

# Groundwater geochemistry and health: an overview

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**Abstract:** The natural geological and geochemical environment, in addition to providing beneficial mineral content and bioessential elements to groundwaters, may also give rise to undesirable or toxic properties through a deficiency or an excess of various elements. In this paper the controls on the release of toxic elements are considered together with the geochemical conditions that give rise to excess and deficiency. Many studies have pointed towards an inverse correlation between water hardness and cardiovascular disease and the associated mobility of metals in soft waters may also be a contributory factor. Under acidic conditions Al and Be as well as other metals may be released, whilst changes in redox conditions as well as pH will affect the mobility of Fe, Mn and As in particular. Some potentially toxic elements such as Ba and F are usually held at acceptable concentrations in groundwaters by the respective solubility controls of barite and fluorite; quality problems arise from these elements when groundwaters contain respectively low sulphate or low calcium concentrations. Deficiencies of Se and I (as well as F) in groundwater are related to the low geochemical abundance of these elements in certain environments. In the context of groundwater pollution it is important first to define the natural baseline concentrations of key elements of health importance.

The provision of safe drinking water as well as water of acceptable quality remain prime targets for both advanced and developing countries. By far the greatest water quality problem in developing countries is the prevalence of water-borne diseases, especially gastro-enteritis which is related to faecal pollution and inadequate hygiene (Tebbutt 1983). Such problems are usually related to poor well siting and construction as well as to insufficient water and water distribution. Pollution from agricultural chemicals, for example nitrate and pesticides, once considered a problem restricted to rich nations, is now also a rapidly growing problem in developing countries.

In addition to the anthropogenic sources, the natural baseline geochemistry of groundwaters and surface waters resulting from interaction with rocks, also creates widespread health and acceptability problems in many parts of the world, mainly on a regional scale. The concentrations of naturally occurring mobile elements often exceed those recommended as the maximum for potable waters, and/or their concentrations may exceed limits of general acceptability for domestic use.

These natural problems of groundwater have been exacerbated during the past two decades by the widespread installation of rural groundwater supplies. Well or borehole water, replacing otherwise unhygienic surface supplies, has all too often been developed in places where specific geochemical conditions may have led to excessive concentrations of toxic or undesirable elements (As, Cr, Fe, Mn, Sb, Al or F).

In the present paper, those elements considered by international organizations to be toxic in natural waters are reviewed with regard to their mobility under various hydrogeochemical conditions. Elements which may give rise to health problems due to their deficiency in water supplies are also considered, as are those elements such as iron which present problems of acceptability in water supplies. It is not possible to review the vast numbers of studies worldwide comprehensively, but rather a selective overview of the current problems is presented using examples mainly from developing countries as a key to future needs, especially work of a remedial or preventive nature.

## Essential and non-essential elements

Nearly all natural waters contain traces of most of the chemical elements but often at extremely low or unquantifiable concentrations. The typical abundance of the elements in natural waters at pH 7 is summarized in Fig. 1. Nine major species ( $\text{HCO}_3^-$ , Na, Ca,  $\text{SO}_4$ , Cl,  $\text{NO}_3^-$ , Mg, K and Si) invariably make up over 99% of the solute content of natural waters. The abundance of minor and trace elements, under 1% of the total, can change significantly from the concentrations shown depending on geochemical conditions. In particular a pH decrease of one unit may lead to an increase of more than one order of magnitude in the concentration of certain metals. A change from oxidizing to reducing conditions may have a similar effect on elements such as iron.

# TRACE ELEMENTS IN GROUNDWATER AND THEIR SIGNIFICANCE IN TERMS OF HEALTH AND ENVIRONMENTAL PROTECTION

## CONCENTRATIONS IN DILUTE, OXYGENATED GROUNDWATER AT pH 7

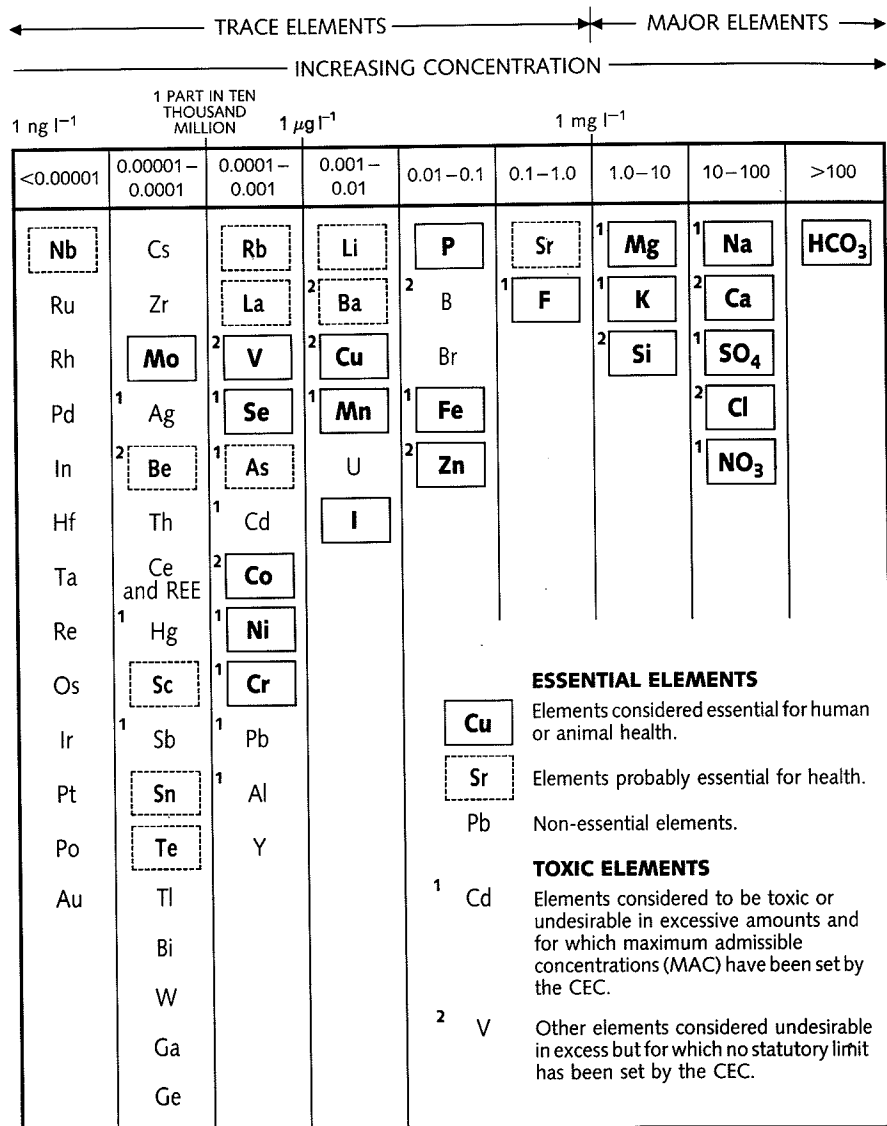


Fig. 1. Major and trace elements in groundwater and their significance in terms of health. Concentrations shown are those typical of dilute oxygenated groundwater at pH 7. Elements outlined are those considered to be essential (or probably essential) for health. Those elements which have guideline or statutory limits set by the CEC or WHO (see Tables 1, 2) are indicated.

