a$</td>
<td>$x = (y - a)/b$</td>
<td>Simple; may result in bias, if the best calibration curve is not 1st order linear or signal errors are not homoscedastic</td>
</tr>
<tr>
<td>Second order linear (quadratic); forced through zero</td>
<td>$y = cx^2 + bx$</td>
<td>$x = (-b + \sqrt{b^2 + 4cy})/2c$</td>
<td>May result in bias at low concentrations or at higher concentrations beyond the calibration range</td>
</tr>
<tr>
<td>Second order linear (quadratic)</td>
<td>$y = cx^2 + bx + a$</td>
<td>$x = (-b + \sqrt{b^2 - 4c(a - y)})/2c$</td>
<td>May result in bias at low concentrations or at higher concentrations beyond the calibration range</td>
</tr>
<tr>
<td>Logarithmic</td>
<td>$y = b \ln(x) + a$</td>
<td>$x = \exp((y - a)/b)$</td>
<td>Useful where there is a logarithmic relationship between concentration and signal</td>
</tr>
<tr>
<td>Logarithmic with offset</td>
<td>$y = b \ln(x + \psi) + a$</td>
<td>$x = \exp((y - a)/b) - \psi$</td>
<td>Useful where there is a logarithmic relationship between concentration and signal and there is also non-zero signal at very low concentrations</td>
</tr>
</tbody>
</table>

**Table 5.5** Commonly used error weighting models.

<table>
<thead>
<tr>
<th>Weighting Model</th>
<th>Equation to Calculate Weighting Factor</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uniform weighting</td>
<td>$W_i = 1$</td>
<td>Simple; may result in very high relative biases at low concentrations in the common case where absolute signal errors are heteroscedastic and higher at higher concentrations</td>
</tr>
<tr>
<td>Weight by inverse of error</td>
<td>$W_i = 1/E_i$</td>
<td>Theoretically difficult to justify in many cases</td>
</tr>
<tr>
<td>Weight by inverse of square of error</td>
<td>$W_i = 1/E_i^2$</td>
<td>Preferred weighting model provided that the added computational complexity is justified by project requirements</td>
</tr>
</tbody>
</table>
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Table 5.6 Equations for calculation of calibration model and estimation of concentration from the calibration model for first order linear calibration without weighting.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>First Order Linear Model with No Weighting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calibration model</td>
<td>( y = bx + a )</td>
</tr>
<tr>
<td>Weighting</td>
<td>( w_i = 1 )</td>
</tr>
<tr>
<td>Mean concentration of ( n ) calibration standards</td>
<td>( \bar{x} = \frac{\sum x_i}{n} )</td>
</tr>
<tr>
<td>Mean signal of ( n ) calibration standards</td>
<td>( \bar{y} = \frac{\sum y_i}{n} )</td>
</tr>
<tr>
<td>Unbiased estimate of slope, ( b ), of calibration curve</td>
<td>( b = \frac{\sum [(x_i - \bar{x})(y_i - \bar{y})]}{\sum (x_i - \bar{x})^2} )</td>
</tr>
<tr>
<td>Unbiased estimate of intercept, ( a ), of calibration curve</td>
<td>( a = \bar{y} - b\bar{x} )</td>
</tr>
<tr>
<td>Unbiased estimate of the concentration of an unknown sample with signal response, ( y_0 )</td>
<td>( x_0 = \frac{(y_0 - a)}{b} )</td>
</tr>
<tr>
<td>Standard deviation of the slope</td>
<td>( s_b = \left[ \frac{s_{y/x}}{\sum (x_i - \bar{x})^2} \right]^{1/2} )</td>
</tr>
<tr>
<td>Standard deviation of the intercept</td>
<td>( s_a = s_{y/x} \left[ \frac{n\sum x_i^2}{n\sum (x_i - \bar{x})^2} \right]^{1/2} )</td>
</tr>
<tr>
<td>( S_{y/x} )</td>
<td>( s_{y/x} = \left[ \frac{\sum (y_i - \hat{y}_i)^2}{n-2} \right]^{1/2} )</td>
</tr>
<tr>
<td>Standard deviation of the estimated concentration of the unknown sample, given that ( g ) (see below) is less than 0.05</td>
<td>( s_{x_0} = \frac{s_{y/x}}{b} \left[ 1 + \frac{1}{n} + \frac{(y_0 - \hat{y})^2}{b^2\sum (x_i - \bar{x})^2} \right]^{1/2} )</td>
</tr>
<tr>
<td>( g )</td>
<td>( g = \frac{t^2}{b^2} \left[ \frac{(s_{y/x})^2}{\sum (x_i - \bar{x})^2} \right] )</td>
</tr>
<tr>
<td>Standard deviation of the estimated concentration of the unknown sample from ( m ) replicate measurements, given that ( g ) (see below) is less than 0.05</td>
<td>( s_{x_0} = \frac{s_{y/x}}{b} \left[ 1 + \frac{1}{m} + \frac{(y_0 - \hat{y})^2}{b^2\sum (x_i - \bar{x})^2} \right]^{1/2} )</td>
</tr>
</tbody>
</table>

Source: After Miller, 1991.
5.6 TOTAL QUALITY MANAGEMENT (TQM), QA & QC

5.6.1 Total quality management

General requirements for the competence of testing and calibration laboratories are set out by the International Standard Organisation, specifically in EN ISO IEC 17025:2005. Accreditation to this standard is monitored through national bodies such as the United Kingdom Accreditation Service (UKAS) in the UK, who monitor; firstly the attainment of accredited status or secondly the maintenance of accredited status. This is achieved through annual visits to laboratories by using independent experts. Laboratories are tested as to whether they are maintaining standard operating procedures which form the basis of a management system and against which they attained accreditation. The laboratory’s management system policy relating to quality, including a quality policy statement shall be defined in a quality manual, which states overall objectives and is reviewed periodically.

“Laboratory facilities for testing and/or calibration, including but not limited to energy sources and environmental conditions [are required to enable appropriate performance and] ensure that “environmental conditions do not invalidate results or adversely affect the quality of” data (ISO/IEC 17025, 2005). Management systems can also consider the laboratories environmental management systems, with guidance provided in ISO 14001:2004. This standard involves the management of waste, control and records of chemical use, storage and disposal, and, in addition, operational activities that may have an environmental impact, such as maintenance of equipment to ensure efficient operation and power consumption.

To ensure the quality of results, laboratories should have “quality control procedures for monitoring the validity of tests and calibrations” (ISO/IEC 17025). This may include “the use of certified reference materials or internal quality control using secondary reference materials, participation in” [inter-laboratory] comparison or proficiency testing programmes or replicate tests” (ISO/IEC 17025, 2005). These data must be “monitored and reviewed and where found to be outside [of] pre-defined criteria, action [should] be taken to correct the problem and to prevent incorrect results from being reported” (ISO/IEC 17025, 2005).

The control of documents should include the maintenance of procedures, instrument and service logs, quality control charts, and training records detailing the competency of a laboratory to undertake specific tests or calibrations. Laboratories should have a procedure to implement when any aspect of testing or calibration work does not conform to its own procedures, with responsibilities assigned for corrective action to be taken. “Records for each test or calibration [should] contain sufficient information to [enable] the identification of factors affecting uncertainty and [allow] for the test to be repeated under conditions as close as possible to the original. [Such] records [should] include the identity of personnel responsible for [each stage] of [a] test” (ISO/IEC 17025, 2005) and include details of the sample from the registration of a sample into a laboratory management system through to the analyses and reporting of data to the client. A clear audit trail could then be established, including details regarding the correct storage and location of samples to demonstrate chain-of-custody or to enable repeat analyses if required and the return of samples to the client.

Laboratories should periodically conduct internal audits by trained and qualified staff, where possible independent of the specific activity “to verify that its operations continue to comply with the requirements of the management system and [the] international standard [against which accreditation is gained]” (ISO/IEC 17025, 2005). Management reviews are necessary to review procedures, the outcome of internal audits, non-conforming tests, customer feedback, sufficient staff training and resources.

5.7 CONCLUSION

Sampling and analysis of waters for arsenic, arsenic speciation and associated parameters ideally requires (i) understanding of the sampling and analytical requirements, including representativeness, accuracy,
Sampling and analysis for monitoring arsenic in drinking water

precision and limits of detection, in the context of project aims; (ii) consideration of sampling, preservation and analytical protocols to achieve the required aims; and (iii) consideration of total quality management requirements including sample and data chains of custody, operator training, use of appropriate control charts and project- and laboratory-specific documentation control.

