4 Water sampling and analysis

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Human exposure to geogenic contamination occurs primarily through consumption of contaminated water. It is therefore essential to identify contaminated water sources. From an institutional perspective, this implies national surveys that help establish i) if there is any contamination; ii) where the regions of contamination might be and iii) where mitigation activities are most urgently required. For local organisations, the survey may be limited to a region of suspected contamination, with much less technical support.

Sampling and analysis of water is a time-consuming and costly process, and planning is one of the most important steps of any field campaign. Often health symptoms provide the first indication of geogenic contamination (see Chapter 1). The first step is always to evaluate already available information, e.g. government agency reports or academic studies on water quality. Our experience shows that relevant data often exist, but sharing these data can be a problem. Next, it needs to be decided where more information is required, which water quality parameters are essential and which instrumentation for the analysis of As and F is available. Finally, the necessary preparations need to be taken before going into the field. The following sections give an overview of sampling and measuring procedures.

4.1 Basic principles

Both fluoride and arsenic are tasteless, odourless and colourless in water. The only way to detect these contaminants is through chemical analysis. If water-quality data are not already available, a field sampling campaign is necessary to find out if arsenic and fluoride concentrations are above the relevant WHO guidelines (10 µg/L for arsenic and 1.5 mg/L for fluoride) and/or national guidelines. In a first step, only a selection of water sources in areas indicated to be at risk, perhaps by the observation of fluorosis or arsenicosis symptoms in local populations, are screened. It may be possible to prioritise certain geographic areas, which are thought to be more vulnerable to geogenic contamination, for testing.

If the screening confirms elevated fluoride or arsenic levels in even a few water sources, then a more time- and resource-intensive testing of all water sources (blanket testing) should be carried out. This needs to be done because contamination levels can vary greatly over short distances. If the financial resources are available, it may be worthwhile not only to measure arsenic and/or fluoride concentrations, but to undertake a full water analysis (sum parameters, major components, minor components), as this gives a much more complete picture of water chemistry and might yield explanations for the occurrence of geogenic contamination. More details can be found in Section 4.4 at the end of this chapter.

Selection of measurement method

Arsenic and fluoride analyses may be carried out directly in the field using semi-quantitative or quantitative field kits. The samples may also be taken back to a laboratory for analysis. Semi-quantitative field test kits are only recommended to classify wells as above or below an acceptable limit, while quantitative measurements provide information on arsenic or fluoride concentrations. Quantitative measurements allow us to evaluate the health hazard and are essential for mitigation planning.

Field testing versus lab testing

Field test kits have the advantage of providing immediate results in the field, allowing water sources to be marked as safe or unsafe straightaway. They also allow a check to be made for alternative safe water sources in the immediate surroundings of the contaminated well. The possibility of sharing safe sources can be discussed on the spot (keeping in mind that microbial contamination may be a problem). However, field measurements are more prone to human error, as they are performed under suboptimal conditions, and often by different testers.

Laboratory equipment will produce results of superior accuracy and precision to field test kits, if correctly operated and maintained by well-trained and dedicated staff. However, there are three main obstacles to the exclusive use of laboratory methods in large screening exercises (Kinniburgh and Kosmus, 2002):

- The lack of sufficient laboratories of the required quality to process large numbers of samples reliably (though a large sampling campaign might allow long-term capacity building and result in improving laboratory performance).
- The lack of management experience to organise the collection and tracking of samples and reporting of results on a large scale, resulting in the risk of results being misreported.
- Logistical problems associated with the transporting of samples from the field to the laboratory and relaying the results back to the field.

Evidence shows that well-designed and well-implemented arsenic survey programmes using field test kits can be reasonably accurate and comparable to laboratory tests (Rosenboom, 2004; Steinmaus et al., 2006; Jakariya et al., 2007, George et al., 2012; Spear et al., 2006). The same can be expected for fluoride surveys.

Testing campaigns have to be carefully planned:

1. Select sampling sites, measurement method and quality-control plan
2. Train staff involved in sampling procedures, preservation and/or transportation of water samples and handling of analytical equipment
3. Prepare monitoring forms Example_Monitoring-Form
4. Prior to each sampling trip: check and carefully pack equipment.
   (Often forgotten: stickers and waterproof pen for labelling, spare batteries, screwdriver for opening battery case, distilled water, pipette, GPS etc.).

Accuracy and precision

Regardless of the equipment used, sample concentrations are obtained by comparing an analytical signal to standards or known samples. While in semi-quantitative methods these may be colour charts, in quantitative methods these will be blanks (distilled or deionised water containing analyte chemicals) and known concentrations. Laboratory analyses of >20 sample batches will usually comprise a blank and standards (between 3 and 8 standards) at the beginning and end of analysis, with one blank and one standard every 10 samples. Ideally, samples will be analysed in duplicate or triplicate. In the field, the number of analytical checks may be reduced (for practical reasons) to one blank and only a few standards at each sampling location. It is therefore recommended to make quality control checks on field kit analyses and to cross-check 5–10% of the water samples with measurements made in reference laboratories (APHA, 2012).

