



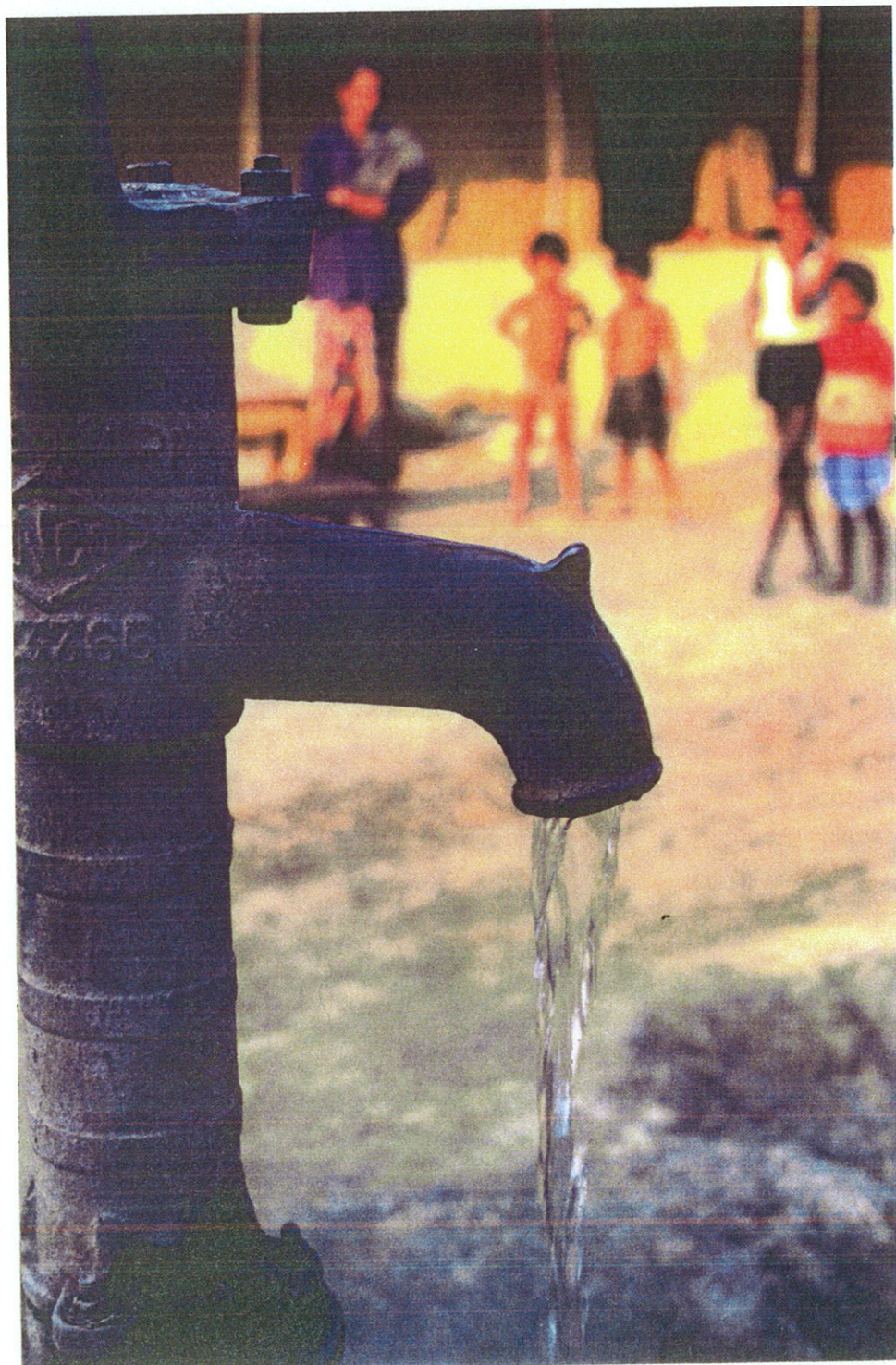
British Geological Survey

ODA

Vulnerability of Shallow Groundwater Quality due to Natural Geochemical Environment

## 1 WATER, GEOCHEMISTRY AND HEALTH - AN OVERVIEW

W M EDMUNDS AND P L SMEDLEY







**ODA**

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## **PREFACE**

This report forms one in a series of three concerning the relationship between water quality resulting from natural processes of water-rock interaction and human health. The first report provides an overview of the constituents in groundwater which at certain concentrations may be detrimental to human health, including arsenic, aluminium, fluorine, iodine, selenium, barium, manganese and beryllium, their health consequences and the geochemical modes of mobilisation in the groundwater environment. The other two reports are the result of field investigations on rural groundwaters in Ghana and Sri Lanka and focus on the particular problems of arsenic, iodine and fluoride in water supplies in parts of these countries. The research has been funded by the British Overseas Development Administration as part of the Technology Development and Research Programme (Project R5552) and the reports represent the culmination of three years' research. The research programmes were carried out in collaboration with Ghanaian and Sri Lankan research workers from the Water Resources Research Institute, Accra and the Institute of Fundamental Studies, Kandy respectively.





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## EXECUTIVE SUMMARY

The natural geological and geochemical environment contributes beneficial mineral content and bioessential elements to water, but may also give rise to undesirable or toxic properties, either through deficiency or excess of various elements. This report describes the controls on the release into solution of some of the most important toxic elements, together with the geochemical conditions that give rise to element excess and deficiency.