5.8 ACKNOWLEDGEMENTS

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Best Practice Guide on the Control of Arsenic in Drinking Water


Chapter 8

Sustainable arsenic mitigation – from field trials to implementation for control of arsenic in drinking water supplies in Bangladesh

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8.1 INTRODUCTION

The widespread occurrence of natural arsenic (As) in groundwater in Bangladesh (Figure 8.1) and its landscape scale of exposure have drastically reduced safe water access across the country (Chowdhury & Jakariya, 1999; Mukherjee & Bhattacharya, 2001; van Geen et al. 2002; Ahmed et al. 2004; Ahmed et al. 2006; Rahman et al. 2009; Ahmed & Bhattacharya, 2014; Chakraborty et al. 2015; Bhattacharya et al. 2016). Since the discovery of arsenic in groundwater in the country in 1993, there has been limited success in overall access to safe drinking water and tens of millions of people are still exposed to As concentrations above the Bangladesh drinking water standard (BDWS; 50 µg/L) (BDWS, 1997) which is even 5 times higher than the WHO guideline (10 µg/L) (WHO, 2004, 2011). The toxic effects of long-term exposure to As, a well known carcinogen, from drinking water are commonly manifested as skin disorders such as leuco-melanosis, melanosis, keratosis, gangrene and lung, kidney and bladder cancer, as well as several other non-carcinogenic
health effects (Smith et al. 2000; Guha Mazumder et al. 2000; Yu & Ahsan, 2004; Kapaj et al. 2006; Smith & Steinmaus, 2009; Argos et al. 2010; Parvez et al. 2013, 2016). The magnitude of the crisis will depend on the rate at which mitigation programmes are implemented (Kabir & Howard, 2007) and at present the main challenge is to develop a sustainable and cost-efficient mitigation option that will be adopted by the people for scaling up safe water access (Jakariya et al. 2003, 2005, 2007; van Geen et al. 2002, 2003; Hoque et al. 2004; von Brömssen et al. 2007; Bundschuh et al. 2010; Inauen et al. 2013; Hossain et al. 2014; SASMIT, 2014).

![Figure 8.1 Distribution of arsenic in groundwater of Bangladesh showing the location of Matlab as a hotspot and the SASMIT study area. (Map produced by KTH-International Groundwater Arsenic Research Group and referred from von Brömssen et al. 2007; Nriagu et al. 2007.)](image)

This chapter provides an overview on how the SASMIT (Sustainable Arsenic Mitigation) study was conducted, developed a strategy and applied to enhance safe water access in arsenic affected areas. SASMIT is an action research project that has developed a community based and cost efficient strategy for installation of safe drinking water tubewells in Bangladesh where arsenic is a major contaminant in groundwater. The installations are optimised on the basis of the demand for safe water among the underserved segments of the society as well as increased knowledge of local hydrogeological settings. The text in this chapter is to a substantial extent based upon the unpublished and published outputs of the SASMIT study, including the PhD thesis of the lead author (Hossain, 2015b) and publications written by the co-authors including SASMIT (2014), Hossain et al. (2014), Bhattacharya et al. (2014, 2015, 2016).

During the last two decades, source and distribution of arsenic (As) in the groundwater and the process of mobilization has been understood to a major extent (Mukherjee & Bhattacharya, 2001; Bhattacharya...
Sustainable arsenic mitigation

et al. 1997, 2001, 2002a, b; Nickson et al. 1998; Harvey et al. 2002; Ahmed et al. 2004; Islam et al. 2004; Zheng et al. 2004; McArthur et al. 2004; Saunders et al. 2005; Harvey et al. 2006; Hasan et al. 2007; von Brömssen et al. 2007, 2008; Mukherjee et al. 2008a, b; Polizzotto et al. 2008; Polya & Charlet, 2009; Polya & Lawson, 2015), but there has been very limited country wide success in the field of As mitigation measures in Bangladesh (van Geen et al. 2002; Jakariya et al. 2003, 2005; Ahmed & Bhattacharya, 2014; Hossain et al. 2015). The limited progress in arsenic mitigation is attributed to:

- limited involvement of the local community to take their own initiative due to lack of suitable methods to identify the safe aquifers and installation of their own wells at relatively low costs
- dependence on government and other NGOs for arsenic safe wells
- inadequate understanding of local geological and hydrogeological constraints
- unplanned development/installations by different agencies where sustainability is not considered and/or assessed

Countrywide in Bangladesh, more than 10 million tubewells provide access to drinking water to the people, although a great proportion of these wells contain As considerably higher than the drinking water guideline of WHO (10 µg/L) and even the Bangladesh Drinking Water Standard (50 µg/L) (BGS/DPHE, 2001; BBS/UNICEF, 2011). Various options have been deployed for arsenic mitigation both at household and community scales over the past two decades. These options include As-removal filters (ARF), rainwater harvesters (RWH), pond sand filters (PSF), dug wells (DW), hand tubewells (HTW) targeted at depths up to 100 m, as well as deep tube wells (DTW) mostly installed at depths of 200–250 m (Jakariya et al. 2005, 2007).

The Swedish International Development Cooperation Agency (Sida)-SASMIT project was conceived by KTH Royal Institute of Technology (KTH-International Groundwater Arsenic Research Group, 2007) together with the Department of Geology, University of Dhaka, NGO Forum for Public Health, Bangladesh and Ramböll Sweden AB, to develop a sustainable mitigation strategy, that rural and disadvantaged community can adopt and implement by themselves. As a part of the SASMIT project, all the options were assessed on the basis of their: (i) acceptability by local community, (ii) technical viability and (iii) their socio-economic implications. Outcomes of this survey, revealed low community acceptance for many of the options, except the As-safe tubewells as an acceptable source of safe drinking water acceptable to communities over the major part of the country (Jakariya et al. 2005, 2007; Kabir & Howard, 2006; Hoque et al. 2004; Ahmed et al. 2006; Hossain et al. 2014, 2015). However, drilling to depths beyond 100 m is difficult through the locally available hand-percussion techniques. The SASMIT project was conceived to develop, systematize and operationalize an approach to identify and target the safe aquifers, considering both hydrogeological suitability and social aspects for tubewell installation to provide safe drinking water to communities exposed to elevated arsenic at low cost. SASMIT also recognized the role of local driller community as the main driving force for installation of tubewells, as majority of tubewells (>90%) in the country are installed privately by local drillers (SASMIT, 2014). The SASMIT project thus also aimed to improve the indigenous skills of the driller community to target safe aquifers for tubewell installation and develop their entrepreneurship.

8.2 THE SASMIT ACTION RESEARCH AND IMPLEMENTATION

8.2.1 Assessing available safe water options

Various alternative drinking water options were provided in the Matlab area, during the Sida supported-AsMat (Arsenic in Matlab) project (2001–2006) (AsMat Report, 2007). These options were evaluated through social survey in the project intervention area (SASMIT, 2014; Hossain et al. 2015). Tubewells are the most preferred and accepted source of safe drinking water especially to women and children, mainly due to ease of installation, operation, availability of water and maintenance (Figure 8.2). The proportion of
safe wells is very limited relative to the overall demand, as the cost for deeper tubewell installation is not affordable by the poor and disadvantaged population (SASMIT, 2014; Hossain et al. 2015).

![Figure 8.2](image)

**Figure 8.2** Performance analysis on different options deployed for arsenic mitigation in the Matlab area of Bangladesh (SASMIT, 2014).

### 8.2.2 Perception of local tubewell drillers and practice for tubewell installation

Tubewell technology was first introduced in Bangladesh (the erstwhile East Pakistan) in 1970 primarily for agricultural development (World Bank, 1970). However, there has been a steady growth of tubewells as source of drinking water supply through interventions by the governmental and non-governmental agencies and 90% of the estimated 10 million tubewells in Bangladesh are installed by tubewell drillers, through the initiatives of the local community and recognized as the main driving force for installation of safe tubewells (Jonsson & Lundell, 2004; von Brömssen et al. 2005, 2007). With growing demand for groundwater exploitation for drinking water supply both in rural and urban Bangladesh, it will be increasingly important that the local tubewell drillers target safe aquifers for drinking water supplies. The drillers commonly categorize the sediments into four colors namely: black, white, red, and off-white. Based on an earlier study in Matlab, Bangladesh (von Brömssen et al. 2007), perception of sediment color by the local drillers, led to the postulation of a four color hypothesis. The four color hypothesis (Figure 8.3) indicates that arsenic risk varies with the sediment color, being highest with the black color sediments and gradually reduces towards red. The relation between sediment color and concentration of As in groundwater was validated through a rigorous hydrogeological investigation, sediment characterization, and water quality monitoring and the results have been used to develop a sediment color tool to be used by the tubewell drillers for installation of shallow tubewells. It is important to note that a number of studies carried out in different parts of the Bangladesh and West Bengal (van Geen et al. 2003; Jonsson & Lundell, 2004; McArthur et al. 2004; Stollenwerk et al. 2007; Pal et al. 2008, 2009; Hossain et al. 2010; Hug et al. 2011; Datta et al. 2011; Biswas et al. 2012; Hossain et al. 2014) have indicated similar findings.

### 8.2.3 Two innovations for installation of safe tubewells

#### 8.2.3.1 Sediment Color Tool for targeting As-safe aquifers at shallow depths

For characterization of sub-surface sediments and installation of piezometers to monitor water quality, test borings were done using the available local technology in 15 locations spread over 410 km² area
of SASMIT project area in Matlab. Sediments were sampled from each 1.5 m (5 ft) section and were characterized by visual inspection for documentation and preparation of lithologs. Targeting shallow, intermediate-deep and deep aquifers (in relative terms) and also sediments of varying colors, 78 depth-specific piezometers were installed in 15 nests (Figure 8.4). In addition, secondary data reflecting the depths of As peaks in groundwater and water table fluctuation were also taken into consideration.

Figure 8.3 The four sand color perceived by the local drillers with corresponding risks of elevated concentration of As in water with varying redox (adapted from von Brömssen et al. 2007).