The multiple analysis of the same sample gives a mean. The precision is the scatter around the mean (UNICEF, 2008a; Fig. 4.1). If the results lie close together, the precision is said to be high. However, their accuracy is dependent on how close they are to the "true" value. The accuracy and precision of an analytical procedure will depend on a number of factors, including the skill of the analyst, the proper operation and maintenance of the equipment and the quality of reagents used.
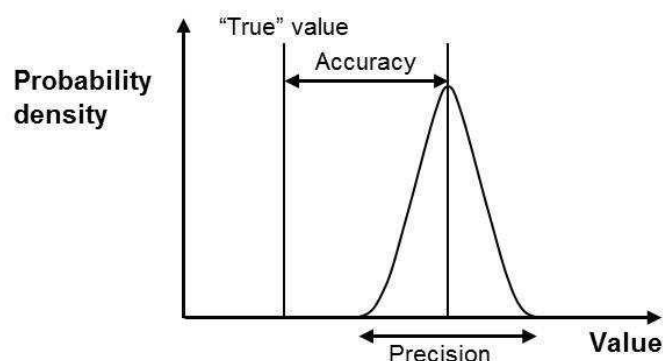

Fig. 4.1   *Difference between accuracy and precision*

For screening, quantitative accuracy may not be essential; if the countrywide drinking-water standard for arsenic is 50 µg/L, a field test kit does not need to be able to distinguish reliably between 200 and 300 µg/L in order to identify the well as contaminated. In India and Bangladesh, arsenic surveys have used field test kits in a semi-quantitative way to classify wells as above or below the acceptable limit of 50 µg/L.

The operation of field test kits is normally easy and explained well in the user manuals of commercially available products. Nevertheless, good training on the use and maintenance of field test kits is a key factor in obtaining accurate measurements. Sophisticated laboratory methods can only be installed and operated by experienced and well-educated laboratory staff.

Some fluoride and arsenic tests might depend on pH or be influenced by competing ions in the water sample. It is important i) to make an in-depth study of user manuals and ii) to consult experts if necessary, to avoid such interferences.

Costs and availability

Analytical costs depend on the number of measurements planned. For instance, the capital costs for an ion-selective electrode (ISE) to measure fluoride is high, so if only few tests are carried out, the cost per sample will be high. However, if many measurements are conducted, the running costs per test are lower for the ISE method than for most of the fluoride field test kits. On the other hand, for arsenic, the costs per measurement are lower for field test kits than for laboratory analyses.

Importing chemicals from abroad can be expensive and complicated, making it preferable to obtain them from a local supplier.

Health and safety

Many of the reagents required for arsenic and fluoride measurements are harmful when in contact with the eyes or skin. They have to be carefully stored during transportation, and safety equipment (gloves and glasses) needs to be worn when handling the chemicals. Children need to be kept away from the work area, and all waste must be taken away from the field and disposed of responsibly.

Another issue related to arsenic field test kits is that they may expose the analyst to unsafe levels of the toxic gas, arsine. One study found that nearly half of the arsine generated during analysis escaped from the reaction vessel (Hussam et al., 1999). Newer kits are better designed, but the analyses still need to be conducted in a well-ventilated area (i.e. outdoors).

The transport of reagents in the cabin or hold of an aeroplane may be prohibited. Cargo companies or postal services are an alternative. Some documentation might be necessary for customs.

Ensuring safety: It is recommended that contaminated water sources be clearly marked (e.g. A red pump spout for contaminated water sources and green spout for uncontaminated water sources (UNICEF, 2008b)), so that it is obvious to local users whether a well is contaminated and that water should not be used for drinking or cooking purposes. Appropriate colours should be determined by consultation with the local population. It is recommended to label the well with its measured As or F concentration, as well as with the date and method of analysis.

4.2 Arsenic sampling and measurement

Inorganic arsenic in groundwater is found in two different oxidation states: As(III) (arsenite) and As(V) (arsenate). There are also organic forms, but these are rare in drinking water. Both As(III) and As(V) are toxic, but the two species behave somewhat differently in the environment. The testing methods described in this manual give total inorganic arsenic concentrations, which are adequate for most general purposes. Specialised techniques are needed to tell whether arsenic is present as arsenite or arsenate.

The detection range of interest is 10 to 50 µg/L (the typical range of national standards for arsenic). Maximum concentrations of naturally occurring arsenic in groundwater can exceed 1000 µg/L.