Table 1. Chemicals of health significance in drinking water

	WHO (1993) guideline maxima (mg l <sup>-1</sup> )	CEC (1980) guideline values (mg l <sup>-1</sup> )	CEC (1980) max. admissible concentrations (mg l <sup>-1</sup> )
Antimony (Sb)	0.005 (P)		0.010
Arsenic (As)	0.01 (P)		0.050
Barium (Ba)	0.7	0.1	
Beryllium (Be)	NAD		
Boron (B)	0.3	1.0	
Cadmium (Cd)	0.003		0.005
Chromium (Cr)	0.05 (P)		0.050
Copper (Cu)	2 (P)	0.1	
Fluoride (F)	1.5		1.5*
Lead (Pb)	0.01		0.05
Manganese (Mn)	0.5 (P)	0.02	0.05
Mercury (Hg) total	0.001		0.001
Molybdenum (Mo)	0.07		
Nickel (Ni)	0.02		0.05
Nitrate (NO <sub>3</sub> )	50	25	50
Selenium (Se)	0.01		0.01
Uranium (U)	NAD		

Data from WHO (1993) with values from CEC (1980) where appropriate. P, provisional value; NAD, no adequate data to permit recommendation of a health-based guideline value; \* climatic conditions, volume of water consumed and intake from other sources should be considered when setting national standards.

Table 2. Substances in drinking water that may give rise to complaints from consumers

	WHO (1993) guideline maxima (mg l <sup>-1</sup> )	CEC (1980) guideline values (mg l <sup>-1</sup> )	CEC (1980) max. admissible concentrations (mg l <sup>-1</sup> )
Aluminium (Al)	0.2	0.05	0.2
Ammonium (NH <sub>4</sub> )	1.5	0.05	0.5
Calcium (Ca)		100	
Chloride (Cl)	250	25	
Sulphide (H <sub>2</sub> S)	0.05		
Iron (Fe)	0.3	0.05	0.2
Magnesium (Mg)		30	50
Potassium (K)		10	12
Sodium (Na)	200	20	150*
Sulphate (SO <sub>4</sub> )	250	25	250
Zinc (Zn)	3	0.1	5

Data from WHO (1993) compared where appropriate with CEC limits. \*More than 80% compliance over a period of 3 years.

Those elements currently considered to be essential for human health and metabolism (Moynahan 1979) are also indicated in Fig. 1, together with elements which are considered to have harmful effects if present in water supplies above certain limits (CEC 1980; World Health Organisation 1993). The currently agreed limits for inorganic constituents of significance in relation to health are summarized in Table 1. It should be noted that for some elements (e.g. Be, U) no agreed limit has been reached despite their known health effects. Some bioessential

elements (e.g. F and Se) may also have a harmful effect if present above certain limits. Those elements that may give rise to acceptability problems are summarized in Table 2; some of the limits quoted in both tables have qualifications placed on them for which reference to the original text is recommended.

### Geochemical baseline conditions

The composition of surface waters and shallow groundwaters will closely reflect the local

geology. Reactions between rainwater and bedrock over a timescale of days or months during percolation, followed by emergence as springs or as inputs to the water table, give the groundwater its essential mineral character. During this process the physical properties of the bedrock and hence mechanisms of flow (i.e. by intergranular or via fractures) will be of importance. The extent of reaction with the host rock will be controlled by the residence times of the water and the primary mineralogy of the aquifer. In this context the initial concentrations of  $\text{CO}_2$  in the soil will determine the amount of reaction of carbonate or silicate minerals that takes place in the aquifer. The geological map may be used to highlight the distribution of carbonate (infinite buffering), from non-carbonate (base-poor) terrains which offer poor buffering capacity and can give rise to acid waters and mobilization of metals harmful to health (Lucas & Cowell 1984; Edmunds & Kinniburgh 1986).

In contrast to shallow environments where the baseline chemistry closely mirrors the surface geology, deeper groundwaters can undergo significant changes in the baseline conditions along flow lines with increasing residence times (Edmunds *et al.* 1987). It is therefore necessary to consider the possible changes taking place not only between areas with different geology but also the sequential changes taking place within an aquifer. Classic examples of health effects relating to differences in water chemistry along flow gradients in aquifers may be found. In the confined Lincolnshire Limestone aquifer in the UK (Lamont 1959), for example, a zonation in dental health could be identified in relation to groundwater use. Once recognized as a fluoride-related problem, blending of high and low F-waters was adopted as a means of eradicating fluorosis and of providing an optimum F concentration in water supplies.

Health and acceptability problems are really only important for a small number of elements and it is convenient to consider these under categories relating to geochemical controls.

### Natural water quality problems

#### Water hardness

It has long been suspected that a causal link exists between water hardness (i.e. principally dissolved Ca and Mg) and cardiovascular disease (Gardner 1976; NAS 1977; Masironi 1979) although water is only one of many factors that might be involved (Shaper *et al.* 1981). In Britain, detailed studies were carried out during the 1960s and 1970s, especially in towns which

had experienced changes in the hardness of their water supplies (Lacey & Shaper 1984). These results supported the hypothesis of a weak causal relationship between drinking water hardness and mortality, especially in men, from cardiovascular disease. More recently the British Committee on Medical Aspects of Food Policy (COMA 1994) as part of a wider review of the nutritional aspects of cardiovascular disease, also found a weak inverse relationship between water hardness and cardiovascular disease mortality, but noted that the size of the effect was small and most clearly seen at water hardness levels below  $170 \text{ mg l}^{-1}$  (as  $\text{CaCO}_3$ ). It was also pointed out (by COMA) that further studies since the 1970s had not altered the balance of evidence for the association and that the explanation for the association remained unknown. Other studies reviewed by Foster (1992) have shown that the relationship between water hardness and heart disease is not straightforward and that the other factors involved (e.g. diet, exercise, smoking) are likely to be more important. On balance, it is probable that hardness may only be a general pointer towards other agents connected with the disease. Several hypotheses for the link with water have been proposed including: (1) potential for Ca and/or Mg to protect against some forms of cardiovascular disease; (2) that some trace elements, more prevalent in hard water, may be beneficial; (3) many metals are more soluble in soft water and hence may promote cardiovascular disease.