Figure 8.4 Design for the assessment of hydrogeological suitability through installation of multi-level piezometer nests in Matlab, Bangladesh targeting the shallow, intermediate deep and deep aquifers.
The sediment color tool was developed through an iterative process, based on (i) the observations on the physical characterization of the sediment samples and their color during the installation of the piezometer nests up to a depth of 100 m, and (ii) a long-term monitoring of the water quality in the different piezometer nest wells. From extensive field-trials in the study area, it was realised that local drillers can drill down to a depth of 100 m by hand-percussion (sludger) method. This situation is true for many other places in the country. In addition to the installed piezometers, some other drinking water wells were also monitored for which the color of sediments at the screen positions were known.

Groundwater samples were collected from 144 wells screened at depths with known sediment color during the period between 2009 and 2011 covering both pre- and post-monsoon seasons, and analysed in the laboratory for detailed water chemistry for major ions and trace elements including arsenic.

In terms of depth and As concentration, wide range of variability was observed for the black sediments, however 50% of wells (n = 33) in black sediments at very shallow depth (10–40 m) revealed average As concentration of 239 µg/L which is manifold above the Bangladesh drinking water standard and WHO guideline (Table 8.1). In the context of probability of As-enrichment in water abstracted from black-colored sediments, it is apparent that these are ‘high-risk’ sediments and recommended to avoid installation of tubewells in black sediments. On the contrary, groundwater from wells installed in shallow, red color sediments found within a depth ranging from 47 to 82 m (n = 39) had As concentration lower than the Bangladesh drinking water standard of 50 µg/L. Average and median values of As collected from the wells installed in the red sediments were below the WHO guideline value of 10 µg/L. Water collected from 25 wells installed in off-white sediments also show a quite similar pattern in terms of depth and As concentration. The white sediments seemed of less importance for installation of tubewells at shallow depths.

<table>
<thead>
<tr>
<th>Color of Aquifer Sediment</th>
<th>Number of Wells</th>
<th>Depth Range (m)</th>
<th>Number of Samples Analyzed</th>
<th>Compliance with BDWS (%)</th>
<th>Compliance with WHO Guideline (%)</th>
<th>Max (µg/L)</th>
<th>Min (µg/L)</th>
<th>Mean (µg/L)</th>
<th>Median (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Black</td>
<td>66</td>
<td>9–91</td>
<td>230</td>
<td>17</td>
<td>9</td>
<td>740.8</td>
<td>5.6</td>
<td>239.2</td>
<td>240.1</td>
</tr>
<tr>
<td>White</td>
<td>14</td>
<td>58–104</td>
<td>49</td>
<td>71</td>
<td>21</td>
<td>150.6</td>
<td>5.6</td>
<td>36.1</td>
<td>27.7</td>
</tr>
<tr>
<td>Off-white</td>
<td>25</td>
<td>24–88</td>
<td>119</td>
<td>88</td>
<td>60</td>
<td>43.9</td>
<td>2.6</td>
<td>12.1</td>
<td>8.4</td>
</tr>
<tr>
<td>Red</td>
<td>39</td>
<td>47–82</td>
<td>123</td>
<td>100</td>
<td>62</td>
<td>21.8</td>
<td>2.6</td>
<td>9.4</td>
<td>8.6</td>
</tr>
</tbody>
</table>


Groundwaters abstracted from black sediments have Ca-Mg-HCO₃ to Na-Cl-HCO₃ as dominant water types, while it is predominantly Na-Cl-HCO₃ type in case of white and red sediments (Figure 8.5). Abundance of Ca and Mg was also observed in waters derived from off-white sediments. Groundwater abstracted from the black sediments had high concentration of HCO₃⁻, DOC, Fe²⁺, NH₄⁺ and PO₄³⁻, concomitant with low Mn and SO₄²⁻ content. In contrast, in waters from wells screened in red and off-white sediments, Mn and SO₄²⁻ concentrations were high with corresponding low levels of HCO₃⁻, DOC, Fe²⁺, NH₄⁺ and PO₄³⁻. However, the levels of Mn in wells in both red and off-white sediments, were higher than the previous WHO guideline value of 0.4 mg/L (Table 8.2). In the revised guideline, WHO (WHO, 2011) has withdrawn the regulatory limit for Mn, on the premises that Mn concentrations in drinking water sources worldwide are well below the health-based guideline value of 400 µg/L and hence there is a need
for re-evaluating the guideline value of Mn in drinking water (Ljung & Vahter, 2007). Although, the levels of Mn in groundwater in the Bengal Basin is in general a matter of concern, it is a crucial determinant for advocating the exploitation of red and/or off-white sand aquifers for installation of shallow tubewells from the perspectives of Water Safety Plan (WHO, 2004).

![Legend](image)

**Figure 8.5** Major ion composition of groundwater derived from the four distinct sediment color groups plotted on a Piper diagram. (SASMIT Database, Hossain et al. 2014.)

From all the 15 locations, 2240 sediment samples were collected up to a depth of 100 m and characterized on the basis of their color and grain size. For assigning color of the sediments, and then to categorize them into four colors as perceived and practised by the local drillers, the following three steps method (Hossain et al. 2014) was used to develop the sediment color tool (Figure 8.6):

**Step-1:** Immediately after collection of sediment sample, each of them was described based on the visual inspection in the moist condition and this color has been recorded as ‘field observed color’.

**Step-2:** Each sample was then compared with the Munsell Color Chart and using this chart Munsell Color and Munsell Code were recorded respectively. These two steps (1 and 2) eventually led to finding all possible color varieties.

**Step-3:** In the narrow down process, each sample was finally assigned to one of the four colors – black, white, off-white and red (Figure 8.3). These four colors are the driller’s perception of sediment color which they have gained through their work experience. During the assignment of four colors, participatory approach was considered with utmost importance taking the opinions of local drillers, field geologists and technical experts into account.
Table 8.2 Statistical summary of redox sensitive elements in groundwaters from four broad color groups of aquifer sediments.

<table>
<thead>
<tr>
<th>Sediment Color</th>
<th>Black</th>
<th>White</th>
<th>Off-White</th>
<th>Red</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. of wells</td>
<td>66</td>
<td>14</td>
<td>25</td>
<td>39</td>
</tr>
<tr>
<td>Number of groundwater samples monitored</td>
<td>230</td>
<td>49</td>
<td>119</td>
<td>123</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Redox Parameters</th>
<th>Max</th>
<th>Min</th>
<th>Mean</th>
<th>Max</th>
<th>Min</th>
<th>Mean</th>
<th>Max</th>
<th>Min</th>
<th>Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn (mg/L)</td>
<td>4.0</td>
<td>0.01</td>
<td>0.7</td>
<td>2.1</td>
<td>0.01</td>
<td>0.5</td>
<td>4.3</td>
<td>0.01</td>
<td>2.0</td>
</tr>
<tr>
<td>Fe (mg/L)</td>
<td>40.3</td>
<td>0.01</td>
<td>6.5</td>
<td>30.9</td>
<td>0.8</td>
<td>7.1</td>
<td>10.8</td>
<td>0.1</td>
<td>2.0</td>
</tr>
<tr>
<td>SO₄ (mg/L)</td>
<td>39.3</td>
<td>0.01</td>
<td>1.9</td>
<td>20.7</td>
<td>0.01</td>
<td>1.4</td>
<td>54.4</td>
<td>0.01</td>
<td>3.9</td>
</tr>
<tr>
<td>HCO₃ (mg/L)</td>
<td>1052</td>
<td>122</td>
<td>454</td>
<td>465</td>
<td>84</td>
<td>276</td>
<td>641</td>
<td>87</td>
<td>227</td>
</tr>
<tr>
<td>DOC (mg/L)</td>
<td>29.6</td>
<td>1.4</td>
<td>9.6</td>
<td>11.5</td>
<td>1.3</td>
<td>4.8</td>
<td>9.8</td>
<td>0.3</td>
<td>3.5</td>
</tr>
<tr>
<td>NH₄-N (mg/L)</td>
<td>57.8</td>
<td>0.01</td>
<td>6.3</td>
<td>10.2</td>
<td>0.01</td>
<td>1.7</td>
<td>12.8</td>
<td>0.01</td>
<td>0.48</td>
</tr>
<tr>
<td>PO₄-P (mg/L)</td>
<td>11.5</td>
<td>0.01</td>
<td>1.7</td>
<td>4.7</td>
<td>0.01</td>
<td>1.1</td>
<td>3.7</td>
<td>0.01</td>
<td>0.3</td>
</tr>
</tbody>
</table>

(SASMIT Database, Hossain et al. 2014).

Figure 8.6 The color scheme based on the 4 color hypothesis with Munsell color and codes for the aquifer sediments recovered at shallow depths (<100 m). (Revised from SASMIT, 2014; Hossain et al. 2014.)
8.2.3.2 A simplified tool for the local drillers

The Sediment Color Tool has been further simplified to make it conveniently usable in the field by the local drillers and other stakeholders. In the process of simplification, all possible color shades under each of the four color groups were again categorized into light (1), moderate (2) and deep (3) shades to cover the entire range of the variability of the respective color (Figure 8.7).

![Simplified prototype of Sediment Color Tool](image)

**Figure 8.7** A simplified prototype of Sediment Color Tool for deployment in the field to be used by the local drillers and other stakeholders.

The local drillers would be able to use this simplified tool for making a decision on the appropriateness of the targeted sediments for the installations of shallow tubewells for drinking water supply.