Sampling and preservation

For both field and laboratory testing, it is important that correct sampling procedures be followed. To ensure that the sample is representative, it should be freshly drawn from the aquifer. The groundwater should be pumped to ensure that at least one well volume of water is removed before collecting a sample. An alternative is to measure dissolved oxygen and/or pH can in the pumped water until the parameters have a constant value, before taking a sample. The acid-washed sampling bottle should be rinsed three times using the pumped water, making sure to keep the lid clean, before the sample is collected for analysis. Depending on the analytical method chosen, the arsenic measurement can be carried out directly on-site at the water source, or as soon as possible back in the laboratory.

If a sample is to be taken back to the laboratory, its volume should suffice for at least 5 arsenic analyses. The sample bottles should be filled to the top. The sample ID should be written on the bottle, or better still, on a label stuck on the bottle, with a waterproof pen BEFORE the sample is taken. A leaky sample bottle can render labels unreadable.

High density polyethylene (HDPE) plastic bottles are recommended. They should be washed with acid (1% HCI) and well rinsed with distilled water (3 times) before use. Water samples should be transported and stored in a cool, dark and clean environment. If the samples are properly preserved, the arsenic measurements will still be reliable even if carried out several months after sampling (This is important when samples are collected for quality checking in a reference laboratory).

To avoid the formation of iron (oxy)hydroxide in the sample (orange colouring commonly associated with groundwater containing iron), which may remove arsenic from solution, the pH of the samples should be reduced to below 2 using acid. Nitric acid is commonly used (hydrochloric acid is another option); the acid should be certified to contain essentially no arsenic. Blank samples (distilled water with and without acidification) should always be tested to ensure that no arsenic is added to the samples along with the acid or the sample bottles. Generally it is sufficient to add 0.2–1% of the filling volume (e.g. 0.2–1 mL acid for a 100 mL sample bottle) of concentrated nitric acid (65%). For safety reasons, it might be advisable to use diluted acid (1:1 or 1:2) in the field.

Water samples can be filtered before acidification (through 0.45 µm filters) to remove any particles that might dissolve arsenic at low pH, which would lead to higher arsenic readings. Filtration increases the precision of the results, as the particulate content is difficult to control. However, if particulate arsenic also contributes significantly to arsenic exposure, then filtering samples will lead to an underestimate of actual exposure. Generally, filtered samples are better for understanding geochemistry, while unfiltered samples are better for public health purposes.

Field test kits

Various arsenic field kits are commercially available (Tables 4.1, 4.2). The most commonly used field test methods rely on the chemical reduction of arsenic present in the sample to arsine gas, which then reacts with other chemicals on a test paper or in an indicator tube to produce a colour with an intensity proportional to the arsenic concentration. The tester then compares the colour with a calibrated colour chart. In some field testing equipment, a digital photometer is used to measure the colour intensity, which eliminates human error.

Bacterial biosensors may offer another alternative for the detection of arsenic contamination in drinking water (Trang et al., 2005). These sensors, which rely on genetically engineered E. coli bacteria that glow when exposed to arsenite, are cheap and easy to use but require some training. The microbiological arsenic test has a great potential in large screening campaigns (see ARSOlux, Table 4.1).

Arsenic analysis in the laboratory

All laboratory analyses must be performed by experienced laboratory staff.

There are various methods of quantifying arsenic concentrations in the laboratory. In order of increasing sophistication (and cost), they are the colorimetric method requiring a (spectro)photometer that uses silver diethyl-dithio-carbamate (SDDC), Anodic Stripping Voltammetry; Graphite Furnace Atomic Absorption Spectrophotometry (GF-AAS); Flame AAS with Hydride Generation apparatus (HG-AAS) and inductively coupled plasma mass spectroscopy (ICP-MS). For a detailed review, see Rasmussen and Andersen (2002).

Table 4.1 *Overview of commercially available semi-quantitative arsenic field test kits (this list does not include all available kits, and is not intended as an endorsement of any of the companies or products listed):*

Industrial Test Systems (Arsenic Quick^{TM})	Available for low- (5–500 µg/L) and high- (20–3000 µg/L) concentration ranges. The test takes 20 minutes. Contains hazardous chemicals. Instruction-Leaflet_(LowRange) Material-Safety-Data-Sheet Where to buy: www.merck-chemicals.com
Hach (Arsenic Test Kit)	Hach offers two arsenic test kits. The Arsenic Low Range Test Kit has a range of 10–500 µg/L and is best for samples containing sulphide or arsenic-iron particles. The EZ Arsenic High Range Test Kit has a range of up to 4000 µg/L, comprises fewer steps, and is more economical. Instruction-Leaflet_(Low-Range) Where to buy: www.hach.com
Industrial Test Systems (Arsenic Quick^{TM})	Industrial Test Systems markets a range of different arsenic test kits. The main product, the Quick™ test, has a range of 5–500 µg/L, with a reported reaction time of only 12 minutes. This kit has been verified by the USEPA's Environmental Technology Verification programme. Further reading on test kit performance: George et al., 2012 Documentation Where to buy: www.sensafe.com
ARSOlux (Biosensor)	ARSOlux offers a biosensor to determine whether arsenic concentrations (in the chemical form of arsenite) are above or below a chosen calibration value (e.g. 10 µg/L). The pH of the water sample has to be between 6 and 8, and it is necessary to incubate the sample for two hours between 20 and 35°C. Information-Leaflet Website: www.arsolux.ufz.de