From the geochemical viewpoint it is considered that more studies are needed that investigate the ratio of Mg to Ca in natural waters in relation to cardiovascular disease, rather than total hardness alone as a factor. Elevated sodium in drinking water is also implicated in contributing to high blood pressure (Calabrese & Tuthill 1981) and it seems important that further work in this area should consider not only sodium (and total mineralization) but also the ratio of Na to other competing ions, especially potassium.

Fewer studies have been carried out in developing countries but Dissanayake *et al.* (1982) for example found a similar negative correlation between water hardness and various forms of cardiovascular disease and leukaemia in Sri Lanka. Links between water hardness and endemic goitre have also been suggested (Day & Powell-Jackson 1972).

#### Acid water and mobilization of toxic metals

Acid groundwater may result either from natural processes such as flow through non-

in the hardness of their (e.g. Shaper 1984). These hypotheses of a weak relationship between drinking water hardness and cardiovascular disease, especially in men, from a wider review of the relationship between water hardness and cardiovascular disease morbidity and mortality, as seen at water hardness (e.g.  $\text{CaCO}_3$ ). It was also suggested that further studies on the effect of altered water hardness on the balance of mineralization and that the relationship remained unexplained by Foster (1992). The relationship between water hardness and cardiovascular disease is not straightforward. Factors involved (e.g. calcium, magnesium) are likely to be more complex, it is probable that the general pointer towards a link with the disease. Several studies with water hardness have been conducted, potential for Ca and/or magnesium in some forms of cardiovascular disease, some trace elements, water, may be beneficial; more soluble in soft water cardiovascular disease. From a viewpoint it is concluded that studies are needed that show the effect of Mg to Ca in natural cardiovascular disease, as well as a factor. Drinking water is also linked to high blood pressure (Hill 1981) and it seems that work in this area should be continued (and total mineralization, Na to other competing ions). Studies have been carried out in Sri Lanka (Dissanayake *et al.* 1991) and a similar negative relationship between water hardness and various diseases and leukaemia has been suggested (Day &

#### Formation of toxic metals

may result either from leaching as flow through non-

carbonate rocks (e.g. granite), from pyrite oxidation or from pollution (acid rain). Acid water is in itself not thought to be a health risk but since many minerals are more soluble in acid water, toxic trace metals (e.g. Al, Be, Cd, Pb) may be present in higher concentrations. Most acid waters are base-poor, soft waters and their Ca and Mg deficiencies may also be implicated in various forms of heart disease referred to above.

Acid groundwaters are common in many parts of Africa, Asia and South America where granitic basement rocks with little acid-buffering capacity compose large areas of the land mass. High trace-metal contents of such waters are likely as a result. Acidic water is, for example, documented in south-western Ghana where Langanegger (1991) found that 45% of groundwaters had pH below 6.5. This is supported by recent work (Smedley *et al.* 1996). Two elements in particular, Al and Be, are worth highlighting as potentially problematic in acid waters.

**Aluminium (Al).** The WHO maximum recommended concentration for Al in drinking water is  $0.2 \text{ mg l}^{-1}$  (WHO 1993). Al is a major element in aluminosilicate minerals and is therefore a common constituent of most rocks. The solubility of Al is strongly pH-dependent and significant environmental concentrations are only found below pH 5.5 where the increasing concentrations are related to the solubility of microcrystalline gibbsite (Bache 1986). The presence of inorganic ligands, notably F and  $\text{SO}_4$  also increase the solubility of aluminium (May *et al.* 1979). At pH greater than 5, it is unlikely that labile, monomeric forms of aluminium will be present in natural waters although colloidal aluminium and other aluminosilicate colloids and particles may contribute to total aluminium in waters. It is customary to measure total aluminium in water on samples filtered through  $0.45 \mu\text{m}$  filters. This will give an early warning of high aluminium problems, although analysis of the monomeric forms (Driscoll 1984) is also needed for health and environmental studies where thermodynamic treatment of aluminium solubility is desirable.

The occurrence of high Al in drinking water has been linked to the development of Alzheimer's disease (e.g. Martyn *et al.* 1989). Recent studies related to Al toxicity have been carried out in relation to acidification by acid rain (Vogt 1986), although concern has also been expressed in relation to the quality of water released from water treatment plants where aluminium salts are used to clarify water by coagulation of organics, particulate matter and bacteria. Alu-

minium in drinking water forms only a small part of the total daily intake. It is more likely to be toxic if present in the labile, monomeric form in which it may make a disproportionate contribution to the amount absorbed from the gastro-intestinal tract. The greater bioavailability of Al in drinking water may therefore render it a relatively more harmful source than food (Martyn *et al.* 1989). The role of aluminium in Alzheimer's disease (let alone the role of Al in water) remains a controversial subject. The WHO guideline of  $0.2 \text{ mg l}^{-1}$  is based on a compromise between reducing aesthetic problems and retaining the efficacy of water treatment; they conclude that it is not presently possible to derive a health-based guideline.

It is likely that high aluminium occurs in groundwater in a number of developing countries where acid waters are generated. However, any health effects are unlikely to have been reported due to the absence of long-term records and the overriding influence of other diseases.

**Beryllium (Be).** Beryllium is known to be toxic at industrial exposure levels (Griffiths *et al.* 1977), yet to date only limited data have been reported on its occurrence and toxicity in natural waters and elsewhere in the environment. Of particular concern is the possibility that beryllium might be mobilized along with aluminium under conditions of increasing acidity (Vesely *et al.* 1989). Beryllium is substituted as a trace component in the silicate lattice of some rock-forming minerals. It is also present as the minerals beryl and bertrandite ( $\text{Be}_4\text{Si}_2\text{O}_7(\text{OH})_2$ ) and is concentrated in residual deposits of silicic volcanic rocks (Brookins 1988). It is especially concentrated in acidic waters, being present as dissolved  $\text{Be}^{2+}$  at pH < 5.5 (e.g. Edmunds & Trafford 1993) but may also be soluble as  $\text{Be}(\text{OH})_x$  complexes at higher pH. Beryllium solubility may also be enhanced by the formation of F-complexes. No WHO guide level has been set for Be in drinking water because of insufficient toxicological data and on the assumption that its concentrations in drinking waters must be very low (WHO 1993).