8.2.3.3 Intermediate Deep Tubewells (IDTW) – Newly explored source of safe drinking water

Tubewells installed by the local drillers are the most widely used and socially accepted drinking water option in rural Bangladesh, which signifies the importance of identification of safe aquifers within a reasonable depth for scaling the safe water access in affected regions of Bangladesh. Depth of the tubewell is a key parameter in the context of groundwater quality and cost of tubewell installation. In Bangladesh, a large proportion of the shallow wells (usually <80 m) are affected by arsenic contamination, and as a mitigation option, deep hand tubewells are installed usually to a depth range of about 250 m, which costs about 4–5 times of the installation cost of shallow tubewells. Compared to the demand for safe water tubewell, the number of deep wells is still very limited mainly because of the cost of installation, which is beyond the affordability of the poor and disadvantaged community of society (Bhattacharya et al. 2015).

The shallow aquifers characterized by sands of red and off-white color are the potential source of As-safe water, but elevated Mn is a concern for the compliance with the previous WHO limits for Mn and thereby
the compliance with the Water Safety Plan (WHO, 2004). Considering the water quality data revealed from the groundwaters derived from red and off-white sediments, and based on field trials and water quality monitoring of piezometers, the SASMIT project made an attempt to find an option which could be suitable for compliance with the Water Safety Plan in the context of both As and Mn. Based on the hydrogeological investigation (hydrostratigraphy and hydrogeochemistry), a strategy was developed systematically, to explore the intermediate-deep aquifer for tapping As-safe and low manganese groundwater. This allowed the discovery of the groundwater resources between traditional shallow and deep aquifers for the installation of tubewells for the first time for drinking water supplies. These aquifers targeted at a depth of 120 m and below have been termed as intermediate deep aquifers (IDA) and the tubewells installed targeting these aquifers are termed as intermediate deep tubewells (IDTW) (Figure 8.4b). Detailed water chemistry results including As, Mn, major ions and other trace elements for 243 IDTWs installed in Matlab “provided promising results which support the strategy for exploitation of IDA as safe sources for installation of drinking water tubewells” (SASMIT 2014; Bhattacharya et al. 2014, 2015). Among 243 wells, only 3 wells exceeded the Bangladesh drinking water standard for As (50 µg/L) “and more than 91% (n = 222) were within the WHO guideline value of 10 µg/L. For Mn, 216 wells (89%) show concentration lower than the previous WHO guideline value of 0.4 mg/L” (SASMIT 2014; Bhattacharya et al. 2015; Hossain, 2015) (Figure 8.8).

**Figure 8.8** Arsenic-safe and low manganese well statistics for the Intermediate Deep Tubewells (IDTW) (referred from SASMIT 2014; Hossain, 2015).

Replication trials conducted in five upazilas, namely Gazaria, Bhedarganj, Shibchar, Palong and Muradnagar in south-central and south-eastern Bangladesh validated the wider applicability of the IDTW as an emerging source for drinking water supplies. The local drillers can target similar sand at this depth in range, the cost of installation per well could be reduced by 50% of the cost of deep tubewell installation. Thus IDTW is considered a novel innovation for promoting safe water access faster by the local community taking into account affordability (SASMIT 2014; Ahmed & Bhattacharya, 2014; Bhattacharya et al. 2014, 2015; Hossain, 2015).

### 8.2.4 Integration of technical and socio-economic aspects for optimisation of safe water access

The process of action research leading to the development of SASMIT strategy involving a novel combination of technical (hydrogeological suitability) and social aspects strengthened the initiative of the local tubewell drillers at the community level and local capacity building for arsenic mitigation. Based on the monitoring of water quality in the piezometer nests and considering safe buffer distances around these piezometer locations, clusters of villages (mauzas) were intervened for selection of sites for safe tubewell
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installation. Social mapping of all the villages within the targeted mauzas were carried out to make an assessment of the availability of safe water options for all clusters of households (baris) (SASMIT, 2014; Bhattacharya et al. 2014; Hossain, 2015). In optimization of site selection, priority was given to the baris with no or limited safe water access and poor and underserved households. The tubewells were installed considering the easy access to the site from all households within the respective cluster (Figure 8.9).

Figure 8.9 (Top) Existing safe water access and household economic status; (Bottom left) Village consultation meetings; and (Bottom right) cluster of households (baris) identified for tubewell installation during SASMIT implementation.

Adapting this strategy, 96% of the newly installed wells were safe with respect to As resulting in scaling up the safe water access from virtually non-existing to up to 40 percent (Figure 8.10). It is also important to mention that as compared to the outcomes of the action research on hydrogeological suitability and the demand for safe drinking water in Matlab, the resources for implementation could only cater improvement
of the safe water access preferentially targeted in areas with poor to very poor access to safe water. The knowledge generated from the current SASMIT research has a potential for expanding the safe water access scenario through continuous implementation in the Matlab region making this a model as sustainable development solution (SDS) to achieve the Vision 2030 UN SDG (UN-SDSN, 2016).

![Figure 8.10 Improved safe water access in the Matlab area from the installed IDTW following the SASMIT methodology (Hossain, 2015).](image)

### 8.2.5 Capacity building of the local drillers

The ever increasing dependence on groundwater in Bangladesh, for drinking water supplies especially in the rural areas, enhances the significance of the role of the local drillers, although widespread As contamination pose a challenge to them in tubewell installation. Local drillers are the main driving force for tubewell installation, and their perception on the nature of the sediments in terms of color, depth and water quality should be taken as a key consideration during implementation of drinking water supply projects. The close interaction and mutual sharing of knowledge and experience between the local drillers and the project team will contribute to optimize the sites for installation of safe tubewells. Involvement of the drillers in the context of capacity building would also help to develop entrepreneurship, in addition to enhancing awareness and knowledge for targeting safe aquifers, and thereby to reduce the exposure to As contamination on a country-wide scale.

### 8.3 COMPLIANCE WITH THE POLICY REGIME OF SUSTAINABLE ARSENIC MITIGATION IN BANGLADESH

Lack of adequate integration of evidence-based research results and the societal aspects, previous efforts of arsenic mitigation could not bring any visible change in the scenario of scaling-up safe drinking water access for millions of population exposed to the risk of chronic arsenic poisoning. Among the three major
challenges for Bangladesh rural water supply, outlined in the Sector Development Plan (FY, 2011–2025) for the Water and Sanitation Sector (Policy Support Unit (PSU, 2011), arsenic has been identified as the priority contaminant due to its adverse health outcomes.

The Sida-SASMIT concept (SASMIT, 2014) offers a unique example for improvement of the safe drinking water access through:

- Providing safe and affordable access to water for the remaining areas in the country where risks of arsenic exposure is high
- Red sand aquifers could be a low-cost option which would minimize the exposure of arsenic
- Intermediate deep aquifers (IDA) could be a feasible option for tackling both arsenic and manganese. Approximately at half of the cost needed for DTW, the IDTWs affordable by the communities would be helpful to enhance the safe water coverage faster
- Wider applicability of SASMIT strategy through mapping of intermediate deep aquifers as safe water source as the action research component of SASMIT during the future implementation process with other sector organizations at a country wide scale
- Incorporate relevant social aspects for implementation of tubewell installation considering the demand and ensuring resource optimization to maximize the number of beneficiaries
- The recognition of the role of the local tubewell drillers as the driving force in tubewell installation is important to regulate the abstraction of water through different wells according to the recently ratified Bangladesh Water Act (2013).

The Sida-SASMIT project implementation has adequately addressed the necessity of the development of the capacity of the local drillers to identify the safe aquifers for installing drinking water wells. This will also form a strong base for their professional development to enabling them to participate and lead the way to work in collaboration within the local institutions and participate in decision making process for installing a new tubewell for the end users.

**8.4 CONCLUSIONS AND FUTURE OUTLOOK**

The SASMIT strategy developed through a combination of hydrogeological suitability and social aspects can improve the safe water access in arsenic affected areas (Bhattacharya et al. 2014; SASMIT 2014). It also helps ensuring the capacity building of the local drillers for identification of safe aquifers for the installation of safe drinking water tubewells. Social mapping has been used as an important tool for optimization of sites for ensuring easy access to new safe well installations for a greater number of beneficiaries. Such mapping would be also useful as a reference for the evaluation of the improvement of safe water access from future implementations (Bhattacharya et al. 2014; SASMIT 2014).

The Sediment color tool developed on the basis of perception of the sediment color by the local drillers and monitoring of water quality is recommended to target safe aquifers for the provision of arsenic-safe drinking water. SASMIT has also discovered intermediate deep aquifers (IDA) for the installation of intermediate deep tubewells (IDTW) producing As-safe and low-Mn water for compliance to the Water Safety Plan (Bhattacharya et al. 2014; SASMIT 2014). Sustainability of the mitigation option needs to be assessed through long term water quality monitoring as prioritized in the Sector Development Plan (2011–2025) for Bangladesh. Collaboration of the Strategic National Partners with the Sida-SASMIT project consortium would facilitate the process of up-scaling the safe water access in the country.

Wider applicability of SASMIT strategy is envisaged for arsenic mitigation in Bangladesh and across the globe in areas with similar hydrogeological environments. Based on the methods developed by SASMIT, implementation of safe well installation carried out in Matlab, has been very much successful
and promising. In addition to the up-scaling of safe water access, this method involved local drillers that ultimately led to their capacity building for entrepreneurship as well as to convey the message (awareness) to the community at large. For validation, replication trials have already been successfully made in some other areas with limited scope and resources.

