Part B
Identifying specific chemicals

4 Naturally occurring chemicals

4.1 General

There are a number of sources of naturally occurring chemicals in drinking-water. All natural water contains a range of inorganic and organic chemicals. The inorganic chemicals derive from the rocks and soil through which water percolates or over which it flows; whereas the organic chemicals derive from the breakdown of plant material or from algae and other microorganisms growing in the water or on sediments. Most of the naturally occurring chemicals for which guidelines have been developed or which have been considered for guideline development are inorganic. Many of the health problems caused by chemical constituents in water supplies throughout the world are due to chemicals of natural origin rather than those from human-made pollution.

4.1.1 Approach to dealing with naturally occurring chemicals

The approach to dealing with naturally occurring chemicals will vary according to the nature of the chemical and the source. For inorganic contaminants, which come from rocks and sediments, it is important to screen possible water sources to determine whether the source is suitable for use or whether it will be necessary to treat the water to remove chemical contaminants of concern along with microbial contaminants. Where a number of different sources of drinking-water are available, dilution of a body of water containing high levels of a contaminant with one containing much lower levels may achieve the desired result. However, in circumstances where there are many small local water supplies, often based on hand pumps, dealing with naturally occurring chemicals may present considerable difficulties, especially if alternative supplies are very limited.

Where possible, authorities should consider which areas are likely to be affected by the chemicals of highest concern and determine how concentrations can be minimized (e.g. by determining the best depth to sink tubewells to avoid contamination). In situations where there are significant concentrations of natural contaminants of concern, it may be appropriate to encourage community-based action to minimize concentrations (e.g. through local treatment or sharing water from wells with the lowest concentrations).

4.1.2 Aesthetic effects

Not all natural constituents are of direct concern for health — some may impact on the aesthetic quality of drinking-water by affecting the taste or odour, or by causing discoloration. Chemicals most commonly causing discolouration are iron and manganese, which are considered to be a high priority for consideration because consumers may find water contaminated with these metals unacceptable and may turn to other sources of drinking-water that may be microbiologically unsafe. High concentrations of sulfate, in association with cations, such as magnesium, may have a laxative effect on people not accustomed to the water. Similarly, chloride in high concentrations can contribute to a salty taste, although neither sulfate nor chloride is harmful in moderate concentrations.

4.1.3 Common health hazards

A number of the most important chemical contaminants (i.e. those that have been shown to cause adverse health effects as a consequence of exposure through drinking-water) fall into the category of naturally occurring chemicals. These are arsenic, fluoride, selenium and, in some circumstances, nitrate. In many parts of the world, the long-term consumption of hazardous, naturally occurring chemicals such as arsenic and fluoride, particularly through drinking groundwater, is a major cause of chronic disease, disablement and premature death.

High concentrations of naturally occurring chemicals generally occur where water has been in contact with rocks or soil for long periods under certain conditions. Such conditions, which generally occur in aquifers where groundwater flow rates are low, are more likely to be found in arid and semiarid regions. To a large extent, health problems caused by naturally occurring chemicals are associated with the use of groundwater as a source of drinking-water in these regions, where there is often no feasible alternative to groundwater. In addition, some springs and (during dry periods) most of the water in rivers may originate from groundwater discharge. Thus, surface water resources for drinking-water supply may also contain high concentrations of naturally occurring chemicals. The high fluoride concentrations found in some parts of India are an example of surface waters being contaminated by a naturally occurring chemical from groundwaters.

It is important that the geological conditions where chemicals are likely to occur at toxic levels are well understood, so that water sources can be located in safe areas, or treated to remove toxic constituents. This is particularly important when sources are being considered for use for drinking-water.

4.2 Environmental factors affecting inorganic constituents in water

Whether or not a naturally occurring chemical constituent in drinking-water is of concern depends on the geology and on the physical and chemical conditions affecting solubility. Climate also has an important role in affecting the way that rocks are broken down and the extent to which minerals are leached into rivers or groundwater.

Table 4.1 lists environmental factors affecting the distribution of naturally occurring toxic chemicals in water and soil. It gives the geological environments in which particular chemicals are most likely to be present in water supplies. An example is the presence of hot springs, which are associated with volcanic activity and may contain very high concentrations of natural chemicals of concern. Such springs can drain to waters that are used as drinking-water sources.