Many studies have identified an inverse correlation between cardiovascular disease and water hardness (calcium and magnesium concentration). The associated mobility of trace metals in soft waters may also be a factor contributing to prevalence of the disease. Links have been made between dietary aluminium intake and the occurrence of Alzheimer's disease. Chronic arsenic exposure is known to lead in particular to skin disorders, cardiovascular problems and internal cancers. High fluoride concentrations give rise to dental and skeletal fluorosis. Ingestion of high concentrations of cadmium has given rise to renal dysfunction and bone disorders in affected communities. In terms of deficiency, inadequate dietary iodine is known to give rise to goitre and related disorders. Selenium deficiency has resulted in Keshan's disease in some affected endemic areas. Low fluoride intake is linked with prevalence of dental caries. Water is only one source of these toxic or bioessential elements, but can exert a major influence on environmental health of large communities, particularly in developing countries where water treatment is seldom practised or where nutrition is poor.

Many trace elements are strongly controlled by pH and redox potential. Under acidic conditions, aluminium and beryllium as well as other potentially toxic metals may be released. Changes in redox conditions (as well as pH) will affect the mobility of iron, manganese and arsenic in particular. Some toxic elements may be held at acceptable concentrations in groundwaters by solubility controls. Barium and fluoride concentrations are for example controlled by the solubility limits of barite and fluorite respectively. Quality problems from these elements arise when groundwaters contain low sulphate or low calcium concentrations respectively. Deficiencies in selenium and iodine (as well as fluoride) in groundwater are related to the low geochemical abundance of these elements in certain environments.

Before pollution can be evaluated in any water resource, it is important first to be aware of the natural baseline concentrations of key elements of health importance in water supplies and to understand the geochemical processes that control them.



## 1 INTRODUCTION

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 gastroenteritis 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. Anthropogenic 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 between water and rocks, 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, either on health or aesthetic grounds.

Natural groundwater-quality problems 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. These include As, F, Fe, Mn, Al and occasionally elements such as Cr, Sb, Cd and Pb.

In this report, some of the most important elements considered by international organisations 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 those of a remedial or preventive nature.



## 2 HYDROGEOCHEMISTRY IN RELATION TO HUMAN HEALTH

### 2.1 Essential and non-essential elements

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 summarised in Figure 2.1. 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 oxidising to reducing conditions may have a similar effect on elements such as Fe.

Those elements currently considered to be essential for human health and metabolism (Moynahan, 1979) are also indicated in Figure 2.1, together with elements considered to have harmful effects if present in water supplies above certain limits (CEC, 1980; WHO, 1993). The currently agreed limits for inorganic constituents of significance in relation to health are summarised in Table 2.1. 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 recommended limits. Those elements that may give rise to acceptability problems are summarised in Table 2.2. Some of the limits quoted in both tables have qualifications placed on them for which reference to the original text is recommended.