SASMIT strategy has been shared through Policy and Strategy Documents, and Best Practices Manual with policy makers and sector agencies towards improvement of safe water access. This strategy allows installing safe wells based on (1) limited hydrogeological investigation to ensure the optimum rate of success and sustainability; and (2) implementation plan using GIS based simple and quick social mapping to ensure relatively uniform distribution to optimize the safe water access with respect to the number of installations.

However, there will always be needs for further monitoring and surveillance and the development of database with open access to see the changes in the improvement of safe water access, complementing the scenario of potential risks of As contamination and the sustainability of arsenic-safe drinking water supplies. Groundwater management is an important determinant for the success, as the proliferation of irrigation wells may impact regional and/or local level hydraulics in the context of cross-contamination. In long-run, it emphasizes the local driller’s education and to bring them under a regulatory framework which will make them more responsible to target safe water sources during tubewell installation practice. Therefore, without further delay in involving further research, it is important to accelerate the mitigation efforts using present knowledge and the developed SASMIT strategy.

### 8.5 ACKNOWLEDGEMENTS

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### 8.6 REFERENCES


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Chapter A3

Estimating the population exposed to arsenic from groundwater-sourced private drinking water supplies in Cornwall, UK

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A3.1 INTRODUCTION

Where connection to mains public supplies is not available, or not utilized, a large number of people worldwide rely on groundwater for drinking water through private water supplies (PWS). Chronic exposure to chemicals in PWS may have an adverse effect on health. Many areas of the world, perhaps most notably Bangladesh, are known to have elevated concentrations of arsenic in groundwater used for drinking or cooking (Ayotte et al. 2003; Henke, 2009; Murcott, 2012; Polya & Lawson, 2015). Such occurrences, albeit
at often lower concentrations, have also been documented in the European Union (Kurttio et al. 1999; Varsanyi & Kovacs, 2006; Lindberg et al. 2006; Hough et al. 2010; Jovanovic, 2017) including in the UK and in particular in Cornwall (Ander et al. 2016) in the South West of England (Figure A3.1). Elevated arsenic concentrations in groundwater are thought to be causally associated with natural mineralisation and the human exploitation of mineral resources. However, notwithstanding the documented detrimental health effects arising from chronic exposure to arsenic in untreated or inadequately treated PWS, there remains uncertainty as to the precise extent of the population substantially exposed both in Cornwall and in many other parts of the European Union. This is due to the variability in the completeness of PWS records and the complexity of the arrangements for the collection and collation of such data.

Figure A3.1 Private water supplies sampled in Cornwall, along with location of shared supplies and arsenic concentrations.
We report here a case study of a recent (2011–2013) sampling and analysis programme of PWS in Cornwall and, in particular, (i) estimates of the population exposed to arsenic from PWS in Cornwall and (ii) estimated distribution of PWS arsenic exposures to that population. We estimate the number of people potentially exposed to arsenic above the Prescribed Concentration or Value (PCV) required by national Regulations (Drinking Water Inspectorate (DWI), 2009), which was implemented from the EU Directive 98/83/EC (Council of the European Union, 1998) and the WHO guideline value (WHO, 2011a) of 10 \(\mu g/L\). The potential health effects of arsenic exposure and a process for communication of risks to users is also outlined.

### A3.2 METHODS

#### A3.2.1 Recruitment of households with PWS

The existing list of households known to use PWS was provided in late 2010 by Cornwall Council and used for two field campaigns, east Cornwall (2011) and west Cornwall (2013). Households were targeted where it was known that they had a groundwater source (borehole, spring capture or traditional large-diameter well), serving a PWS. Properties using public supplies, PWS surface water sources, or not using the PWS for domestic drinking water were excluded. Larger PWS serving businesses were also excluded. A total of 3095 records were retained. There were 33 (1%) records removed due to the use of surface water, rather than groundwater, for the PWS. Some records were incomplete, and these were clarified on contact with potential volunteer householders to ensure that the PWS met the study design criteria.

A stratified, random design was used: records were classified into one of 10 geological categories, within which the records were randomised for sequence of contacting. It is, however, important to note that participation was entirely on a voluntary basis.

Where contact details of residents were incomplete (37%), these were amended by searching the council records (e.g. environmental health records, council tax records), the electoral roll and telephone or other online directories: where a valid address could not be established the record could not be used (~30% of records). Contact was made by letter (>2000 in total) and follow-up phone call to ensure adequate recruitment. In east Cornwall a local newspaper advertisement was also used.

Householders were encouraged to participate by the provision of the measured chemical data for their property, free-of-charge. After a two week recruitment drive for each phase, 497 households volunteered for the study and had their PWS drinking water sampled in spring (March/April) 2011 and 2013. A further fifteen properties were sampled when householders were absent in 2011, leading to ambiguity in knowing the extent of treatment used in water serving exterior taps: this was avoided in 2013 sampling. These data were not used as drinking water samples.

On recruitment, the head of the household and/or PWS owner were asked a series of questions by telephone, about the nature of the water supply, water treatment methods, the number of people living in the property and the number of properties the supply served. From this, the total number of residents served by the sampled PWS and the total number of properties served by the sampled PWS was calculated.

Further sampling design and chemical data collection methods are detailed in Ander et al. (2016). There were 497 samples taken to assess the chemical quality of drinking water from groundwater-sourced PWS (Figure A3.1).

#### A3.2.2 Estimating the number of PWS and residents served in Cornwall

The exact number of PWS in Cornwall serving domestic properties is not known. The most recent record of domestic PWS currently registered in Cornwall (\(n = 2995\)) was used (DWI, 2015) as a starting basis. This was considered a more up-to-date assessment originating from Cornwall Council than the database
version used in the original study planning. The average number of residents per household was calculated on a pro rata basis using the telephone householder questionnaires. These were also the source for information on numbers of further domestic properties served by a PWS source.

There were a number of households which also ran businesses with temporary residents on their property (caravan sites, holiday lets, holiday bed and breakfast). Only permanent residents at these sites were included in this assessment.

A3.2.3 Estimating the population exposed to arsenic in PWS

The distribution of arsenic concentrations in the surveyed tap water samples (Ander et al. 2016) was applied to the modelled number of PWS and the residential population served in Cornwall.

A3.3 RESULTS

A3.3.1 Estimating the number of PWS residents included in the survey

From the telephone recruitment questionnaire, it is known that 1263 residents were served by the PWS, at 94% (n = 467) of the sampled households, giving an average of 2.7 individuals per household. Using a Geographical Information System (GIS) and the National Population Database (NPD) (HSL, 2015) shapefile, we estimate that an additional 81 people are likely to live in the 30 households (6%) for which we do not have records, giving a total of 1344 residents served by the sampled PWS. This average occupancy rate is higher than the 2011 Census data (mean 2.3) (Cornwall Council, 2012).

In this study, 62% (n = 308) of households were the only users of the PWS, with 31% (n = 154) sharing their supply with other properties, based on questionnaire responses (7% not known). We found a higher proportion of small shared supplies than the DWI estimate of 14% (n = 533) on shared supplies (z score test shows a difference in the proportions, p < 0.001).

The shared supplies provide a further 352 households, in addition to the 154 which were sampled, using telephone questionnaire responses (n = 126) and otherwise estimated using GIS (Figure A3.2). We predict these contained 950 residents. Thus 849 properties are estimated to have 2294 people using drinking water from the PWS that we sampled.

![Figure A3.2](data.png)

**Figure A3.2** Distribution of the number of additional dwellings served by the sampled PWS in Cornwall (data available for 126 PWS).
A3.3.2 Estimated Cornish population using PWS, from official records

The DWI (2015) estimated that there are some 37,717 PWS in England, of which 67% (25,270) serve a single household, known as ‘Single Domestic Dwellings’ (SDDW). In Cornwall 65% (n = 2462) are recorded as SDDW PWS.

DWI (2015) estimated that 5.25% of the population in Cornwall are served by 3811 PWS, considering all types of PWS. Given a total population of 545,335 in 2014 (ONS, 2015a), this implies 28,630 people are drinking water from PWS. Using the ONS Rural Urban Classification of land use (ONS, 2015b), we find that 97% of sampled PWS were in rural hamlets (77%) or rural villages (20%), with the remainder in more urban settings. The total Cornish population (2011 Census) for these rural hamlet and village areas was 182,655, implying that 16% of the population in these settings may be using PWS.

A3.3.3 Estimating the population exposure distribution to drinking water arsenic

The number of households that exceeded the PCV (10 µg/L) for arsenic was 27 (5.4%). These served 66 residents and it was known that 15 additional properties (serving 21 people) also shared these PWS, giving 87 users. We assume that their drinking water concentrations are identical to that of the sampled property, and not affected in any way by individual household treatment which may be installed. We also calculate the residents potentially exposed to arsenic categories of <1, 1–5, 5–10 and >10 µg/L by the same method.

Of the 28,630 people estimated to be using PWS drinking water in Cornwall, and assuming 5.4% exceeding the As PCV, we infer that there could be approximately 1,432 residents in Cornwall using tap water which exceeds the As PCV. Caveats in this calculation include the assumption that only a negligible proportion of PWS are not sourced from groundwater, and the (unquantified) uncertainty on the 5.25% estimate of the population using PWS in Cornwall. Applying the As concentration distribution found in the 497 samples to the wider population calculated to be using PWS, Table A3.1 summarises the number of households and people predicted to be exposed to varying levels of arsenic measured in the PWS in Cornwall.