#### Redox-related controls

The complete reduction of oxygen in an aquifer is accompanied by a sharp decrease in the redox potential. The mobility of some species ( $\text{NO}_3$ , Se, U for example) is favoured under oxidizing conditions whilst others (especially Fe) have increased mobility under reducing conditions. A redox boundary will be found at shallow depths especially in soils or aquifers high in organic matter or sulphide minerals which will act as the

main substrate (electron donor) for the reduction of oxygen but in organic-deficient sediments, oxidizing conditions may persist for thousands of years.

**Nitrate.** Nitrate is often a major concern in developed countries as a result of well documented concerns about its potential health problems, including links with methaemoglobinemia and stomach cancers. It is not discussed in detail here because excessive nitrate concentrations are related mainly to pollution and have been comprehensively reviewed elsewhere (Foster *et al.* 1982; Chilton *et al.* 1994). Two points are emphasized, however, in the context of this review on geochemical controls. In many arid regions the natural baseline concentrations may well exceed the recommended limits due to natural rather than anthropogenic factors, for example fixation by leguminous plants (Edmunds 1994) or micro-organisms (Barnes *et al.* 1992). Secondly, concentrations of  $\text{NO}_3$  will persist under oxidizing conditions but *in-situ* denitrification will rapidly take place once oxygen has reacted completely if electron donors are available in the system.

**Iron and manganese.** Under reducing conditions concentrations of dissolved Fe and Mn can reach several  $\text{mg l}^{-1}$ , although much may be in colloidal rather than truly dissolved form. The solubility of Fe and Mn is also greater at low pH. Manganese is an essential element and is readily absorbed. There is limited evidence that it may be toxic at high concentrations (Loranger *et al.* 1994) and a provisional limit of  $0.5 \text{ mg l}^{-1}$  has been set (WHO 1993). Water with high Mn and/or Fe concentrations is usually unpalatable in terms of taste, odour, staining of laundry and discoloration of food (Gale & Smedley 1989). These aesthetic problems may be exacerbated by the presence of Fe bacteria (e.g. *Thiobacillus ferro-oxidans*, *Gallionella*) which obtain energy from the oxidation of Fe(II) and are responsible for biofouling of aquifers in some Fe-rich areas.

Most Fe problems relate to dissolution of Fe-bearing minerals but problems may also arise from corrosion of ferrous casing, pumps and pipework in supply boreholes. Iron especially is a very common problem in groundwater globally. The problem is well documented in developing countries where communities may be poorly equipped to treat affected supplies. Iron problems are reported for example in parts of India, Ghana (Pelig-Ba *et al.* 1991), Thailand (Ramnarong 1991) and Sri Lanka, Malaysia, Vietnam, Indonesia (Lawrence & Foster 1991), South Africa (Chibi 1991) and the former Soviet

Union (Kraynov & Solomin 1982).

**Arsenic.** Arsenic is toxic and carcinogenic. Hyperpigmentation, depigmentation, keratosis and peripheral vascular disorders are the most commonly reported symptoms of chronic arsenic exposure (Matisoff *et al.* 1982; Chen *et al.* 1994; Morton & Dunette 1994), but skin cancer and a number of internal cancers can also result. Toxicity depends on the form of As ingested, notably the oxidation state and whether in organic or inorganic form. Reduced forms of As are apparently more toxic than oxidized forms, with the order of toxicity from greatest to least being arsine, organo-arsine compounds, arsenite and oxides, arsenate, arsonium, native arsenic (e.g. Welch *et al.* 1988) although there is some evidence for *in-vivo* reduction of arsenate species (Vahter & Envall 1983). Arsenic intake by humans is probably greater from food (e.g. seafood) than from drinking water; however, that present in fish is overwhelmingly present as organic forms of low toxicity. Drinking water therefore represents by far the greatest hazard since the species present in groundwater are predominantly the more toxic inorganic forms (Ferguson & Gavis, 1972; Smedley *et al.* 1996). WHO has recently reduced its recommended limit for As in drinking water from  $50 \mu\text{g l}^{-1}$  to  $10 \mu\text{g l}^{-1}$  in response to evidence from toxicological studies. Regulatory bodies such as the EU and US-EPA are currently considering similar revision of the maximum value.

The crustal average As concentration is  $2 \text{ mg kg}^{-1}$  (Tebbutt 1983). Arsenic occurs as a trace element in many rocks and minerals but is especially concentrated in sulphide minerals such as orpiment ( $\text{As}_2\text{S}_3$ ), arsenopyrite ( $\text{FeAsS}$ ), realgar ( $\text{AsS}$ ) and enargite ( $\text{Cu}_3\text{AsS}_4$ ). Coal may contain about  $2000 \text{ mg kg}^{-1}$  As (Onishi 1969) and phosphorite may also be enriched.

Arsenic species in aqueous systems consist principally of arsenite ( $\text{H}_n\text{AsO}_3^{3-n}$ ) and arsenate ( $\text{H}_n\text{AsO}_4^{3-n}$ ) oxyanions. These species are highly soluble over a wide range of Eh and pH conditions. However, under reducing conditions in the presence of sulphide, As mobility is reduced due to precipitation as orpiment, realgar or arsenopyrite (although at low pH, the aqueous species  $\text{HAsS}_2$  may be present). Biomethylation of As may also take place resulting in the production of monomethylarsonic acid (MMAA) and dimethylarsinic acid (DMAA). In natural waters these are usually rare compared to the organic forms but may be present in relatively high concentrations in organic-rich waters.

Arsenic is strongly sorbed onto, or coprecipi-

min 1982).

toxic and carcinogenic. Hyperpigmentation, keratosis and other skin disorders are the most common symptoms of chronic arsenic poisoning (e.g. *et al.* 1982; Chen *et al.* 1994), but skin cancer and other cancers can also result. The form of As ingested, the oxidation state and whether in dissolved or particulate form. Reduced forms of As are more toxic than oxidized forms. The toxicity from greatest to least is: arsine compounds, arsenate, arsonium, native arsenic (e.g. 1988) although there is some reduction of arsenate to arsenite (e.g. 1983). Arsenic intake is generally greater from food (e.g. 1982) than from drinking water; however, in some areas it is overwhelmingly present as arsenic in drinking water. Drinking water is generally the greatest hazard at in groundwater are toxic inorganic forms (e.g. 1992; Smedley *et al.* 1996). It has reduced its recommended limit for drinking water from  $50 \mu\text{g l}^{-1}$  to  $10 \mu\text{g l}^{-1}$ . There is evidence from toxicological studies such as the EU study (1994) and recently considering similar values.