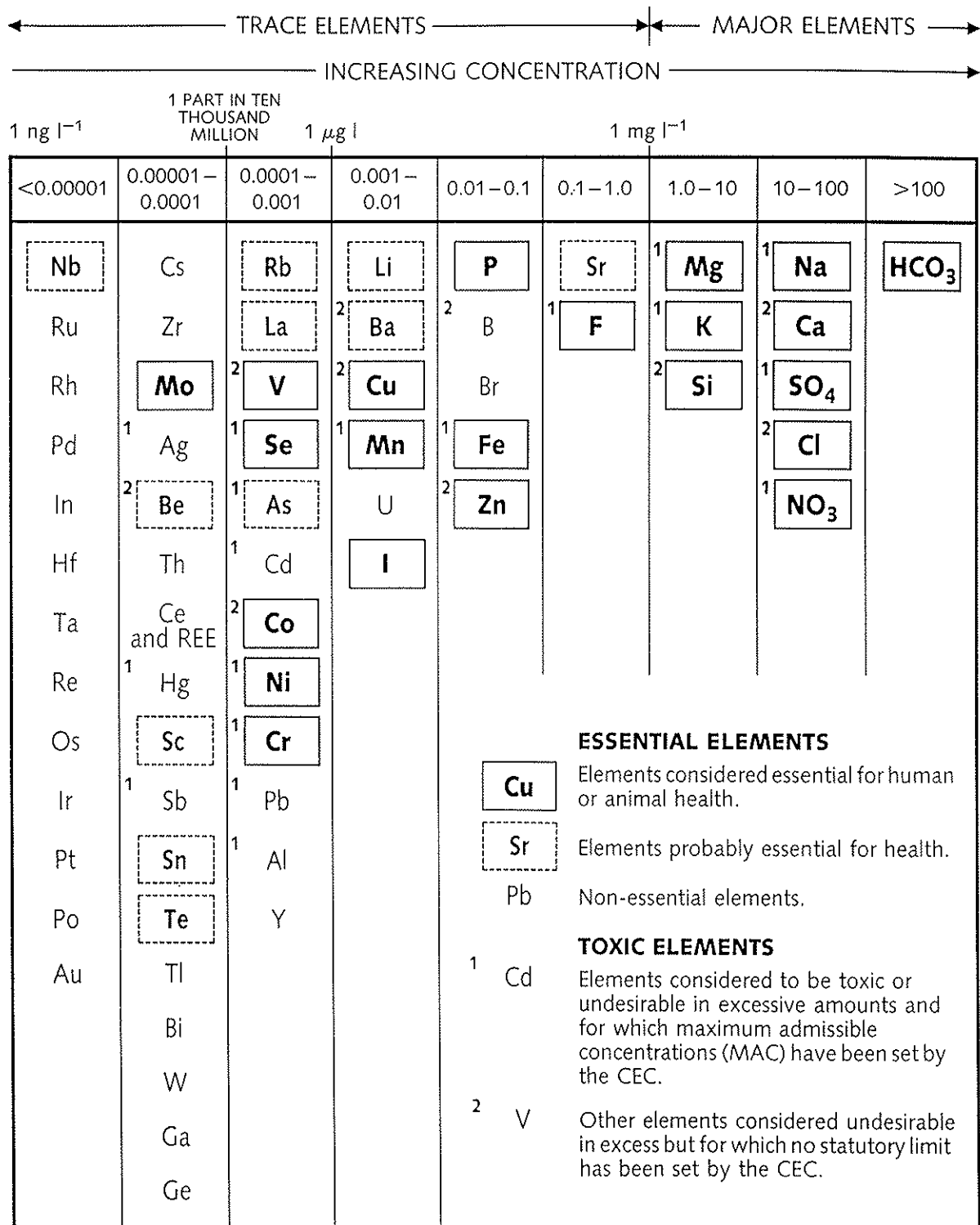
### 2.2 Geochemical baseline conditions

The composition of surface waters and shallow groundwaters closely reflects 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 (ie. 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 mobilisation of metals harmful to health (Lucas and Cowell, 1984; Edmunds and 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 may be found of health effects relating to differences in water chemistry along flow gradients in aquifers. 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 recognised as a fluoride-related problem, blending of high and low-F waters was adopted as

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

### CONCENTRATIONS IN DILUTE, OXYGENATED GROUNDWATER AT pH 7



**Figure 2.1.** 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.



**Table 2.1.** Chemicals of health significance in drinking water (data from WHO (1993) with values from CEC (1980) where appropriate).

	<b>WHO (1993) Guideline Value (mg l<sup>-1</sup>)</b>	<b>CEC (1980) Guideline Value (mg l<sup>-1</sup>)</b>	<b>CEC (1980) Max. Admissible Concentration (mg l<sup>-1</sup>)</b>
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)	2.0 (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)	0.001		0.001
Molybdenum (Mo)	0.07		
Nickel (Ni)	0.02		0.05
Nitrate (NO <sub>3</sub> -N)	10	5.7	11.3
Selenium (Se)	0.01		0.01
Uranium (U)	NAD		

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.

a means of eradicating fluorosis and of providing an optimum F concentration in water supplies.

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

## 2.3 Natural water-quality problems

### 2.3.1 Water hardness and sodium

It has long been suspected that a causal link exists between water hardness (ie. principally dissolved Ca and Mg) and cardiovascular disease (Gardner, 1976; NAS, 1977; Masironi, 1979; Pocock et al., 1985) although water is only one of many factors that might be involved (Shaper et al., 1981). During the 1960s and 1970s in Britain, detailed studies were carried out, especially in towns which had experienced changes in the hardness of their water supplies (Lacey and Shaper, 1984). These results supported the hypothesis of a weak causal relationship between drinking-water hardness and mortality from cardiovascular disease, especially in men. More recently, the British Committee on Medical Aspects of Food Policy

**Table 2.2.** Substances in drinking water that may give rise to complaints from consumers (data from WHO (1993) compared, where appropriate, with CEC limits).

	WHO (1993) Guideline Value (mg l <sup>-1</sup> )	CEC (1980) Guideline Value (mg l <sup>-1</sup> )	CEC (1980) Max. Admissible Concentration (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

\*More than 80% compliance over a period of 3 years.

(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 mg l<sup>-1</sup> (as CaCO<sub>3</sub>). It was also pointed out (COMA, 1994) that further studies since the 1970s have not altered the balance of evidence for the association and that the explanation for the association remains unknown. Other studies reviewed by Foster (1992) have shown that the relationship between water hardness and heart disease is not straight forward 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 quality have been proposed, including:

1. potential for Ca and/or Mg to protect against some forms of cardiovascular disease;
2. potential benefits of some trace elements which are more prevalent in hard water;
3. higher concentrations of many potentially toxic trace metals which are more soluble in soft water.

From the geochemical viewpoint, it is considered that further investigation is deserved of the ratios of Ca to Mg in natural waters in relation to cardiovascular disease, rather than variations in total hardness alone.

Fewer studies of cardiovascular disease and water quality have been carried out in developing countries but Dissanayake et al. (1982) also found a 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 and Powell-Jackson, 1972).

Elevated sodium in drinking water is also implicated in contributing to high blood pressure (e.g. Calabrese and Tuthill, 1981), despite the fact that water is a relatively minor Na source (usually <9% of dietary intake) compared to food (Calabrese, 1983). Sodium is a major component of rocks and minerals (especially feldspars, clays and evaporite minerals) and as a result of the high concentrations achievable in waters before solubility limits are approached, observed concentrations can be very variable, potable waters often having in excess of 100 mg l<sup>-1</sup>. The WHO guideline limit for Na in drinking water based on acceptability is 200 mg l<sup>-1</sup> (Table 2.2).

There is limited evidence that the effect of Na on hypertension can be partly mitigated by higher intakes of dietary potassium, leading to reduced risk of high blood pressure and strokes (COMA, 1994). It seems important therefore, that further work in this area should consider not only sodium (and total mineralisation) but also the ratio of Na to other competing ions, especially K.