Table 4.1 Environmental factors affecting the distribution of naturally occurring toxic chemicals in water and soil

Geological setting[1]	Source of water	Climate	Naturally occurring toxic chemicals that may be found in water	Land uses that may increase concentrations of possible constituents of water	Additional chemicals that may be released from natural sources, due to land uses given in previous column
Granite-like igneous rocks (e.g. granites, pegmatites)	Groundwater from fractured bedrock and from regolith overlying bedrock	Humid, arid	As, Ba, B, F, Rn, U; concentrations of B, F, U likely to be higher in drier areas	Irrigated agriculture, mining	B, Mo, Pb
Alkaline igneous and volcanic rocks	Groundwater from fractured bedrock and from regolith overlying bedrock	Humid, arid	As, Ba, B, F, Rn, U; very high concentrations of F occur in groundwater in these rock types in East Africa	Irrigated agriculture, mining	Mo, Pb
Basalts and magnesium-rich igneous and volcanic rocks (e.g. serpentine, talc-rich rocks)	Groundwater from fractured bedrock and from between lava flows	Humid, arid	SO_4^{2-}	Drainage, mining, groundwater pumping	Co, Cr, Ni
Contact metamorphic rocks	Groundwater from fractured bedrock	Humid, arid	Mo, U, Rn	Drainage, mining, groundwater pumping	Other metals, depending on mineralization
Iron-rich sedimentary rocks (e.g. sandstones, siltstones)	Groundwater from porous rock, fractures	Mainly arid	As, Se, Co	Irrigated agriculture	Ni
Manganese-rich sedimentary rocks	Groundwater from porous rock, fractures	Mainly arid	As, Ba, Mo	Irrigated agriculture	Co, Mo, Ni
Phosphorus-rich sedimentary rocks (limestones, mudstones, siltstones)	Groundwater from porous rock or from karst features (limestone, dolomite and calcrete)	Mainly arid	F, U, Rn	Irrigated agriculture	Mo, Pb
Black shales	Groundwater from fractured bedrock	Humid, arid	As, Mo, Sb	Drainage, mining, groundwater pumping	Ni, Pb

Geological setting[1]	**Source of water**	**Climate**	**Naturally occurring toxic chemicals that may be found in water**	**Land uses that may increase concentrations of possible constituents of water**	**Additional chemicals that may be released from natural sources, due to land uses given in previous column**
Sulfide mineralization	Groundwater from fractured bedrock	Humid, arid	Al, As, Co, Cd, Cr, Pb, Mo, Ni, Sb, Se	Drainage, mining, groundwater pumping	
Gold mineralization	Groundwater from fractured bedrock	Humid, arid	As	Drainage, mining, groundwater pumping	Hg
Alluvial plains and deltas, mainly in coastal areas (including buried channels)	Groundwater from extensive alluvial aquifers (the most significant source of water in many areas of the world)	Humid, arid	As, Se, U	Drainage, groundwater pumping	Co, Cd, Cr, Pb, Mo, Ni, Sb, SO_4^{2-}
All	Groundwater from fractured bedrock, alluvial aquifers or calcrete	Arid	NO_3 — high concentrations may occur where there are leguminous plants (e.g. *Acacia* species), and widespread termite activity		
All	Surface water	Humid	Cyanobacterial toxins	Agriculture	
All	Groundwater from organic rich sediments or stagnant surface water bodies	Humid	NH_3	Intensive animal husbandry, agriculture	
All	Groundwater from fractured bedrock and surface drainage	Humid	I — very low concentrations occur in areas of very high rainfall or very high relief		
All	Surface runoff and groundwater in seasonally submerged soils	Humid	As	Agriculture involving flooding of fields (e.g. rice paddies), aquaculture ponds	

[1] Geological association of inorganic constituents based on data presented by Rose et al. (1979)

4.3 Data sources

Authorities at the national, regional or local level may develop water supply systems. Where the water supply developer has not established a comprehensive profile of chemicals in water sources (which is often the case), it may be appropriate to seek additional information from other sources. In many countries, government geological survey departments and the geology departments of universities have information on naturally occurring chemicals in the soil and on the risk of these chemicals being found in water sources. Mining companies can also be an important source of geological information. The presence of a significant local mining industry should be taken as a sign that extra caution is required with regard to water quality of groundwater and, in some cases, surface water. All relevant sources of data and information should be consulted.

4.4 Indicator parameters and simple tests

Indicator parameters are measurements that give information about the chemical condition of groundwater or a surface water body. These parameters are easily measured in the field and are valuable in guiding further investigations. For example, pH is an important indicator of the ability of water to dissolve minerals from rocks and soil; dissolved oxygen concentration indicates whether the water is aerobic or anaerobic; and redox potential can indicate whether or not the water is reducing in nature. The results of measurements of such parameters can indicate the potential presence of hydrogen sulfide or dissolved iron and manganese. An example of a very simple test would be to shake a water sample in a bottle to aerate it — if the water becomes brown, this would indicate the presence of dissolved iron or manganese in a water that was anaerobic.