As concentration is low. Arsenic occurs as a trace element in rocks and minerals but is concentrated in sulphide minerals such as arsenopyrite ( $\text{FeAsS}$ ), arsenite ( $\text{Cu}_3\text{AsS}_4$ ). Coal may contain up to  $1 \text{ mg kg}^{-1}$  As (Onishi 1969) and can be enriched.

Aqueous systems consist of arsenite ( $\text{AsO}_3^{3-}$ ) and arsenate ( $\text{AsO}_4^{3-}$ ). These species are highly mobile over a range of Eh and pH. Under reducing conditions, arsenite is precipitated as arsenopyrite, As mobility is high (although at low pH, arsenite may be present). Arsenite may also take place in the oxidation of monomethyl- and dimethylarsinic acid. In waters these are usually in inorganic forms but may be precipitated at high concentrations in

tated with, ferric hydroxide ( $\text{Fe(OH)}_3$ ), the arsenate forms (5+ oxidation state) being more strongly sorbed than the arsenite forms (3+ oxidation state). This results in potentially much greater concentrations of dissolved As under reducing conditions, not only because of the lower sorption affinity but also because  $\text{Fe(OH)}_3$  is more soluble at low Eh. Many studies of groundwater and sediments have detected correlations between As concentration and both Fe and Eh (e.g. Matisoff *et al.* 1982; Belzile 1988; Varsányi *et al.* 1991). However, As may also be present in oxidizing waters, particularly in groundwater environments where oxidation of sulphide minerals is occurring (Smedley *et al.* 1995, 1996). Arsenic is also readily sorbed onto aluminium hydroxide ( $\text{Al(OH)}_3$ ), except at low pH where Al is itself stable in dissolved ionic form.

Occurrences of high As in drinking water are relatively rare. Most recorded cases are associated with sources of natural sulphide minerals, most notably pyrite and arsenopyrite, and these are often exacerbated by sulphide-mining activity. In the latter case the high As may be generated by oxidation *in situ* or by the processing and disposal of mine wastes. Incidences of high As have been noticed particularly in Taiwan (Tseng *et al.* 1968), S. America (Zaldivar 1974; Henriquez & Gischler 1980), Mexico (Cebrian *et al.* 1994), Ghana (Smedley *et al.* 1996), India (Chatterjee *et al.* 1995; Das *et al.* 1995) and Thailand (Ramnarong 1991).

#### *Element deficiencies related to geology*

Some water-related health problems are created by element deficiencies rather than excesses. Such diseases are most apparent in rural communities where water and food are locally derived and little exotic produce is consumed. In 'developed' societies, such deficiencies have normally diminished due to broader diet, wider provenance of foodstuffs and dietary supplements. It is possible to delineate large areas containing element deficiencies which are closely related to the local geology and/or geographical location. Three elements (Se, F, I) have well documented deficiency-related health problems, although Se and F also give rise to disease if present above threshold values defined earlier.

**Selenium.** Trace concentrations of Se are essential in the diet of humans and animals (e.g. Oldfield 1972) and Se deficiency may promote a health problem. Symptoms include muscular degeneration, impeded growth, fertility disorders, anaemia and liver disease (Låg 1984;

Peereboom 1985). However, at high ingested concentrations of  $10 \text{ mg day}^{-1}$  or greater, other problems such as gastro-intestinal ailments, skin discoloration and tooth decay may occur (Tebbutt 1983). Selenium toxicity in American Indians has been reported by Beath (1962). The WHO recommended limit for Se in drinking water is  $10 \mu\text{g l}^{-1}$ , but concentrations in natural water rarely exceed  $1 \mu\text{g l}^{-1}$ .

The geochemistry of Se is similar to that of sulphur. It occurs naturally in four oxidation states: 2-, 0, 4+ and 6+. In its 2- state, Se occurs as  $\text{H}_2\text{Se}$ , a highly toxic and reactive gas which readily oxidizes in the presence of oxygen. In elemental form ( $\text{Se}^0$ ), Se is insoluble and therefore non-toxic. The element occurs in the 4+ oxidation state as inorganic selenite ( $\text{SeO}_3^{2-}$ ) which is highly toxic. However, under reducing and acidic conditions selenite is readily reduced to elemental Se (NRC 1976; Howard 1977). Oxidizing and alkaline conditions favour the stability of the 6+ form, selenate ( $\text{SeO}_4^{2-}$ ), which is highly soluble. Selenium mobility should therefore be greater in oxidizing aquifers, although its dissolved concentration may be limited by the fact that it readily sorbs onto ferric hydroxide which precipitates under such conditions (Howard 1977).

Selenium has a strong affinity for organic matter and is readily incorporated into sulphide minerals. It is therefore often associated with sulphide-bearing hydrothermal veins and is present in relatively high concentrations in U deposits (Naftz & Rice 1989). It may also form the mineral ferroselite ( $\text{FeSe}_2$ ) if present in sufficiently high concentrations.

Few studies of Se in drinking water in developing countries have been carried out, but Iyengar & Gopal-Ayengar (1988), for example, cited the incidence of endemic Keshan disease, a chronic cardiomyopathy thought to be related to Se deficiency, in many parts of China. The disease afflicted several thousand people, principally in hilly and mountainous districts (altitude > 1600 m). There is also some evidence that remoteness from the sea may lead to Se deficiency (Låg 1984).

**Iodine.** The association of I deficiency in the human diet with endemic goitre has long been recognized. Goitre results from enlargement of the thyroid in order to compensate for I deficiency in hormone production. The condition has been recognized in many areas all over the world (e.g. Kelly & Sneddon 1960).

Iodine is not a major element in minerals and does not enter readily into the crystal lattice. It is, however, chalcophile and may be found in

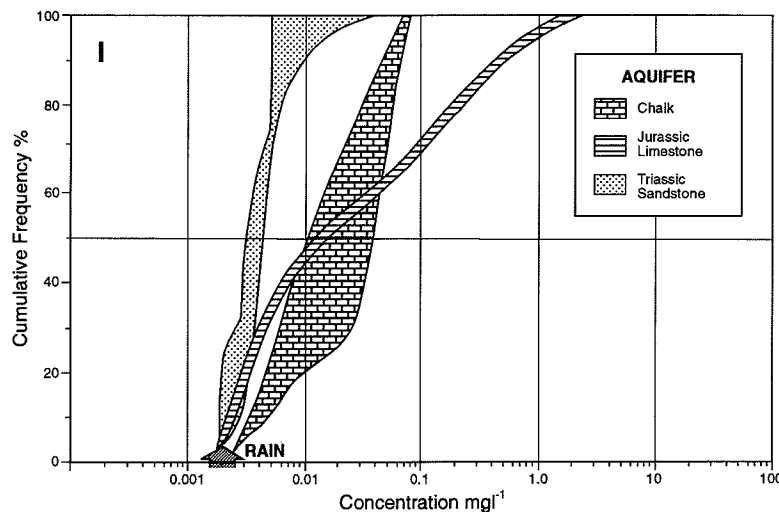


Fig. 2. Iodine concentrations in groundwater from UK aquifers (Chalk, Jurassic limestones, Triassic sandstones). Note that only carbonate rocks contribute I from water-rock interaction, over and above rainfall inputs.

higher concentrations in association with organic carbon (e.g. Fuge & Johnson 1986). Iodine is also readily adsorbed onto Fe and Al oxides (Whitehead 1984).