### 2.3.2 Acid water and mobilisation of toxic metals

Acid groundwater may result either from natural processes such 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 and soft and their Ca and Mg deficiencies may also be implicated in the occurrence 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 concentrations in 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., 1995a, b). Two elements in particular are worth highlighting as potentially problematic in acid waters: Al and Be.

#### Aluminium

Aluminium is a major element in aluminosilicate minerals and is therefore a common constituent of most rocks. It comprises about 8% of the earth's crust. The solubility of Al in water is strongly pH-dependent and significant concentrations are generally only found below ca. pH 5.5 where they are related to the increasing solubility of microcrystalline gibbsite (Bache, 1986). However, the presence of inorganic ligands, notably F and SO<sub>4</sub>, also increases the stability of dissolved Al (May et al., 1979). At pH greater than about 5, it is unlikely that labile, monomeric forms of Al will be present in natural waters although colloids of Al and other aluminosilicate compounds as well as particulate Al may contribute to total Al in waters. It is customary to measure total Al in water on samples filtered through 0.45µm. This will give an early warning of high-Al problems, although analysis of the monomeric forms (Driscoll, 1984) is also needed for health and environmental studies where thermodynamic investigation of Al solubility is desirable.

Drinking-water acidification by acid rain may increase Al concentrations in water significantly (Vogt, 1986). Concern has also been expressed about the quality of water released from water-treatment plants where aluminium salts are used to clarify water by coagulation of organic material, particulate matter and bacteria (Ho and Tso, 1992).

The concentrations of Al in drinking water have received much attention in recent years since they have been linked to the development of various forms of dementia, particularly Alzheimer's disease. However, evidence is frequently conflicting and the links are somewhat tenuous. Anomalously high concentrations of Al have been found in neuritic plaques and neurofibrillary tangles in the brains of patients affected by Alzheimer's disease (e.g. Candy et al., 1992), but whether accumulation of Al is causal or merely an effect of regulatory dysfunction due to disease is still in dispute. Recent studies have also claimed that high Al in senile plaques of affected patients are simply an artefact of the analytical technique used (Landsberg et al., 1992).

Alzheimer-like symptoms have also been recognised in patients undergoing long-term dialysis as a result of renal failure. Aluminium, given in large doses through dialysis and orally-administered phosphate binders, was found to accumulate in the brains of affected patients (e.g. Copestake, 1993).

Circumstantial evidence for the link between Al and Alzheimer's disease also derives from epidemiological investigations associating drinking-water quality with disease prevalence. Martyn et al. (1989) found a slightly increased risk of Alzheimer's disease (1.5 times greater) in parts of England and Wales where the mean Al concentration in drinking water is greater than 0.11 mg l<sup>-1</sup> compared with areas where concentrations are less than 0.01 mg l<sup>-1</sup>. Vogt (1986) found a higher prevalence of dementia in areas of Norway with elevated concentrations of Al in drinking water as a result of acid rain and tentatively suggested that Al may be an important factor in development of the disease. However, more epidemiological data are needed to confirm the link.

The WHO recommended limit for Al in drinking water is 0.2 mg l<sup>-1</sup> (WHO, 1993). This is based on a compromise between reducing aesthetic problems and retaining the efficacy of water treatment. WHO conclude that there are at present insufficient data to derive a recommended limit based on health criteria.

Aluminium in drinking water forms only a small part (<10%) of the total daily intake. However, since water is more likely to contain Al in the labile, monomeric form, it is thought to make a disproportionate contribution to the amount absorbed from the gastrointestinal tract. Therefore, if Al is a factor involved in the development of neuro-degenerative diseases, the greater bioavailability of Al in drinking water may render it a more harmful source than food (Martyn et al., 1989). This is supported to some extent by the fact that studies investigating the role of Al-rich antacids in the development of Alzheimer's disease have failed to show any association (Copestake, 1993).

Many of the published data concerning links between Al and various forms of dementia are for industrialised nations: few data exist for developing countries. It is likely that high Al occurs in groundwater in a number of developing countries where acid waters are generated, although 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

Beryllium is known to be toxic at industrial exposure levels (Griffitts 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. Increased mortality in fish has been observed in acid waters (pH 4.5) with Be concentrations of  $10 \mu\text{g l}^{-1}$  (Jagoe et al., 1990) but effects on human populations are largely unknown. Concentrations in water are usually  $<1 \mu\text{g l}^{-1}$ .

Beryllium is substituted as a trace component in the silicate lattice of some rock-forming minerals. It is also present in the minerals beryl ( $\text{Be}_3\text{Al}_2(\text{Si}_6\text{O}_{18})$ ) 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  $<5.5$  (Edmunds and Trafford, 1992) but may also be soluble as  $\text{Be}(\text{OH})_x$  complexes at higher pH. Of particular concern is the possibility that Be might be mobilised along with Al under conditions of increasing acidity (Vesely et al., 1989), particularly due to acidification by acid rain. Like Al, dissolved Be concentrations may also be enhanced by the formation of Be-F complexes. No WHO guide level has been set for Be in drinking water due to insufficient toxicological data and on the assumption that its concentrations in drinking waters must be very low (WHO, 1993).