<table>
<thead>
<tr>
<th>Arsenic Concentration Range (µg/L)</th>
<th>Proportion of Total Groundwater Supplied PWS (%)</th>
<th>Predicted Number of Households</th>
<th>Predicted Number of Residents</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;1</td>
<td>71</td>
<td>7650</td>
<td>20,327</td>
</tr>
<tr>
<td>1–5</td>
<td>20</td>
<td>2155</td>
<td>5726</td>
</tr>
<tr>
<td>5–10</td>
<td>4</td>
<td>431</td>
<td>1145</td>
</tr>
<tr>
<td>&gt;10</td>
<td>5</td>
<td>539</td>
<td>1432</td>
</tr>
<tr>
<td>Total</td>
<td>100%</td>
<td>10,774</td>
<td>28,630</td>
</tr>
</tbody>
</table>

A3.4 DISCUSSION

A3.4.1 Guideline values, standards and health effects of arsenic in drinking water

The UK PCV (2009) and WHO (2011a) provisional drinking water guideline value for arsenic of 10 µg/L is set to protect health. Long-term (many years) exposure to relatively high arsenic drinking water levels
can produce skin lesions (e.g. hyperpigmentation and hypopigmentation), peripheral vascular disease, peripheral neuropathy and an increased risk of skin, lung and bladder cancer (HPA, 2011; WHO, 2011b). The International Agency for Research on Cancer (IARC) determined that long term exposure to inorganic arsenic (the form most commonly found in water) can cause cancer of the lung, skin and bladder (IARC, 1987, 2004, 2012; WHO, 2011b). The WHO consider that it is not possible to identify a level of exposure to arsenic that is completely free from cancer risk and Leonardi et al. (2012) suggest possible detrimental health impacts arising from chronic exposure through drinking water with sub-PCV concentrations. Therefore, exposure to inorganic arsenic from drinking water should be as low as reasonably practicable (ALARP) (WHO, 2011a).

Arsenic accumulates in the placenta where it may impair function and lead to a reduction in the efficiency of nutrient transport to the foetus. Additionally, it can cross the placenta and may then cause toxic effects (UKTIS, 2012). There is some evidence that arsenic exposure to the unborn baby or infants may adversely affect the developing nervous system (e.g. impaired cognitive functions, such as learning and memory) and lead to reduced birthweight (EFSA, 2009). Therefore, Public Health England (PHE) advises that women who are pregnant should avoid drinking water containing arsenic at levels above the UK PCV (updated advice from HPA, 2011).

A3.4.2 Public health advice given to households with exceedances

For any households that had one or more exceedance of PCVs, PHE and Cornwall Council sent chemical specific advice in the form of public health advice sheets. This was sent alongside the results of the chemical testing that summarised the main sources of the contaminant, outlined the potential acute and chronic health effects, and suggested action to be taken to reduce exposure to the contaminant [see for example http://www.bgs.ac.uk/sciencefacilities/laboratories/geochemistry/igt/Biomonitoring/arsenicSW.html]. The local authority supported with advice on mitigation measures to reduce arsenic concentrations in PWS.

The advice given to households with arsenic exceedance included some immediate, precautionary, health advice that included the following:

- Recommendation to avoid drinking and cooking with tap water containing arsenic above the PCV on a long-term basis.
- Pregnant women should avoid drinking water containing arsenic above the PCV.
- For any exceedances found, further testing was advised as there are different factors such as seasonal variation (particularly wet or dry months) that could affect the results. If the results further exceed the PCV, PHE recommended not drinking or cooking with the PWS tap water on a long-term basis.

The advice to anyone who had been regularly consuming water from the affected supply and had adverse effects consistent with excessive arsenic consumption was to seek advice from their general medical practitioner (GP). GPs were also sent briefings to advise them of the sampling programme and advised to seek specialist clinical toxicological advice from the National Poisons Information Service (NPIS, 2015).

The results of the water testing were sent back to the householders via letters, along with the advice sheets and any high or excessive exceedances were individually followed up with phone calls to raise awareness of the problem and advise of action to take.

The majority of enquiries received from the feedback of results were regarding what action to take and seeking assurance of the health risk posed. When a subset of households were contacted a year later, asking if they would take part in a follow–on biomonitoring study (Middleton et al. 2016a, 2016b), feedback was
gained on the actions they had taken following the results of the water testing. Some households had taken action on the advice given; undertaking maintenance of treatment systems or switching to bottled water for drinking, whilst others hadn’t.

A3.4.3 Evaluating arsenic PCV exceedances

Between 2010 and 2014, the DWI reported that 5.6% (14/249) of arsenic tests on SDDW in England failed the PCV (DWI, 2015). This is comparable to our overall study finding 5.4% failure in Cornwall alone. In this study, a substantial number of PWS shared the supply with other properties (31%), greatly increasing the number of residents served by these supplies.

DWI (2015) estimated that 5.25% of the population in Cornwall are served by private supplies, including larger shared supplies – using that value would appear to indicate ~10,800 properties with PWS (based on 28,630 users and an average household occupancy of 2.7), a somewhat higher figure than the ~3100 number on the register). There is anecdotal information that these records may be incomplete, particularly for the SDDW properties, probably because SDDW are not required to risk assess and monitor the PWS being used (DWI, 2009). In Northern Ireland (NI), where 99% of PWS are from groundwater, records of SDDW (n = 128) were an under-representation by ~1,100 properties, as calculated by subtraction of the known public and private supplies from the total households in NI (DWINI, 2014). These unregistered PWS were thought to be SDDW. The numerical inconsistencies and the DWINI report indicate the potential scale of the knowledge gap in relation to domestic use of PWS.

A3.4.4 Representativeness of samples and caveats

Drinking water samples were collected from 497 household PWS, approximately 17% of the ~3100 households on the original public register. Visits to households took place in the day, from 08:00 to 18:00, with some appointments available in the evenings and through the weekend to allow for the working population. There may be over-representation of older people in this survey, perhaps influenced by their more flexible availability for appointments, as was seen in the follow-up biomonitoring study (Middleton et al., 2016a,b). Business and commercial users of PWS were excluded from the study, unless they used a PWS for domestic drinking water.

In west Cornwall in 2013, 12% of households declined to take part when invited. The reasons for refusal included:

- The resident had their PWS tested regularly and therefore didn’t think it was necessary to have an additional sample taken.
- The resident didn’t want the additional hassle of having their PWS sampled (not convenient).
- The resident was not available during the water sampling programme.
- The resident did not use their PWS for drinking, but used mains water instead.

Similar reasons were given for refusal in east Cornwall in 2011.

Representativeness of the sample is reflected in our recruitment methods; based on the characteristics of recruited households, such as householders being retired or working, household size, number of shared supplies, land use classification, property type and geological classification. Characteristics of un-recruited households may differ in terms of these parameters.

Bias may occur through our recruitment methods. We could only contact and invite households if they were known to have a PWS, and if their details were up to date or known to various directories or council sources. Recruitment stopped when all appointment slots were booked. Householders less concerned with the quality of their supplies, or not wishing to be on an official register, may not have responded to the
The sample size depended upon the budget and resources available to the sampling team. It was necessary for householders to be available within the sampling programme or otherwise provide consent for access to their PWS and/or tap water supply. A small proportion of households were sampled as a result of meeting field teams on-site or word of mouth between neighbours, for which many of these were not on the central register.

The estimates of population exposure depended upon the accuracy of the source data, although DWI estimates are summaries of data reported by each council annually. Information on the number of residents per property depended upon residents reporting true occupancy in the questionnaire. The NPD is modelled on census returns and ad-hoc administrative surveys. Both can be subject to reporting biases and inaccuracies. Information on shared supplies depended upon respondents giving accurate responses to the questionnaire. There were some missing data in the form of non-response or ‘not known’ for some questions. Some inaccuracies were recorded as the water treatment method was unknown or incorrectly stated by the householder, as validated by the field notes taken by BGS at the time of visits against resulting data (Ander et al. 2016).

A3.5 CONCLUSIONS
A survey of 497 households in Cornwall between 2011 and 2013, recorded 5.4% of households to be utilising drinking water from PWS with arsenic concentrations exceeding the PCV of 10 µg/L. A further 4% of households recorded PWS arsenic concentrations between 5 and 10 µg/L, whilst 30% of households had PWS arsenic concentrations above 1 µg/L.

On the basis of a representative PWS population sampled in Cornwall, an estimation of the total population in Cornwall utilising PWS for drinking water was calculated to inform the distribution of the population exposed to 1, 5–10 and 10 µg/L arsenic in their PWS drinking water. Private water drinking supply user estimates and surveyed PWS arsenic concentrations indicated that approximately 1432 people in Cornwall are likely to be chronically exposed to arsenic through their PWS at concentrations exceeding the PCV of 10 µg/L; a further 1145 are likely to be exposed at concentrations between 5 and 10 µg/L and a likely total of over 20,300 exposed at concentrations above 1 µg/L. Public health advice sheets were prepared to outline the chronic risks of drinking water with elevated arsenic. Householders were sent advice if their water exceeded the PCVs. Cornwall Council continue to risk assess PWSs and recommend or enforce remediation where appropriate. In identifying the risk of arsenic the intention is to communicate the risk to those affected and local communities. It is hoped that in the future where similar situations arise, local authorities could utilise the advice sheets as a resource to highlight the risks to PWS users.