The principal natural source of I is sea water (mean value  $58 \mu\text{g l}^{-1}$ ; Fuge & Johnson 1986), but additional sources are formation waters, fluid inclusions and volcanic emanations. Iodine concentrations in the environment are increased by man's activities. I is used in herbicides, fungicides, sterilants, detergents, pharmaceuticals and the food industry. Iodine is also released into the environment from fossil fuel combustion, car exhausts and from sewage. The geochemical cycle of I involves volatilization to atmospheric I (as iodine gas,  $\text{I}_2$  or as methyl iodide,  $\text{CH}_3\text{I}$ ), atmospheric transport and subsequent loss to the biosphere and lithosphere as wet and dry deposition (e.g. Whitehead 1984; Fuge & Johnson 1986; Fuge 1989). Iodine in rainfall over coastal areas is therefore generally higher ( $1.5\text{--}2.5 \mu\text{g l}^{-1}$ ; Whitehead 1984) than over inland areas ( $1 \mu\text{g l}^{-1}$  or less; Fuge 1989).

Soils generally have higher concentrations of I than their parent rocks, especially shallow soils, presumably owing to the addition of I from the atmosphere (Fuge & Johnson 1986). Whitehead (1979) found a range of  $0.5\text{--}98.2 \text{ mg kg}^{-1}$  (dry weight) in surface soils from the UK, the highest being in fen peat and the lowest in podzolic sands poor in organic carbon. Soil I concentration has in some places been enhanced by

addition of seaweed as a fertilizer (Whitehead 1984). High natural baseline I concentrations may be found in carbonate aquifers probably derived from the oxidation of organic matter (Edmunds *et al.* 1989). This is well illustrated for the Chalk aquifer of the London basin (Fig. 2) where the median concentration is  $32 \mu\text{g l}^{-1}$  and the I/Cl ratio is  $5.84 \times 10^{-4}$  which is about four times higher than for non-carbonate aquifers in the UK.

About 20% of the daily I requirement of humans is likely to come from drinking water, the remaining 80% being derived from food (Fuge 1987). Dairy products, meat and fish are especially enriched in I, as is iodized salt where available. Since drinking water is a relatively minor I source, links between concentrations in water and occurrence of endemic goitre must be relatively tenuous. Nonetheless, they can serve as an indicator of I levels in the local environment (e.g. soils, local vegetation) and will therefore be useful for the determination of local health risk.

Total I concentrations in drinking waters range between  $0.01$  and  $c. 70 \mu\text{g l}^{-1}$ , depending on location, topography and rainfall pattern (mean river water content  $5 \mu\text{g l}^{-1}$ ; Fuge & Johnson 1986; Fuge 1989). Concentrations much below this mean value are frequently associated with the occurrence of goitres. Day & Powell-Jackson (1972) for example reported concentrations of  $< 1 \mu\text{g l}^{-1}$  in goitrous areas



**Table 3.** Impact of fluoride in drinking water on health (from Dissanayake 1991)

Concentration of fluoride ( $\text{mg l}^{-1}$ )	Impact on health
Nil	Limited growth and fertility
0–0.5	Dental caries
0.5–1.5	Promotes dental health resulting in healthy teeth, prevents tooth decay
1.5–4.0	Dental fluorosis (mottling of teeth)
4.0–10.0	Dental fluorosis, skeletal fluorosis (pain in back and neck bones)
> 10.0	Crippling fluorosis

of Nepal. Kelly and Sneddon (1960) produced maps of the distribution of endemic goitre and found that almost all countries regardless of climate, race or wealth had some recorded evidence of the problem although for reasons stated above the problem today tends to be restricted to rural areas of developing countries (Wilson 1953; Coble *et al.* 1968; Mahadeva *et al.* 1968; Kambal *et al.* 1969; Fuge & Johnson 1986; Rosenthal & Mates 1986). It has frequently been associated with mountainous areas, especially the Alps, Himalayas and Andes and regions distant from the coast (Fuge 1987).

There is therefore a very clear association between the geochemical occurrence of iodine, especially in natural waters, and the incidence of goitre. Remediation through dietary supplement is generally effective such that goitre now remains a political rather than a geochemical problem.

#### Mineral-saturation control

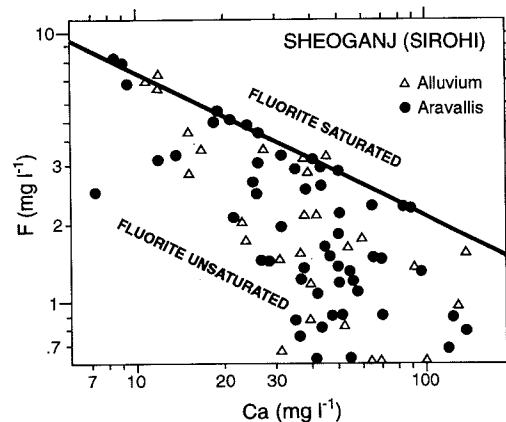
The upper limits of solubility for some elements are naturally maintained due to saturation with certain minerals. Health-related problems usually emerge when abnormally low concentrations of associated ions allow the concentrations of the harmful element to increase. These increases can be predicted from and described by the relevant solubility product ( $K_s$ ). Mineral saturation exerts a strong control on F and Ba concentrations.

**Fluorine.** An extensive literature exists on the occurrence of F in natural waters, both in industrialized and developing countries. This is because it is a fairly common trace element and its health effects have been recognized in many parts of the world. At low concentrations of less than about  $0.5 \text{ mg l}^{-1}$  total F, dental caries may result, whilst at higher concentrations chronic exposure can result in dental fluorosis (mottled enamel) or skeletal fluorosis (e.g. Rajagopal & Tobin 1991). Concentrations above which these

become problematic are around  $2 \text{ mg l}^{-1}$  and  $4 \text{ mg l}^{-1}$  respectively (Table 3), although poor nutrition is also recognized as an important contributory factor. The effects are permanent and incurable. High F concentrations in drinking water have also been linked with cancer (Marshall 1990). The WHO recommended limit for F in drinking water is  $1.5 \text{ mg l}^{-1}$ .