### 2.3.3 Redox-related controls

The complete reduction of oxygen in an aquifer is accompanied by a sharp decrease in the redox potential. The mobilisation of some species (e.g.  $\text{NO}_3$ , Se, U) is favoured under oxidising conditions whilst others (especially Fe) have increased mobility under reducing conditions. In soils and aquifers which contain organic matter or sulphide minerals, the main electron donors for reduction reactions, a redox boundary may be found at relatively shallow depths. However, in organic- and sulphide-deficient sediments, oxidising conditions may persist to significant depths and 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 methaemoglobinaemia and stomach cancer. The WHO recommended maximum for  $\text{NO}_3\text{-N}$  in drinking water is  $10 \mu\text{g l}^{-1}$  (Table 2.1). Nitrate is not discussed in detail here because excessive concentrations are related mainly to anthropogenic pollution and have been comprehensively reviewed elsewhere (e.g. Foster et al., 1982; Chilton et al., 1994). However, two points concerning geochemical controls are emphasized in the context of this review. Firstly, in many arid regions, baseline concentrations may well exceed the recommended limit due to natural rather than anthropogenic factors, for example fixation by leguminous plants (Edmunds, 1994) or microorganisms (Barnes et al., 1992). Secondly, concentrations of  $\text{NO}_3$  will persist under oxidising conditions, but *in-situ* denitrification will take place rapidly under reducing conditions if electron donors are available in the system and once oxygen has reacted completely.

## Iron

Iron has no known toxicological effects, indeed it is important in the production of haemoglobin. However, high-Fe waters are usually unpalatable due to taste, odour, staining of laundry and discoloration of food (Gale and Smedley, 1989). Such 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 bio-fouling of aquifers in some Fe-rich areas. The WHO recommended limit for Fe in drinking water based on aesthetic criteria is 0.3 mg l<sup>-1</sup>. Under reducing conditions, concentrations can reach several mg l<sup>-1</sup>, although much may be in colloidal rather than truly dissolved form. The solubility of Fe minerals is also greater at low pH.

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 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 groundwaters in parts of India (e.g. Smedley, 1991), Ghana (Pelig-Ba et al., 1991), Thailand (Ramnarong, 1991), Sri Lanka, Malaysia, Vietnam, Indonesia (Lawrence and Foster, 1991), South Africa (Chibi, 1991) and the former Soviet Union (Kraynov and Solomin, 1982). In impacted areas, such Fe-rich waters are frequently abandoned in favour of traditional surface-water sources with lower Fe concentrations. This can lead to indirect health problems as surface waters are commonly polluted with faecal and other bacteria.

## Manganese

Like Fe, Mn concentrations in water tend to be higher under reducing and acidic conditions and the two elements are often found in close association. However, the principal dissolved form of Mn, Mn<sup>2+</sup>, is significantly more stable than Fe<sup>2+</sup> in aerated water and Mn therefore tends to be more mobile in the oxidising environment (Hem, 1985). As with Fe, bacteria can be influential in the oxidation reaction. The bacterium *Hyphomicrobium* has for example been found in deposits of Mn oxides in pipelines (Tyler and Marshall, 1967).

Manganese is an essential element in the metabolism and is readily absorbed. However, there is some evidence that it is toxic at high concentrations (Loranger et al., 1994). Some links have been postulated between Mn occurrence and prevalence of a form of motor neuron disease, Guamian amyotrophic lateral sclerosis, particularly prevalent in the Pacific region (Guam, Japan, New Guinea, Australia; Foster, 1992). Former mineworkers from a Mn-ore mine in northern Australia who presented neurological symptoms (known locally as 'bird disease') had high blood Mn concentrations (Cawte et al., 1987). Iwami et al. (1994) found correlations between high Mn in food and the prevalence of motor neuron disease in the Kii Peninsula of Japan, although deficiency of Mg in the drinking water was cited as an important contributory factor. Calcium deficiency is also thought by some workers to be a causal factor in the disease (Foster, 1992 and references therein). However, statistical data for Mn intake and the occurrence of motor neuron disease (classical amyotrophic lateral sclerosis) in the United States failed to find a link (e.g. Foster, 1992).

Water is estimated to contribute less than 1% of the total dietary intake of Mn, but may be much higher in populations drinking reducing groundwater (Loranger et al., 1994). WHO has set a provisional limit of 0.5 mg l<sup>-1</sup> for the element in drinking water (Table 2.1).

## Arsenic

Unlike many elements where toxicity at concentrations found in drinking water is postulated but as yet not proven, As is a known toxin and carcinogen. The most common health problems associated with chronic ingestion of high-As drinking water are skin disorders, notably pigmentation disorders, keratosis and skin cancer, but peripheral vascular disorders, as well as renal, haematological, respiratory and neurological problems can result (e.g. Matisoff et al., 1982; Morton and Dunette, 1994; Chen et al., 1994). A number of internal cancers including bladder, kidney, liver, lung and prostate cancer have also been linked to chronic As ingestion (Smith et al., 1992; Gibb, 1995). Large populations in the developing world suffering from various forms of chronic As poisoning have been identified, notably in Taiwan, Mexico, Chile, Argentina, El Salvador, India (West Bengal) and Bangladesh (e.g. Tseng et al., 1968; Zaldivar, 1974; Henriquez and Gischler, 1980; Cebrián et al., 1994; Chatterjee et al., 1995; Das et al., 1995). Some of the As-associated health problems experienced in West Bengal are shown in Plates 2.1 and 2.2.

The WHO recommended limit for As in drinking water has recently been reduced from 50 µg l<sup>-1</sup> to 10 µg l<sup>-1</sup> in response to recent toxicological evidence. Regulatory bodies such as the EC and US-EPA are currently considering similar revision of the maximum value. Arsenic concentrations in drinking waters used by populations in the affected areas listed above are well in excess of these limits, sometimes at concentrations greater than 1 mg l<sup>-1</sup>. In these poor rural areas, treatment of water prior to use to remove the As is rarely a practical or affordable option.