4.5 Guidance on selecting relevant chemicals

The facilities and resources available may be sufficient to allow a comprehensive analytical assessment of the inorganic constituents in a source.[1] However, such an assessment is often not possible; in which case, the following sections and Table 4.1 indicate the naturally occurring chemicals that should be considered in setting priorities for chemicals in drinking-water sources.

Arsenic, fluoride, selenium and, in certain circumstances, nitrate should be given high priority. As noted in Chapter 2, the presence of these chemicals in drinking-water has been shown to cause health effects. These chemicals are relatively common in water supplies around the world in both developing and developed countries; therefore, they should be assumed to be potentially present, and consideration should be given as to whether they are actually present in concentrations of concern.

[1] Guidance on analytical methodology to determine the inorganic constituents and their concentrations in drinking-water is outlined in the WHO *Guidelines for Drinking-water quality* (WHO, 2004).

4.5.1 Catchment information

If groundwater is being used, it is important to know where wells and tubewells are located, because there may be localized areas where chemicals in the groundwater are of concern. Also, groundwater may be stratified, with water at different depths having different chemical profiles. In such cases, it is important to understand the potential variation in chemicals caused by the stratification.

When there is no geological information for a water supply catchment, or there is no information relating the siting of wells and tubewells and surface sources to the geology of the catchment, chemicals of natural origin (i.e. arsenic, fluoride, selenium, nitrate, iron and manganese) should be regarded as being present in the water.

Appendix 1 of this document, and the WHO *Guidelines for Drinking-water Quality* (WHO, 2004), contain additional comments on individual chemicals.

Box 4.1 summarizes the main risk factors associated with the catchment.

Box 4.1 Risk factors — catchment information

Chemicals such as arsenic, fluoride, selenium or nitrate present in unusually high concentrations in rocks, soil or groundwater in a catchment area.

4.5.2 Acidity and potential acidity

A low pH is likely to lead to greater leaching of inorganic constituents from rocks and soil, thereby increasing the probability that naturally occurring inorganic substances will be present at higher concentrations than would otherwise be expected. When groundwater or surface water used for water supply has a pH of less than 5.5 and there are nearby mineral deposits containing metals, it would be appropriate to consider those metals in particular. Low pH is widely encountered in groundwater from the weathered crystalline basement rocks that provide water supplies for villages and small towns in much of sub-Saharan Africa and peninsula India; thus, mobilization of iron and manganese is to be expected, and indeed is frequently observed, in these areas.

Box 4.2 summarizes the main risk factors associated with acidity and potential acidity.

Box 4.2 Risk factor — acidity and potential acidity

The pH of groundwater or surface water used for a water supply is less than 5.5.

4.5.3 Algal toxins

Cyanobacteria (also known as blue–green algae) occur widely in lakes, reservoirs, ponds and slow-flowing rivers. Many species are known to produce toxins, a number of which are of concern for health. Several different cyanotoxins, varying in structure, may be found within cells or released into water. There is wide variation in the toxicity of known cyanotoxins (including among different varieties of a single toxin, such as the microcystins), and it is likely that there are further cyanotoxins, yet to be discovered.

Health hazards from algal toxins are primarily associated with overgrowth (bloom) events. Algal blooms may develop rapidly and be of short duration; they are generally seasonal and are frequently associated with the presence of nutrients, particularly phosphate. Levels of nutrients are often increased by human activity (see also chapters 5, 6 and 7), increasing the likelihood of cyanobacterial blooms.

Analytical standards are frequently not available for algal toxins, and analysis of the toxins is slow and difficult (although rapid methods are becoming available for a few of these toxins, such as the microcystins). Therefore, the preferred approach is to monitor source water for evidence of blooms, or bloom-forming potential, and to increase vigilance where such events occur. Chemical analysis of cyanotoxins is not the preferred focus of routine monitoring, and it is used primarily in response to bloom events.

Various actions can be used to decrease the probability of bloom occurrence, and some effective treatments are available for removal of cyanobacteria or their toxins.

Box 4.3 summarizes the main risk factors associated with algal blooms.

Box 4.3 Risk factor — occurrence of algal blooms

High concentrations (blooms) of cyanobacteria (blue–green algae), such as *Microcystis* sp. and *Anabaena* sp. occur in slow moving or still surface waters with a moderate to high concentration of nutrients, particularly phosphorus. Blooms can occur in both deep and shallow waters, but are more usual in relatively still periods with a moderate to high light intensity. It is difficult to predict whether a bloom will produce toxins, but experience in a number of countries has shown that more than 50% of blooms will generally produce toxins at some stage.

4.6 References

Rose AW, Hawkes HE, Webb JS (1979). *Geochemistry in mineral exploration*. Academic Press, London.

WHO (2004). *Guidelines for drinking-water quality*, 3rd ed., World Health Organization, Geneva.