During the 1950s in the USA and Europe, it was found that introduction of F in toothpaste and fluoridation of public water supplies to a concentration of about  $1 \text{ mg l}^{-1}$  reduced the incidence of dental caries by more than 50% (Diesendorf 1986). The benefits of water fluoridation in recent years have been much less pronounced, probably as a result of long-term use of topical F, increased dietary F, improved dental health education and reduced sugar intake.

The average crustal abundance of F is  $300 \text{ mg kg}^{-1}$  (Tebbutt 1983). Fluorite ( $\text{CaF}_2$ ) is the most common F-bearing mineral but it is also present in apatite ( $\text{Ca}_5(\text{Cl},\text{F},\text{OH})(\text{PO}_4)_3$ ) and in trace quantities in amphibole, mica, sphene and pyroxene. Fluoride occurrence is



**Fig. 3.** Fluoride concentration in groundwaters from Rajasthan, India showing solubility control by fluorite (from Handa 1975).

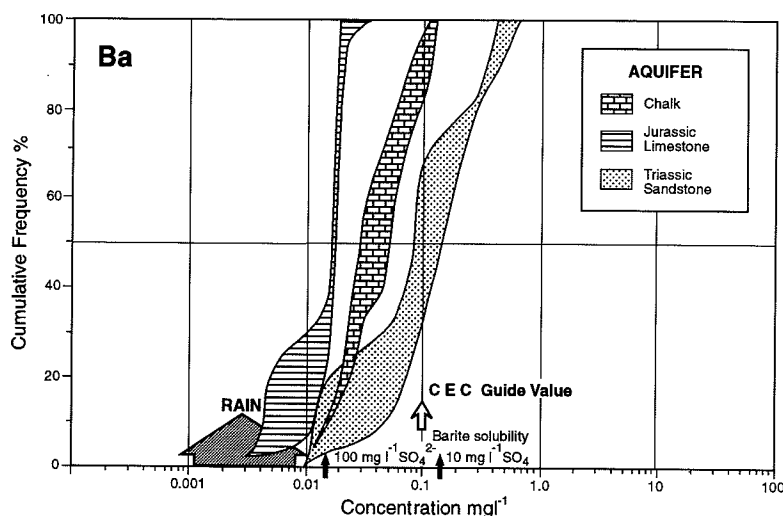


Fig. 4. Barium concentrations in groundwater from UK aquifers (Chalk, Jurassic limestone, Triassic sandstone). The Ba concentrations in rain and in groundwaters at saturation with 10 and 100 mg l<sup>-1</sup> SO<sub>4</sub> are also shown. Note that highest concentrations of Ba occur in sandstone aquifers.

commonly associated with volcanic activity (being especially high in volcanic glasses), geothermal fluids and granitic rocks. Thermal, high pH waters have especially high concentrations.

The principal form of F in water is as free dissolved F<sup>-</sup> but at low pH, the species HF<sup>0</sup> may be stabilized (at pH 3.5 this may be the dominant species; Hem 1985). F readily forms complexes with Al, Be, Fe<sup>3+</sup>, B and Si. Concentrations of F in water are limited by fluorite solubility, such that in the presence of 10<sup>-3</sup> M Ca, F should be limited to 3.1 mg l<sup>-1</sup> (Hem 1985). It is therefore the absence of Ca in solution which allows higher concentrations of F to be stable (Fig. 3). High F concentrations may therefore be expected in groundwater in Ca-poor aquifers and in areas where F minerals (or F-substituted minerals e.g. biotite) are common. Fluoride concentration will also increase in groundwaters where cation exchange of Ca for Na takes place.

In many developing countries high F concentrations have been reported in association with rift zones, volcanic rocks and granitic (Ca-poor) basement rocks (Bugaisa 1971; Kilham & Hecky 1973; Hadwen 1975; Nanyaro *et al.* 1984). High F concentrations are noted in the Kenyan part of the African Rift Valley (Ockerse 1953; Gaciri & Davies 1993) and in Uganda (Møller *et al.* 1970) where incidences of dental fluorosis have been linked with concentrations of F up to 3 mg l<sup>-1</sup>.

Fluoride problems have also received much

attention in Asia. Teotia *et al.* (1981) note that endemic fluorosis affects nearly one million people in India, the high concentrations of dissolved fluoride in drinking water resulting from dissolution of fluorite, apatite, francolite and topaz in the bedrocks. Handa (1975) noted the general negative correlation between F and Ca concentration in Indian groundwater (Fig. 3). Dissanayake (1991) found concentrations of F in the Dry Zone of Sri Lanka up to 10 mg l<sup>-1</sup> associated with dental fluorosis and possibly skeletal fluorosis. In the Wet Zone, intensive rainfall and the long-term leaching of F from rocks is probably responsible for low groundwater F concentrations. Here, the incidence of dental caries is reported to be high. Excessive F concentrations in water have also been found in Algeria and Kenya (Tjook 1983), Turkey (Pekdeger *et al.* 1992), South America (Lloyd & Helmer 1991), Ghana (UN 1988; Amoah 1990; Smedley *et al.* 1995) and Ivory Coast (especially in granitic areas; Akiti *et al.* 1990), Thailand (Ramnarong 1991; Table 4) and China (Zhaoli *et al.* 1989).

**Barium.** Barium occurs as a minor element in many rock types but is most abundant in acid igneous rocks. It is readily released during water-rock interaction but its solubility is controlled by the solubility of barite. Thus concentrations of barium in natural waters should be inversely proportional to the sulphate concentrations. High barium concentrations are

to be anticipated mainly where sulphate reduction has occurred and where  $\text{SO}_4$  concentrations are less than  $10 \text{ mg l}^{-1}$ . Barium has a possible association with cardiovascular disease (Brenniman *et al.* 1981; WHO 1993) and a guideline maximum value for drinking waters of  $0.7 \text{ mg l}^{-1}$  is given by WHO.

The concentration of Ba rarely exceeds  $1 \text{ mg l}^{-1}$  in natural waters (Edmunds *et al.* 1989). Median concentrations in waters unsaturated with respect to barite tend to be highest in groundwaters from non-carbonate aquifers (Fig. 4) and this reflects the lower geochemical abundance in carbonate rocks and the higher Ba in silicate minerals such as K-feldspar.