Other semi-quantitative field test kits

The Asia Arsenic Network, an early player in arsenic testing and kit development, continues to market an inexpensive kit with a range of 20–700 µg/L in Bangladesh. A variation on this kit, measuring arsenic from 10–500 µg/L, was developed by the Environment and Public Health Organization, Nepal.

A joint project between UNICEF and the Rajiv Gandhi National Drinking Water Mission in India has developed specifications for a field kit that does not use the conventional mercuric-bromide paper. Instead, a detector tube is filled with a granular medium coated with a secondary colour reagent that reacts with arsenic and mercuric bromide to produce a pink colour. Following completion of the test, the arsenic concentration (10–110 µg/L) is read directly by measuring the extent of pink colour penetration in the detector tube. Specifications for the kit are available from the Rural Water Supply Network.

UNICEF also supported the development of locally manufactured arsenic test kits in China, Thailand and Vietnam, and in China and Thailand, they are still in use. The Thai kit, developed and marketed by Mahidol University, has a detection range of 5–500 µg/L and is used in Thailand and in other countries in the region.

Table 4.2 *Overview of commercially available quantitative arsenic field test kits (this list does not include all available kits, and it is not intended as an endorsement of any of the companies or products listed):*

Wagtech/Palintest (Digital Arsenator, DigiPAsS)	The Digital Arsenator detects arsenic within a reported range of 2–100 µg/L. Wagtech also produces a Visual Arsenic Detection Kit, which uses a visual reference colour chart instead of the optical photometer. It has a reported range of 10–500 µg/L. It has been widely used in Bangladesh, Kenya and other countries. Operation-Leaflet_1 Material-Safety-Data-Sheet_(Sachets) Material-Safety-Data-Sheet_(Tablets) Where to buy: www.wagtech.com, www.palintest.com
Merck (Spectroquant®, Nova 60A)	Merck sells a digital photometer arsenic kit (Spectroquant®) with a reported range of 1–100 µg/L. The Merck photometers are typically used in a laboratory setting, but one model (Nova 60A) comes with a battery pack and can be used as a portable instrument. Operation-Manual Material-Safety-Data-Sheet Where to buy: www.merck-chemicals.com

4.3 Fluoride sampling and measurement

Fluoride concentrations in drinking water normally range from below 0.1 mg/L up to 10 mg/L, but can in some cases reach 20 mg/L or more. At fluoride concentrations of >20 mg F/L, the water is often saline and therefore not used for drinking or cooking. The WHO guideline value (and that of many national standards) is 1.5 mg/L, so quantification in this range is critical.

Fluoride measurement methods can be divided into colorimetric/photometric methods (semi-quantitative and quantitative) and potentiometric methods (using an ion-selective electrode, ISE). More sophisticated methods (e.g. ion chromatography, IC) do not deliver more accurate results than a carefully calibrated ISE and are not discussed in this manual (basic information on IC can be found in Fawell et al., (2006)).

Sampling and preservation

For both field and laboratory testing, it is important that correct sampling procedures be followed. To ensure that the sample is representative, it should be freshly drawn from the aquifer. The groundwater should be pumped to ensure that at least one well volume of water is removed before collecting a sample. An alternative is to measure dissolved oxygen and/or pH can in the pumped water until the parameters have a constant value before taking a sample. The sampling bottle should be rinsed three times using the pumped water, making sure to keep the lid clean, before the sample is collected for analysis. Depending on the analytical method chosen, the fluoride measurement can be carried out directly on-site at the water source, or as soon as possible back in the laboratory.

If a sample is to be taken back to the laboratory, its volume should suffice for at least 5 fluoride analyses. The sample bottles should be filled to the top. The sample ID should be written on the bottle, or better still, on a label stuck on the bottle, with a waterproof pen BEFORE the sample is taken. A leaky sample bottle can render labels unreadable.

Plastic bottles are recommended, as glass bottles can easily break. Water samples should be transported and stored in a cool, dark and clean environment. If the samples are properly preserved, the fluoride measurements will still be reliable even if carried out several months after sampling (This is important when samples are collected for quality checking in a reference laboratory). However, it is better to analyse the samples as soon as possible, because some fluoride might precipitate in the presence of other ions.