Arsenic toxicity depends on the form ingested, notably the oxidation state and whether in organic or inorganic form. Reduced forms of As are apparently more toxic than oxidised forms, the order of toxicity decreasing from arsine through organo-arsine compounds, arsenite and oxides, arsenate, arsonium to native arsenic (e.g. Welch et al., 1988) although there is some evidence for *in-vivo* reduction of arsenate species (Vahter and 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 potentially a far greater hazard since the species present in groundwater are predominantly the more toxic inorganic forms (Ferguson and Gavis, 1972; Smedley et al., 1995a, b).

The crustal average As concentration is 2 mg kg<sup>-1</sup> (Tebbutt, 1983). Arsenic occurs as a trace element in many rocks and minerals but is especially concentrated in sulphide minerals such as orpiment (As<sub>2</sub>S<sub>3</sub>), arsenopyrite (FeAsS), realgar (AsS) and enargite (Cu<sub>3</sub>AsS<sub>4</sub>) as well as pyrite and chalcopyrite (Table 2.3). Sulphide-rich coal may contain up to about 1000 mg kg<sup>-1</sup> As (Onishi, 1969). Iron oxide is also commonly enriched in As (sorbed or co-precipitated), particularly when the oxide forms as a result of oxidation of sulphide precursors. Since As is in the same group of the periodic table as P, phosphorite may also have elevated As concentrations, up to about 200 mg kg<sup>-1</sup> (Table 2.3).

**Table 2.3.** Arsenic concentrations in common rocks and minerals. Data are principally from Onishi (1969) and White et al. (1989).

	Range (mg kg <sup>-1</sup> )
Quartz	0.4 - 2
Feldspar	0.02 - 2
Biotite	1.4
Amphibole	<1 - 2
Pyroxene	0.05 - 1
Olivine	0.1 - 0.2
Magnetite	0.1 - 40
Apatite	0.4
Galena	<50 - 1000
Sphalerite	<80 - 1000
Chalcopyrite	<80 - 5000
Pyrite	<80 - 13000
Limestone	0.1 - 20
Phosphatic limestone	7 - 25
Phosphorite	<1 - 188
Sandstone	<1 - 9
Marine shale	3 - 500
Freshwater clay	3 - 10
Coal	100 - 1000
Fe/Mn nodules	100 - 1000
Soil	<1 - 70

Arsenic species in aqueous systems consist principally of arsenite ( $H_nAsO_3^{3-n}$ ) and arsenate ( $H_nAsO_4^{3-n}$ ) oxyanions which are stable in soluble form under reducing and oxidising conditions respectively. Redox potential and pH are the most important controls on As mobility. Arsenite and arsenate are stable in soluble form over a wide Eh-pH range, but under reducing conditions in the presence of sulphur, As mobility is reduced due to stabilisation of As sulphides (although at low pH, the aqueous species  $HAsS_2$  may be present).

Arsenic is strongly sorbed onto, or co-precipitated with, ferric hydroxide ( $Fe(OH)_3$ ), the arsenate (As(V)) forms being more strongly sorbed than the arsenite (As(III)) forms. This results in potentially much greater concentrations of dissolved As under reducing conditions, not only because of the lower sorption affinity but also because  $Fe(OH)_3$  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).

Sorption onto ferric hydroxide is also strongly pH-dependent, being greatest in the near-neutral pH range. Since the point-of-zero-charge of ferric hydroxide and oxide minerals lies in the range pH 7.5-8.5 (Appelo and Postma, 1993), sorption affinity for the As oxyanions





**Plate 2.1.** Hyperkeratosis on the palms from chronic exposure to arsenic in drinking water, West Bengal, India.



**Plate 2.2.** Hyperkeratotic nodules on the soles of the feet of a middle-aged man, West Bengal, India.



is greater at pH values less than this range. Sorption affinity is lower under acidic conditions (less than pH ca. 3; Dzombak and Morel, 1990), presumably due to the increased solubility of ferric hydroxide under such conditions. Arsenic is also readily sorbed onto aluminium hydroxide ( $\text{Al}(\text{OH})_3$ ), although again, sorption is low at low pH where Al is itself dissolved. Biomethylation of As may take place, resulting in the production of monomethylarsonic acid (MMAA) and dimethylarsinic acid (DMAA). In natural waters, particularly groundwaters, these are usually rare compared to inorganic forms but may be more important in organic-rich waters.

Most recorded cases of high-As water are associated with sources of natural sulphide minerals, notably pyrite and arsenopyrite. Mobilisation of As may be exacerbated by oxidation of the sulphide minerals, particularly by the introduction of oxygen by either mining activity or dewatering of aquifers (e.g. by overabstraction). Arsenic mobility in the groundwater environment is discussed in more detail in Volume 2, in a case study of the Obuasi gold-mining area of southern Ghana (Smedley et al., 1995b).

#### 2.3.4 Element deficiencies related to geology

Some water-related health problems are created by element deficiencies rather than excesses. Such diseases are most apparent in poor 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, I, F) have well-documented deficiency-related health problems, although these are also potentially toxic if present above threshold values.

#### Selenium

Trace concentrations of Se are essential in the diet of humans and animals (e.g. Oldfield, 1972) and chronic 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 oxidises 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). Oxidising 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 oxidising aquifers, although its dissolved concentration may be limited by the fact that it sorbs readily 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 and 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 and Gopal-Ayengar (1988) for example cited the incidence of endemic Keshan's 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 greater than 1600 m). There is also some evidence that remoteness from the sea may lead to Se deficiency (Låg, 1984).