#### Other elements

**Lead.** Lead is present as a major element in galena ( $\text{PbS}$ ) and is a common constituent in hydrothermal mineral veins. Its average crustal abundance is  $16 \text{ mg kg}^{-1}$ . Pb is also produced from smelting, motor-vehicle exhaust fumes and from corrosion of lead pipework. Lead solubility is controlled principally by  $\text{PbCO}_3$  and low-alkalinity, low-pH waters can have higher Pb concentrations (Hem 1985). The WHO maximum recommended concentration for Pb has recently been reduced from  $50 \mu\text{g l}^{-1}$  to  $10 \mu\text{g l}^{-1}$  because of concerns about chronic toxicity, although this concentration is rarely exceeded in natural waters. There is an extensive literature on lead in the environment derived from leaded petrol and from lead pipes in soft water areas.

Lead is a cumulative poison, initiating tiredness, irritability, anaemia, behavioural changes and impairment of intellectual functions in affected patients (Tebbutt 1983). Ramnarong (1991) cites a case of lead poisoning in Thailand, where five out of ten patients died in 1979. Water from the local well was found to contain  $53.5 \text{ mg l}^{-1}$  Pb and soils contained  $0.13\text{--}4.92 \text{ mg kg}^{-1}$  as a result of pollution from leachate derived from a local refuse dump. Pelig-Ba *et al.* (1991) also reported relatively high natural Pb concentrations (around  $0.15 \text{ mg l}^{-1}$ ) in acid water from granitic terrains in Ghana.

**Cadmium.** Cadmium occurrence in the environment is from both natural and human sources. It is usually associated with zinc ores and may be present in volcanic emissions and released from vegetation (Robards & Worsfold 1991). Environmental levels are greatly enhanced by industrial operations as Cd is commonly used as a pigment, in paint, plastics, ceramics and glass manufacture, in metal fabrication and finishing. It is also released from smelting of copper ores

and from sewage sludge (Nicholson *et al.* 1983). Cadmium is an acute toxin, producing symptoms such as giddiness, vomiting, respiratory difficulties, cramps and loss of consciousness at high doses. Chronic exposure to the metal can lead to anaemia, anosmia (loss of sense of smell), cardiovascular diseases, renal problems and hypertension (Mielke *et al.* 1991, Robards & Worsfold 1991). There is also evidence that increased Cd ingestion can promote Cu and Zn deficiency in humans, both necessary elements in metabolic processes (Petering *et al.* 1971). Cd may also be a carcinogen (Tebbutt 1983).

Exposure of humans to Cd is likely to be greatest from food intake and inhalation. Drinking water should have lower Cd concentrations unless water sources are affected by volcanic exhalations, landfill leachate, or mine waters. Evidence of endemic Cd poisoning was, for example, found in Toyonia Prefecture, Japan. This resulted from the consumption of rice grown in irrigation water contaminated by local mining effluent (Robards & Worsfold 1991).

The WHO limit for Cd in drinking water is  $5 \mu\text{g l}^{-1}$  but Nicholson *et al.* (1983) detected renal damage in seabirds as a result of exposure to both Cd and Hg at concentrations below this limit. Cadmium solubility is limited by  $\text{CdCO}_3$  (Hem 1985) and is therefore found in higher concentrations at low pH. Cd may also be sorbed onto organic substances such as humic and fulvic acids and hence organic-rich waters may have higher Cd concentrations given a local Cd source. Few data are available on Cd in drinking water in developing countries. Concentrations are generally expected to be low, but acid waters and especially those close to mines and sewage effluents may have higher concentrations.

#### Conclusions

Not all elements relevant to human health have been considered in detail in this paper. Other potentially harmful dissolved constituents in some groundwaters include U, Sb, Th, CN, Hg, Ni and Cr. It is clear that health relates not only to excesses of trace elements in drinking water supplies, but may also relate to deficiencies (e.g. Se). With some elements health depends upon a delicate balance between the two (e.g. I, F, Se). The relationships between trace elements in water and health are very complex. Water is not their only dietary source and often relationships may be masked by the effects of other elements. Competition between different elements in the body for example, can

either exacerbate health problems or effect some form of protection (e.g. the protective effects of Fe, Cu and Zn on Cd toxicity; Underwood 1979). Water may, however, be a useful indicator of the local environmental levels of trace elements (e.g. in food, soils, rocks, atmosphere). The links between excesses or deficiencies of particular trace elements and health are likely to be more noticeable in developing countries especially in rural areas because of a much greater dependence on water and food of local provenance.

Trace element mobility is dependent upon physico-chemical conditions and interaction of other chemical constituents but varies with each individual element. Al, Be, Pb, Cd, Fe and Mn for example are preferentially mobilized under acidic conditions. Arsenic (along with Fe and Mn) may be more soluble under reducing conditions, whilst Se and U are more mobile in oxidizing environments. Fluoride is most mobile in alkaline conditions, given low dissolved Ca concentrations and I may be a largely conservative element, depending mainly on I concentrations in local input sources. Deficiency in both I and Se have been observed in regions remote from the sea, particularly at high altitudes. Microbiological processes also exert an important influence on trace element speciation. Disregarding the additional effects of industry and agriculture on trace element content of groundwater, acid-mobile elements should be concentrated in mining effluent, especially those associated with pyrite oxidation, and in hydrothermal and geothermal areas. Likewise, As, Se and U should have elevated concentrations in groundwater of hydrothermal and geothermal areas. High F concentrations have been reported in zones of extensional tectonism and volcanism (e.g. the East African Rift) and in association with F-bearing hydrothermal mineral veins.

Further geochemical work on natural baseline variations in the chemistry of surface and groundwaters is still required for those elements for which few data currently exist. In addition there is a need to convey more information on natural baseline conditions to those working in water agencies who may wrongly assign anomalous inorganic concentrations to pollution origins. Geochemical studies have sometimes been 'ahead' of related epidemiological and especially clinical studies and it is recognized that it is much easier to define a particular geochemical province for a given element than to establish the relationships with health effects. Water of high quality is nevertheless of such a high priority worldwide that hydrogeochemical databases are an essential component in epi-

demiological studies.

From the practical point of view, some conclusions may be drawn in relation to studies connected with rural water schemes. The problem of arsenic which is mainly related to sulphide oxidation can be avoided or minimized by preventing oxidation through good management practice (e.g. avoiding excessive draw-down). The other main area of concern, fluoride, is difficult to manage, although groundwater with shorter residence times in general should be more likely to contain lower levels of fluoride. Those responsible for development schemes must be aware of these geochemical provinces likely to give rise to problems. Furthermore, there is a tendency in many aid schemes to specify a certain depth and design and then to complete many boreholes to this specification. If concentrations of iron and manganese are too high, villagers will abandon the wells. Therefore, it is most important that a pilot investigation of the water quality is carried out before large wellfield projects are undertaken.

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