Field test kits

A large number of fluoride field kits based on colorimetric techniques are commercially available (Tables 4.3, 4.4). The final colour of a test paper or a water sample is either compared visually with a colour scale (semi-quantitative) or more precisely against standard measurements using a photometer (quantitative). The colouring reagent SPADNS (1,8-dihydroxy-2-(4-sulfophenylazo)naphthalene-3,6-disulfonic acid) is commonly used as a reagent for fluoride determination.

The ease of operation of the photometers makes them attractive for organisations without well-trained laboratory staff. Some photometers are designed for field use. A drawback of all fluoride field test kits is the low upper detection limit; water samples often have to be diluted, increasing the risk of miscalculation.

Table 4.3 *Overview of commercially available semi-quantitative fluoride field test kits (this list does not include all available kits, and it is not intended as an endorsement of any of the companies or products listed):*

Kyoritsu (Pack Test Fluoride)	Measuring range up to 8 mg/L (though quite imprecise for concentrations above 3 mg/L). Dilution of the water samples might be necessary (distilled water is required). Measuring time is 10 minutes. Instruction-Leaflet Where to buy: www.kyoritsu-lab.co.jp
Macherey-Nagel (Fluoride Test)	Measuring range up to 100 mg/L, though the accuracy is not very high. Measuring time is 5–7 minutes. The test kit contains hydrochloric acid but in a concentration that does not have to be declared as hazardous. Instruction-Leaflet Material-Safety-Data-Sheet Where to buy: www.mn-net.com
Merck (Aquamerck® Fluoride Test)	Detection range from 0.15–0.8 mg/L. Due to the low upper detection limit, dilution of the water samples is always necessary (distilled water is required). The test takes 12 minutes. Contains hazardous chemicals. Instruction-Leaflet Material-Safety-Data-Sheet Where to buy: www.merck-chemicals.com

Other semi-quantitative field test kits

Two field test kits are available in India; however, it might not be possible to ship these to other countries. The Orlab test kit (www.orlabindia.com) and the test kit are developed by the National Chemical Laboratory in Pune and are distributed by the Chem-In Corporation (www.chemicorp.com).

Fluoride analysis in the laboratory

Ion-selective electrodes (ISE) are widely used for fluoride analyses. TISAB (total ionic strength adjustment buffer) is added to the diluted or undiluted water sample, which is stirred during the measurement. The electropotential is measured with an ion-selective electrode. This analytical method requires more laboratory experience than a photometric method.

Table 4.4 *List of commercially available quantitative fluoride field test kits (this list does not include all available kits, and it is not intended as an endorsement of any of the companies or products listed):*

Hach (Fluoride Pocket Colorimeter) 	Hach offers a simple-to-use photometer for qualitative fluoride measurements using SPADNS reagent. The measuring range is 0.1–2 mg/L. The water sample often has to be diluted (distilled water is required). The SPADNS solution is hazardous. Please note that phosphate ions may interfere with measurements. Hach sells SPADNS either in small glass ampoules or in 1 L bottles. This method is practical, as the water can be directly sucked into the ampoules. On the other hand the ampoules are more expensive, are breakable and are bulky to transport. Operation-Manual Where to buy: www.hach.com
Wagtech/Palintest (Photometer 7100) 	The Photometer 7100 from Wagtech/Palintest can be used for measuring fluoride as well as other water-"quality" parameters. For fluoride, the measurement range is 0.1–1.5 mg/L. The water sample often has to be diluted (distilled water is required). Operation-Manual Reagents Material-Safety-Data-Sheet Where to buy: www.wagtech.com, www.palintest.com

The fluoride electrode has to be calibrated before use. The preparation of 3–8 standards with fluoride concentrations ranging between 0.05 mg/L and 2 mg/L is recommended. Dilution will be necessary if concentrations exceed 2 mg/L, so that sample concentrations lie within the calibrated range. Please note that high concentrations of dissolved aluminium in the sample can interfere with the ISE fluoride analysis. Suppliers of ISE provide manuals with information on calibration. A list of some suppliers and operation manuals is provided below:

- Hach   (www.hach.com)   Operation-Manual

- Metrohm   (www.metrohm.com)   Operation-Manual

- Mettler   (www.mt.com)   Operation-Manual

- Thermo Orion (www.thermo.com)   Operation-Manual

4.4 Detailed water analyses

The planning of a water survey can be restricted to the measurement of arsenic and fluoride concentrations, but measuring further parameters may be helpful:

- To identify other contaminants that may be present
- To interpret the causes of geogenic contamination
- To physically and chemically characterise the groundwater

A comprehensive analysis of water composition can be costly, as extensive laboratory analysis is involved. The usefulness of the information must therefore be weighed against the cost. Sometimes a parameter that was not initially considered may later become important. The most important parameters are presented here to aid the reader to decide which water-quality parameters to include in a survey.