This work highlights the importance of testing for arsenic in SDDW and shared PWS particularly in areas of high geological risk. Further research is being carried out to more accurately estimate the population exposure from biomonitoring samples provided by a subset of these PWS householders and will be the subject of further publications (e.g. Middleton et al. 2016a,b). This work can inform the risk assessment of consumption from PWS and in the planning and implementation of public health prevention strategies. Further information on the project is available from:

http://www.bgs.ac.uk/sciencefacilities/laboratories/geochemistry/igf/Biomonitoring/arsenicSW.html

A3.6 ACKNOWLEDGEMENTS
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A3.7 REFERENCES


Chapter A14

Groundwater sampling, arsenic analysis and risk communication: Cambodia case study

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A14.1 INTRODUCTION

As part of an on-going (2002-present) study of the controls on arsenic in shallow groundwater in Cambodia, a team from the University of Manchester working in collaboration with the Royal University of Phnom Penh, undertook a survey of arsenic and other chemical parameters in two transects through shallow aquifers in Kandal Province, Cambodia in 2013 and 2014. We report here procedures used for water sampling and preservation and chemical analysis, particularly for groundwater arsenic, as well as for the subsequent communication of arsenic-attributable health risks to those people drinking water from the same aquifers.

A14.2 DATA REQUIREMENTS & METHODS

A14.2.1 Overall aims of monitoring

The overall aim of the sampling programme was to understand better the origins of and controls on the concentrations of geogenic arsenic in shallow aquifers in circum-Himalayan aquifers, which are extensively used by hundreds of millions of people as a drinking water source. The programme targeted a region in Kandal Province in Cambodia because (i) it represents an ideal area, relatively un-impacted by massive...
scale irrigation and potentially enabling a better understanding of arsenic mobilising processes to be developed (Charlet & Polya, 2006); (ii) extensive background geographical and geological data existed for the area (Polya et al. 2005; Polizzotto et al. 2008; Rowland et al. 2008; Benner et al. 2008; Buschmann & Berg, 2009; Polya et al. 2010; Lawson et al. 2013; Richards et al. 2015; Lawson et al. 2016) (iii) logistical positives, including 10 years’ experience in the area; and (iv) known groundwater arsenic concentrations over a wide range, viz. 0.1 to 1000 µg/L (Polya et al. 2005; Rowland et al. 2008; Sovann & Polya, 2014).

A14.2.2 Representativeness
The aims of the study required the samples obtained to be collectively representative of two contrasting transects oriented broadly parallel to the inferred predominant directions of groundwater flow. Accordingly, for each transect, samples were obtained at roughly equally spaced intervals over the 3 km – 5 km length of the transect and over a 6 m–45 m depth range, being typical of the overall exploited thickness of the aquifers being studied. Thus results may be justifiably used to interpret how groundwater compositions vary with position with respect to groundwater flow paths from recharge to discharge zones. Since the aim of the study was not to undertake an area survey, the aggregate results may only be used in an indicative way of the overall arsenic concentrations in the study area.

A14.2.2.1 Speciation
Previous studies have determined that groundwater arsenic speciation in this area is dominated by inorganic arsenic and particularly As(III), with minor concentrations of methylated arsenicals. Nevertheless, further speciation measurements (not reported here) were carried out using a cartridge-based field separation technique after Watts et al. (2010).

A14.2.2.2 Spatial and temporal variations
Water samples were largely taken from previously drilled and developed boreholes (Lawson et al. 2013; Richards et al. 2015) using a flow cell apparatus to monitor sample homogeneity and after flushing typically 2 to 3 borehole volumes depending upon the nature of the aquifer being sampled (cf. Richards et al. 2015) to obtain a sample more representative of the aquifer at the depth of the well screening rather than the borehole used to obtain the sample.

Since groundwater flow directions are known to be strongly seasonally dependent (Benner et al. 2008), samples were taken in both pre-monsoon and post-monsoon seasons, with a number of samples taken at other time intervals to better establish temporal variations in groundwater composition. The frequency of such temporal sampling was largely determined by logistical and financial constraints.

A14.2.2.3 Contamination during sampling
Contamination of samples was minimised through (i) thoroughly washing sample vessels with nitric acid and then deionised water and then furnace at 450°C (for glass vessels) prior to field work; (ii) sample rinsing with the sample to be collected during field work; and (iii) flushing of several borehole volumes through a flow cell prior to sample collection. The lack of contamination introduced from leaching of sampling vessels or from the addition of nitric acid preservative was checked through the analysis of procedural blanks, whilst LiCl tracers provided information on the likely extent or otherwise of drilling fluid contamination in recently drilled boreholes (Richards et al. 2015).
A14.2.2.4 Preservation

Samples for arsenic analysis were filtered (0.45 µm cellulose and polypropylene syringe filters) and acidified with Aristar nitric acid to ensure a pH of lower than 2. The pH of the acidified samples was checked given the frequent presence of high (200–1100 mg/L) concentrations of HCO$_3$ (aq) which can neutralise added acid by the reaction:

\[
\text{HCO}_3^-(aq) + \text{H}^+ (aq) \rightarrow \text{H}_2\text{CO}_3(aq)
\]

Non-acidified samples (still filtered to 0.45 µm) were also collected for analysis of anionic components. After collection, all samples were stored in an ice-box on the day of sampling and then subsequently refrigerated prior to analysis.

A14.2.3 Data & Data Quality Objectives (DQOs)

Analytes requiring determination were arsenic as well as many further geochemical parameters, measurement of which was considered likely to assist in understanding arsenic biogeochemistry.

A14.2.3.1 Field site related parameters

Sampling was informed by conceptual groundwater models (Benner et al. 2008; Polizzotto et al. 2008) and ERT (electrical resistivity tomography) investigations (Uhlemann et al. 2015). In order to model groundwater flow, piezometric levels were determined and groundwater level relative to local datum constrained using a combination of GPS and total station measurements.

A14.2.3.2 Analytes

In addition to arsenic, other analytes determined included (i) field-determined pH, Eh, dissolved oxygen, electrical conductivity (as a field proxy for total dissolved solids), and the potentially labile constituents sulphide, ammonium, nitrate, nitrite, iron, manganese, fluoride and orthophosphate; (ii) laboratory determined chemical analytes including Na, K, Mg, Ca, Si, Cl, HCO$_3$, SO$_4$, Sr, Ba, Cu, Pb, Zn, Li, Al, DOC (dissolved organic carbon), DIC (dissolved inorganic carbon) and (iii) laboratory determined isotopic analytes $\delta^{18}$O, $\delta^D$, $\delta^{13}$C, $^{87}$Sr/$^{86}$Sr, $^{14}$C, $^3$T, $^3$He, $^4$He, $^{20}$Ne and $^{22}$Ne.

A14.2.3.3 DQOs – required chemical measurement performance characteristics

Analytical requirements for arsenic arising from the project aims included: accuracy better than 5%; precision better than 5%; and detection limit better than 0.2 µg/L.

A14.3 ANALYTICAL METHODS & TOTAL QUALITY MANAGEMENT

A14.3.1 Analytical methods

Total arsenic was determined by ICP-MS (Agilent, 7500 cx) after shipping of preserved water samples to the Manchester Analytical Geochemistry Unit (MAGU) at the University of Manchester. Arsenic speciation was determined by a field separation method, followed by elution and subsequent determination by ICP-MS of the eluted separated fractions following the method of O’Reilly et al. (2010) and Watts et al. (2010).
A14.3.2 Analytical & data reduction protocols

A14.3.2.1 Control samples & standards

Calibration standards, with arsenic concentrations between 0 and 500 µg/L (range of anticipated sample arsenic concentrations) were used at a frequency of approximately 1 set of 8 calibration standards per 10 sample analyses. Procedural blanks were used to estimate contamination from sample processing. Blank samples were used to assess any contamination from in-laboratory handling, including dilutions where appropriate, whilst wash samples were used to determine the extent if any of any “carry over” from one sample to the next during an analytic run. Precision was estimated through triplicate analysis of samples and repeat analysis of samples at different times in an analytical session or in different analytical sessions. A mixed internal standard spike (containing 10 µg/L each of Ge, Sc, Rh and Ir) was used, although its efficacy in improving analytical accuracy and precision was ambiguous. The project requirements for geochemical modelling, including saturation index calculations, of the analysed groundwater necessitated the use of certified reference materials, notably SPS-SW1 (LGC Standards, UK), SRM1643 (National Institute of Standards and Technology, USA), TM25.2 (National Water Research Institute, Environment Canada) to ensure accuracy.

A14.3.2.2 Order of analysis – randomisation

Randomisation of presentation of samples for analysis was partially carried out although not comprehensively: any bias introduced by any systematic changes in analytical sensitivity over the course of an analytical session were monitored to ensure that this slight deviation from best practice did not materially impair analytical quality.

A14.3.2.3 Data reduction – calibration models

Calibration curves were calculated using least square methods using (i) unweighted; and (ii) inverse variance weighted first order linear models. The utility of using an internal standard was also assessed. The appropriateness of calibration curve models was assessed following the recommendations of Polya and Watts (2017).

A14.3.3 Total quality management

As a university-based laboratory undertaking a wide variety of analyses and exploratory studies and with resource constraints, our laboratory does not currently operate as a formally accredited laboratory under, for example, ISO 14001:2004. However, the laboratory follows good laboratory practice (cf. Polya & Watts, 2017) and confidence in the laboratory’s data has been obtained through longer-term involvement in inter-laboratory comparison schemes, such as run by EAWAG (Duebendorf, Switzerland) (Berg & Stengel, 2009).