## Iodine

Iodine is an essential element in human metabolism. Iodine-deficiency disorders (IDDs) are well-documented, the most common symptom being goitre (Plate 2.3), but hypothyroidism and cretinism may also result (Taylor, 1956; Dunn and Van der Haar, 1990). Less well-accepted associations have been reported between iodine deficiency and multiple sclerosis, motor neuron disease, Parkinson's disease and Alzheimer's disease (Foster, 1992). Endemic goitre has been a global problem, but today is largely restricted to rural areas of developing countries (e.g. Kelly and Sneddon, 1960) where food and water are of local provenance and iodine supplements are not administered or not sufficiently well-distributed. It still affects many millions of people in the poorest communities (e.g. Wilson, 1953; Coble et al., 1968; Mahadeva et al., 1968; Kambal et al., 1969; Fuge and Johnson, 1986; Rosenthal and Mates, 1986).

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 higher concentrations in association with organic carbon (e.g. Fuge and Johnson, 1986). Iodine is also readily adsorbed onto Fe and Al oxides (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), but carbonate minerals may also be a source. The high I concentrations in groundwaters from carbonate aquifers are illustrated by the Chalk aquifer of the London basin and the Jurassic Lincolnshire Limestone (Figure 2.2), where median I concentrations are  $32 \mu\text{g l}^{-1}$  and  $30 \mu\text{g l}^{-1}$  respectively and I/Cl (weight) ratios are  $5.85 \times 10^{-4}$  and  $2.86 \times 10^{-4}$  respectively, values far higher than for groundwaters in non-carbonate aquifers in the UK.

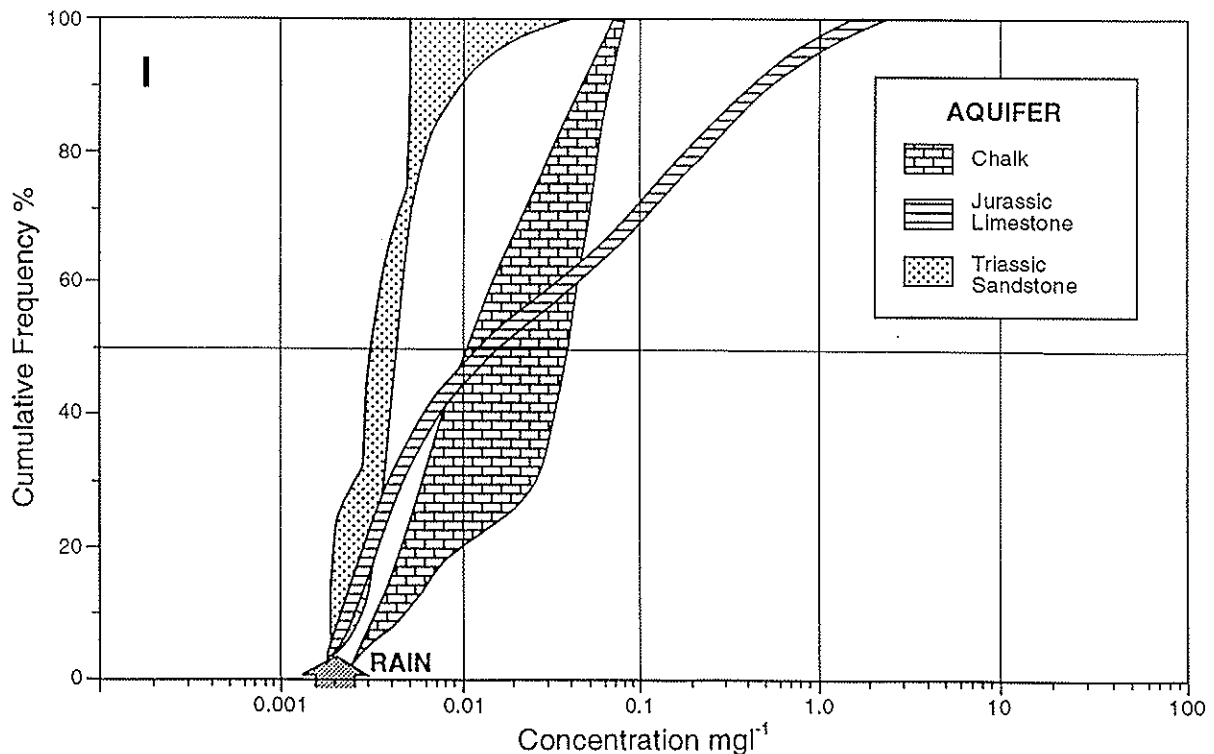
The principal natural source of I is seawater (mean value  $58 \mu\text{g l}^{-1}$ ; Fuge and Johnson, 1986), but additional sources are formation waters, fluid inclusions and volcanic emanations. Iodine concentrations in the environment are increased by man's activities. Iodine is used in herbicides, fungicides, sterilants, detergents, pharmaceuticals and the food industry. It is also released from fossil fuels during combustion and from car exhausts and sewage.

The geochemical cycle of I involves volatilisation 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 and 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 and Johnson, 1986). Whitehead (1979) found a range of 0.5–98.2 mg kg<sup>-1</sup> (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 fertiliser (Whitehead, 1984).