The composition of groundwater is affected by a combination of processes (Appelo and Postma, 1993) including:

- Weathering, dissolution and precipitation of minerals
- Evaporation and evapotranspiration
- Decay of organic matter
- Selective uptake of ions by vegetation, e.g. potassium and phosphate
- Mixing and dilution
- Ion exchange

All these processes in combination affect ion concentrations in solution, i.e. water composition. In-depth hydrogeological studies would be necessary to fully understand water composition, but in the context of this handbook, it is sufficient to capture the waters that are characteristic for geogenic contamination. Here we focus on sum parameters (Table 4.5), major components (Table 4.6), redox parameters (Table 4.7) and minor components and contaminants (Table 4.8).

The sum parameters pH, Eh (redox potential) and EC (electrical conductivity) can be measured with portable instruments in the field and give a general indication of water quality (Table 4.5). Redox potential, and the related parameter, dissolved oxygen, are liable to atmospheric contamination, making it very important to avoid contact between samples and air.

Major ion chemistry, together with a knowledge of sum parameters, provides an understanding of the type of water that the measurement of the sum parameters alone does not provide. Some examples are:

- The chemical composition of a groundwater with a pH value of 7 to 8 and with calcium as the predominant cation may be controlled by the mineral calcite ($CaCO_3$). In the presence of calcium, elevated concentrations of fluoride would not be expected.

- The chemical composition of a groundwater with a pH value of around 5 to 6 and a low ion content may indicate a crystalline rock environment, for example, granite. Fluoride content could be elevated.
- A neutral to alkaline groundwater (pH range 7 to 8 or above) with high ion content is indicative of arid conditions. High evaporation rates can lead to an increase in salinity (particularly $NaHCO_3$). Under these conditions, calcite ($CaCO_3$) tends to be insoluble, resulting in a low calcium content. Depending on the composition of the source rock, geogenic contaminants might be present.

Table 4.5 Description of sum parameters

Parameter	Description
pH	pH is a measure of the activity of free protons (H+) in solution. It is a number on a logarithmic scale from 0 to 14, on which a value of 7 represents neutrality. Values of pH <7 indicate increasing acidity, while values of pH >7 indicate increasing alkalinity. Each unit of change represents a tenfold change in H+ activity. The definition of pH is: $$pH = -\log \{H+\}$$ where {H+} is the activity of protons in moles per litre (mol/L).
Electrochemical potential (Eh) Unit: mV	Eh is a measure of the reducing/oxidising (redox) state of the water. Eh values in natural waters can range from -400 mV (highly reducing) to +800 mV (highly oxidising). Positive Eh values indicate oxidising conditions with dissolved oxygen present. Negative values indicate that conditions are reducing (low in dissolved oxygen) and predominated by reduced chemical species, such as Mn(II) and NH4+ in mildly reducing conditions and dissolved iron (Fe(II)), sulphide (S(-II)) and methane (CH4) under highly reducing conditions. Arsenic is often found in highly reducing environments. The measurement of Eh in the field can be very imprecise. A more reliable alternative is to determine dissolved oxygen content (and concentrations of reduced species). Dissolved oxygen can be measured potentiometrically with an electrode.
Electrical conductivity (EC) Unit: mS/cm, µS/cm	EC is a measure of Total Dissolved Solids (TDS). The approximate relationship between EC and TDS is $$EC \ (mS/cm) \approx TDS \ (mg/L) / 640$$ A high electrical conductivity therefore indicates high ion concentrations. EC values in drinking water usually range from 0.05 to 0.5 mS/cm or ≈30–320 mg/L TDS. Fluoride is often found in groundwater in arid climates and can be associated with high EC.

A groundwater with negative redox potential or no measureable oxygen may contain reduced species (Table 4.7) irrespective of the major ions present. An elevated dissolved organic carbon content might be expected. Under these conditions, soluble reduced

arsenic might be present.

The quality of the measurements can be verified by comparing the sum of the cations with the sum of the anions. As aqueous solutions cannot be charged, the two should be equal ("charge balance"). If the calculation shows an excess positive or negative charge (i.e. too few cations or anions), this indicates that the analysis is incorrect or that a parameter is missing. Care has to be taken during the calculation that the units are the same. For example, all units should be measured in milligrams per litre (mg/L). For the charge balance, values then need to be converted to mmol/L by dividing the values in milligrams per litre (mg/L) by the molecular weight of the respective ions. The final step is to multiply the millimolar concentration by the respective charge (z) of the ion, which gives the milli-equivalents of charge per litre (meq/L) for a particular ion. The total charge of the cations and anions is obtained by summing the meq/L as shown below:

Σ cations (meq/L) = Σ cation concentration (mmol/L) $\times$ z (charge)

Σ anions (meq/L) = Σ anion concentration (mmol/L) $\times$ z (charge)

Mole units

One mole is equal to 6.02×10^{23} atoms or molecules of a chemical substance. This number is derived from the number of atoms in 12 grams of carbon (^{12}C).