A14.4 PRELIMINARY RESULTS

Measured arsenic concentrations using a simple unweighted first order linear calibration model ranged from 2 to 918 µg/L with a mean of 211 µg/L and a median of 130 µg/L. Analytical precision was strongly and systematically dependent upon concentration, varying from about ±0.3% at 500 µg/L to ±3% at 2 µg/L, the concentration dependence of analytical precision being adequately modelled by an exponential fit.

The following QA/QC check results are noted:

(i) The residuals from a first order unweighted calibration curve (see Figure A14.1, top left) show that there is no substantial correlation of the mean residuals with count rate/concentration. However the
data are clearly heteroscedastic, i.e. the magnitude of the residuals are correlated with count rate/concentration invalidating one of the assumptions of least squares fitting. This is also confirmed by the evident relationship between standardised residuals and count rate/concentration;

(ii) The Q-Q plot of standardised residuals (Figure 14A.1, top right) shows that they are for the most part normally distributed but the distribution is nevertheless “light-tailed”;

(iii) It is clear from inspection of a plot of standardised residuals vs leverage (Figure 14A.1, bottom right), there is a disproportionate leverage of the calibration curve best-fit parameters from data related to the highest concentration calibration standards;

(iv) The concentration of some of the samples exceeded that of the top calibration standards, accordingly the data for these samples are taken to be indicative only (and the samples were subsequently diluted and re-analysed);

(v) The range of analytical precisions, ±0.3% to ±3% was compliant with the analytical precision required by the project;

(vi) The detection limit determined to be around 0.5 µg/L is somewhat higher than the value ideally required by the project;

(vii) Agreement between the determined arsenic concentrations of calibration standards measured as unknown samples and the known concentrations were largely within the determined analytical precisions, with the exception of certain 0 µg/L and 1 µg/L standards – closer inspection of the data with reference to run order showed that elevated concentrations of As were measured in all 0 µg/L and 1 µg/L standards and wash samples where they immediately followed a sample with > 200 µg/L As – accordingly the removal of the impacted standards from the calibration standards was indicated and re-analysis of all the impacted samples was indicated, although in the case of the latter the estimated biases where always less than 10% and mostly less than 0.5%;

(viii) Analytical sensitivity for calibrations between 5 and 500 µg/L was determined to increase by around 20% during the course of an analytical session – this necessitates a drift correction, using for example, the 74Ge internal standard;

(ix) Arsenic spikes and standard additions (not reported here) were used to determine the magnitude of any likely matrix effects;

(x) Wash samples contained either undetectable or less than 0.7 µg/L arsenic; blank samples contained as much as 0.7 µg/L arsenic – both sets of samples indicate a level of carry-over from the previously analysed sample of as much as 0.13%;

(xi) Measured arsenic concentration in the CRMs analysed were in agreement with the certified values to within analytical precision, viz. SRM1643 (found 58 ± 6; known 60.45 ± 0.72 µg/L); TM-25.2 (found 9 ± 1; known 7.1 µg/L) and SPS-SW1 (found 11 ± 2; cf. known 10 ± 0.1 µg/L);

(xii) The total arsenic concentration method used here agreed to within 2 ± 10% of an independent method, viz. summing individual species determined by coupled ion chromatography ICP-MS, although it was noted that there were a considerable number of outliers, which are thought to relate to operator/operator training issues in field-based cartridge separation used as part of the speciation method;

(xiii) Previous inter-laboratory schemes resulted in agreement of samples analysed using the same method as reported here with agreed values to within analytical precision (cf. Berg & Stengel, 2009);

(xiv) Electrical charge balances for the samples were largely within 15% – somewhat higher than ideal and again thought to be related to operator/training issues for some field-based determinations;
Lastly, it is noted that the range of arsenic concentrations is similar to that determined by previous studies (cf. Polya et al. 2005; Polizzotto et al. 2008; Rowland et al. 2008; Sovann & Polya, 2014).

![Figure A14.1](image)

**Figure A14.1** Analysis of calibration model (unweighted first order linear) for arsenic determination by ICP-MS. (a) Residuals as a function of mass spectrometry count rates at m/z = 75; (b) Standardised residuals as a function of count rate; (c) Q-Q curve for standardised residuals; (d) Standardised residuals vs leverage.

Inspection of analytical data particularly of control samples has indicated where further post-instrument analysis and further instrumental analysis is required.

### A14.5 RISK COMMUNICATION

Information on groundwater compositions and possible health risks associated with chronic consumption of such groundwater for drinking was particularly sought by landowners and tenants who had given permission for work to be carried out on their land. Notwithstanding that the majority of the boreholes sampled as part of this study were not used as drinking water wells, but rather were drilled for the purposes of scientific investigation, information to landowners and tenants, who might otherwise access the groundwaters through drilling their own wells, was considered to be an important element of the communication plan for the overall
Groundwater sampling, arsenic analysis and risk communication

A template letter providing such information is shown in Figure A14.2 – it represents a balance between brevity and comprehensiveness and in particular highlights the appropriate agencies from where to seek more detailed information. The letter was provided in both English and the local language, Khmer (not shown here).

**SCIENTIFIC INVESTIGATION OF HIGH ARSENIC GROUNDWATERS IN KANDAL PROVINCE, CAMBODIA**

**REPORT ON COMPOSITION OF WATER SAMPPLED FROM BOREHOLE [RXX-XX]**

Borehole [RXX-XX] was sampled in the year 2014 and analysed for a limited selection of chemicals. The purpose of the analysis was scientific - to better understand why high arsenic occurs in many groundwaters in Kandal province, Cambodia as well as in many other parts of the world, including parts of Bangladesh, India, Vietnam and China.

The purpose of the analysis was not to provide an assessment of water quality. However, for the information of those (e.g. landowners, tenants) with interests in the quality of groundwater in the nearby area – results for 4 chemicals, arsenic (As), manganese (Mn), nitrate (NO₃⁻) and nitrite (NO₂⁻) are shown below. The results are all expressed in units of μg/L (micro-gram per litre) – this is approximately equivalent to the unit of “parts per billion” or “1 part in 1,000,000,000”. The results are compared to the current World Health Organization (WHO) guide values (or equivalent derivable value) for the maximum recommended concentrations of these chemicals in drinking water.

Please note: (i) Uncertainties of the reported results are typically better than 10% or 2 μg/L, whichever is the higher; (ii) Groundwater/borehole water compositions may vary over time and from place to place; (iii) arsenic concentrations of greater than 10 μg/L (the WHO Guide value) were found in over 80% of the borehole waters analysed in this study; (iv) The overall fitness to drink of water depends also upon the concentrations of other chemicals and particularly of pathogenic organisms – the concentrations of such organisms have not been determined in this study because it was not the purpose of this study to determine the fitness of water to drink; (v) well water or other water sources to be used for drinking should be thoroughly tested for its suitability before use.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Result (μg/L)</th>
<th>WHO guide value (μg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic (As)</td>
<td>XX</td>
<td>10 ^</td>
</tr>
<tr>
<td>Manganese (Mn)</td>
<td>XX</td>
<td>4,000 ^</td>
</tr>
<tr>
<td>Nitrate (NO₃⁻)</td>
<td>XX</td>
<td>50,000 ^</td>
</tr>
<tr>
<td>Nitrite (NO₂⁻)</td>
<td>XX</td>
<td>3,000 ^</td>
</tr>
</tbody>
</table>

^ formal value; * derivable health-based value; not a formal WHO Guideline value

If the result for any chemical is higher than the WHO guide value then this indicates that drinking the water on a regular basis may result in unacceptably high added risks of bad long term health outcomes. For manganese these outcomes may include developmental issues in children. For nitrate and nitrite these outcomes may include “blue baby syndrome”. For arsenic these bad health outcomes may include cancers, heart disease and premature death.

In order to prevent accidental drinking of borehole waters that may contain harmful concentrations of arsenic and other chemicals, boreholes drilled as part of this study have not been fitted with pumps or wellheads and are either being removed (i.e. filled in) (particularly where requested by landowners or tenants) or locked (where further useful monitoring is indicated and the landowner or tenant as appropriate is agreeable).

Further information on health risks arising from chemicals in drinking water and on water remediation and testing is provided by the WHO. Information on local groundwater and regulation may be sought from relevant national, regional and local government authorities. To comment or for further information on the chemicals found in this borehole water please email the project team at laura.richards@manchester.ac.uk, david.polya@manchester.ac.uk or chanphotosheak@gmail.com. We aim to reply within 30 days to emails received by the end of December 2018.

We thank all those who have helped us to undertake this scientific study. Key results and a summary are anticipated to be available from www.manchester.ac.uk/research/david.polya or the email addresses above by February 2017.

University of Manchester Groundwater Arsenic Team, Phnom Penh, December 2015

In the event of any discrepancies between the Khmer and English versions of this document, the original English version takes precedence.

**Figure A14.2** Template of Report on Water Chemistry to Landowners/Tenants.
A14.6 CONCLUSIONS
This case study illustrates the importance of inspection of analytical data, particularly that of control samples and standards, and the importance of consideration of the most appropriate methods for detecting and correct for, when appropriate, instrumental drift and contamination – including cross-sample contamination.

A14.7 ACKNOWLEDGEMENTS
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A14.8 REFERENCES