The mole is widely used in chemistry instead of units of mass or volume, because it is a convenient way to express the number of atoms, molecules or other units of reactants or products in chemical reactions. For example, one mole of calcium (Ca^{2+}) will react with 2 moles of fluoride (F^-) to form one mole of fluorite (CaF_2).

The values represent the equivalents of charge of cations and anions, which – as stated before – should be equal. Agreement to within 10% is excellent. If values differ by more than 20%, the samples must be re-analysed or a missing factor sought. Organic acids can make a significant contribution to the anionic charge in surface and contaminated waters. NOTE: The ion balance is usually limited to the major ions (Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, SO_4^{2-}, HCO_3^-, Table 4.6). For most groundwater samples, this is sufficient.

The redox potential is of particular significance in arsenic-contaminated waters, as arsenic is a redox-sensitive element. The measurements of Eh can be substantiated by measuring the concentrations of redox-sensitive species (Table 4.7). The cause of reducing conditions is generally the oxidation of organic carbon (as may be found in young organic-rich sediments) by microbes. The microbes use different oxidising agents in a specific order: oxygen, nitrate, manganese oxides, then iron oxides and sulphate. These are themselves reduced.

Table 4.6 *Major ions found in water samples*

Cations		Anions	
Sodium	Na^+	Chloride	Cl^-
Potassium	K^+	Sulphate	SO_4^{2-}
Magnesium	Mg^{2+}	Bicarbonate	HCO_3^-
Calcium	Ca^{2+}		
Also (representing influence from agricultural activities and the mineralisation of organic carbon):			
Ammonium	NH4+	Nitrate	NO_3^-
		Phosphate	PO_4^{3-}
Optional			
Borate	BO_3^{3-}	Borate can be associated with volcanic rocks and hydrothermal activity	
Aluminium	Al_3^+	Solubility limited in neutral pH by the precipitation of $Al(OH)_3$ (solid)	
Silicic acid	H_4SiO_4	Solubility limited to a maximum of 28 mg/L by precipitation of H_4SiO_4 (solid)	

Total organic carbon (TOC) or dissolved organic carbon (DOC) content can be an indicator of these processes. Oxic groundwater generally contains ≤ 2 mg DOC/L. It should also be noted that dissolved ammonium (NH_4^+) is often associated with biodegradation processes and may result from the microbial reduction of nitrate.

Table 4.7 *Redox species*

Order	Parameter		Description
1	reduced manganese	Mn^{2+}	Solutions that only contain manganese are generally not reducing enough to release reduced arsenic.
2	reduced iron	Fe^{2+}	Arsenic is generally found in association with reduced iron, but not sulphide (as insoluble arsenic-sulphides are formed). These species are oxidised rapidly in the presence of oxygen and are unstable. Appropriate sampling and preservation procedures must be followed.
3	sulphide	S^{2-}	

Table 4.8 Minor and potential contaminant species

Ions	Most frequent chemical form	Description
Possible geogenic contaminants		
Fluoride	F^-	These species may sometimes be found in high concentrations where arid conditions coincide with rocks/sediments containing elevated contaminant concentrations.
Arsenate	AsO_4^{3-}	
Uranyl	UO_2^{2+}	These species are negatively charged and their solubility controlled by calcium. In sodic waters dominated by $NaHCO_3$ with low calcium content, these species can be soluble. (Note that arsenic is present in oxidised form).
Borate	BO_3^{3-}	
Molybdate	MoO_4^{2-}	It is more common to find elevated fluoride, borate and perhaps arsenate and uranyl concentrations.
Selenate	SeO_4^{2-}	
Vanadate	VO_4^{3-}	
Arsenite	$As(OH)_3$	This reduced arsenic species is soluble.
Chromate	CrO_4^{2+}	Chromate is derived from the oxidation of chromium released from ultramafic rocks.
Heavy metals		
Copper	Cu^{2+}	These heavy metals are generally associated with anthropogenic activities such as mining, industrial activities, airborne contamination to soils etc. Other than in very acidic conditions (e.g. acid mine drainage) their solubility is limited to the low microgram per litre range.
Lead	Pb^{2+}	
Cadmium	Cd^{2+}	
Zinc	Zn^{2+}	
Mercury	Hg^+	

The choice of trace metals and metalloids to analyse is dependent on the type of geogenic contamination (Table 4.8).

- For reducing conditions where groundwater may be contaminated with arsenic, it is sufficient to quantify arsenic and possibly iron, manganese and sulphide (noting that sulphide would indicate the absence of arsenic). Arsenic is one of the very few elements (including manganese and iron) that is more soluble in reduced form than in its oxidised state.

- Where fluoride might be expected, usually under oxidising conditions, the analysis of further potential contaminants, including arsenic and uranium, would be beneficial.

Sampling and the preservation of the water samples for the determination of minor and contaminant species should follow guidelines provided by the laboratory (APHA, 2012). The measured values are assessed by comparing them with the WHO Drinking-Water Guideline values or with national standards where applicable.

References and further reading

APHA, American Public Health Association. (2012) Standard methods for the examination of water and wastewater, 22nd Edition. American Water Works Association.

Appelo C.A.J., Postma D. (2005) Geochemistry, groundwater and pollution, 2nd Edition. A.A. Balkema, Rotterdam.

Fawell J., Bailey K., Chilton J., Dahi E., Fewtrell L., Magra Y. (2006) Fluoride in drinking-water. Chapter 6: Analytical Methods. World Health Organization. IWA Publishing, London, 134. www.who.int/water_sanitation_health/publications/fluoride_drinking_water/en/

George C.M., Zheng Y., Graziano J.H., Bin Rasul S., Hossain Z., Mey, J.L., van Geen A. (2012) Evaluation of an arsenic test kit for rapid well screening in Bangladesh. Environ. Sci. Technol. 46(20), 11213−11219.

Hussam A., Alauddin M., Khan A.H., Rasul S.B., Munir A.K.M. (1999) Evaluation of arsine generation in arsenic field kit. Environ. Sci. Technol. 33(20), 3686–3688.

Jakariya M., Vahter M., Rahman M., Wahed M.A., Hore S.K., Bhattacharya P., Jacks G., Persson L.Å. (2007). Screening of arsenic in tubewell water with field test kits: Evaluation of the method from public health perspective. Sci. Total Environ. 379(2–3), 167–175.

Kinniburgh D.G., Kosmus W. (2002) Arsenic contamination in groundwater: some analytical considerations. Talanta 58(1), 165–180.

Langmuir D. (1997) Aqueous environmental geochemistry. New Jersey: Prentice Hall.

Rasmussen L., Andersen K.J. (2002) Chapter 2: Environmental health and human exposure assessment. United Nations synthesis report on arsenic in drinking water. World Health Organization, Geneva. www.who.int/water_sanitation_health/dwq/arsenic3

Rosenboom J.W. (2004). Not just red or green: An analysis of arsenic data from 15 upazilas in Bangladesh. Dhaka: DPHE/APSU/UNICEF.

Spear J.M., Zhou Y.M., Cole C.A., Xie Y.F. (2006). Evaluation of arsenic field test kits for drinking water analysis. J. Am. Water Works Assoc. 98(12), 97–105.

Steinmaus C.M., George C.M., Kalman D.A., Smith A.H. (2006) Evaluation of two new arsenic field test kits capable of detecting arsenic water concentrations close to 10 microg/L. Environ. Sci. Technol. 40(10), 3362–3366.

Sundaram B., Feitz A.J., deCaritat P., Plazinska A., Brodie R.S., Coram J., Ransley T. (2009) Groundwater sampling and analysis – A field guide. GeoScience Australia, No. 27, GeoCat 68901, 295. www.ga.gov.au/image_cache/GA15501.pdf

Trang P.T.K., Berg M., Viet P.H., Mui N.V., van der Meer J.R. (2005). Bacterial bioassay for rapid and accurate analysis of arsenic in highly variable groundwater samples. Environ. Sci. Technol. 39(19), 7625–7630.

UNICEF (2008a). Water quality handbook. New York: United Nations Children's Fund.

UNICEF (2008b). Arsenic primer – Guidance for UNICEF country offices on the investigation and mitigation of arsenic contamination. United Nations Children's Fund, New York.

Van Geen A., Cheng Z., Seddique A.A., Hoque M.A., Gelman A., Graziano J.H., Ahsan H., Parvez F., Ahmed K.M. (2005). Reliability of a commercial kit to test groundwater for arsenic in Bangladesh. Environ. Sci. Technol. 39(1), 299–303.

WHO, World Health Organization (1997) Water Sampling and Analysis. In: Volume 3 - Surveillance and control of community supplies, WHO Guidelines for Drinking-Water Quality, 2nd edn., 51–72. World Health Organization, Geneva. www.who.int/water_sanitation_health/dwq/gdwq2v1/en/index2.html

WHO, World Health Organization (2011) Guidelines for drinking-water quality, 4th edition. World Health Organization, Geneva. www.who.int/water_sanitation_health/publications/2011/dwq_guidelines/en/index.html