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 iodised 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 about 70 µg l<sup>-1</sup>, depending on location, topography and rainfall pattern. The mean river-water concentration has been given by Fuge and Johnson (1986) and Fuge (1989) as 5 µg l<sup>-1</sup>. Concentrations much below this value are frequently found to be goitrous. Areas remote from the coast tend to have lower I concentrations and indeed, goitre prevalence is relatively high in many continental compared to coastal areas. It has frequently also been associated with mountainous areas, especially the Alps, Himalaya and Andes (Fuge, 1987). Day and Powell-Jackson (1972) for example described goitrous areas of Nepal with drinking-water I concentrations of < 1 µg l<sup>-1</sup>.



**Figure 2.2.** Iodine concentrations in UK groundwaters from the Chalk, Jurassic Limestone and Triassic Sandstone. Only carbonate rocks contribute I from water-rock interaction, over and above rainfall inputs.





**Plate 2.3.** Goitre (enlargement of the thyroid gland) is still common in many parts of the developing world. This is one example from northern Ghana.



**Plate 2.4.** Young boys with dental fluorosis due to high F concentrations in drinking water, Sri Lanka.

The relationship between dietary I deficiency and endemic goitre is one of the most clear-cut environmental health associations known. Nonetheless, many workers have postulated other factors contributory to the development of the disorder, such as dietary goitrogens (thiocyanate, thiouracil, e.g. Ekpechi, 1967) and synergistic effects of other inorganic constituents such as F (e.g. Wilson, 1941), Ca, Mg, Mo, As, Co and Zn (Fuge, 1987; Stewart, 1990). Iodine represents the single most important factor and only in I-deficient areas are other factors likely to be involved in development of the disease. Remediation through dietary supplement is generally effective such that goitre now remains largely a political rather than a geochemical problem. Further discussion of I and its relationship with human health is given in Volume 2 (Smedley et al., 1995b) and a case study from the Bolgatanga area of northern Ghana is described.

### 2.3.5 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 ( $K_s$ ). The two elements of particular interest from a health viewpoint are F and Ba.

#### Fluorine

An extensive literature exists on the occurrence of F in natural waters, both in industrialised and developing countries. This is because it is a fairly common trace element and its health effects have been recognised 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. At higher concentrations, chronic exposure can result in dental fluorosis (mottled enamel; Plate 2.4) or skeletal fluorosis (Rajagopal and Tobin, 1991). Concentrations above which these become problematic are around  $1.5\text{--}2 \text{ mg l}^{-1}$  and  $4 \text{ mg l}^{-1}$  respectively (Table 2.4), although poor nutrition is also recognised as an important additional 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  $1.5 \text{ mg l}^{-1}$  (Table 2.1). Many millions of people throughout the developing world are drinking water with F concentrations in excess of this limit and dental fluorosis probably represents the single most important health problem related to inorganic water quality globally today.

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 (toothpastes, mouth washes), increased dietary F, improved dental health education and reduced sugar intake.

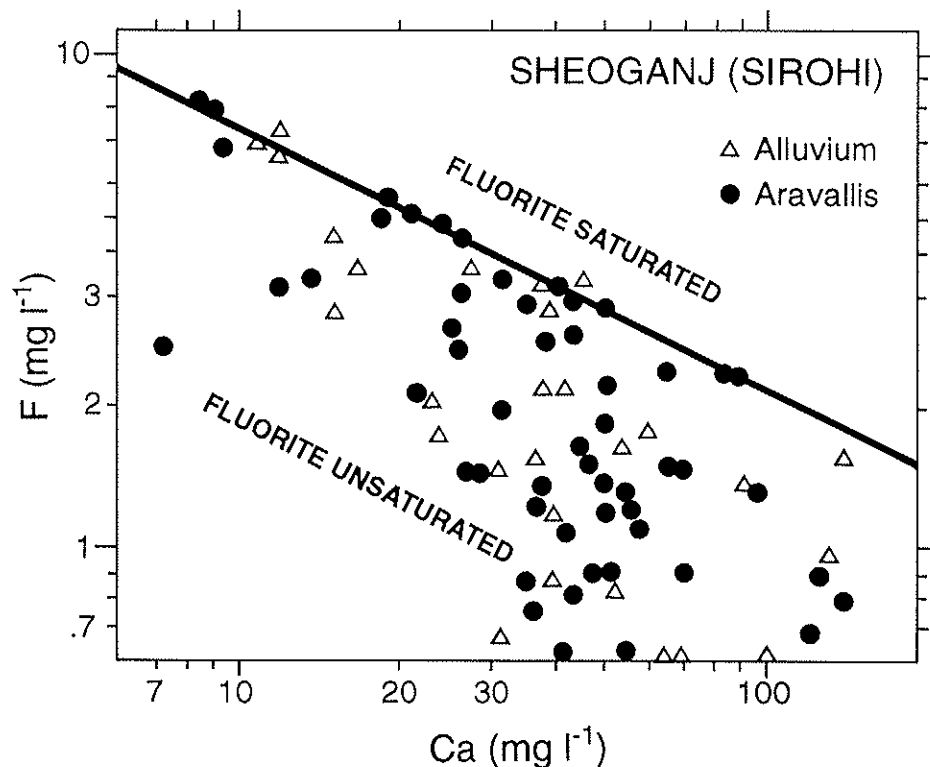
The average crustal abundance of F is  $300 \text{ mg kg}^{-1}$  (Tebbutt, 1983). Fluorite ( $\text{CaF}_2$ ) is the most common F-bearing mineral but it is also present in apatite ( $\text{Ca}_5(\text{Cl},\text{F},\text{OH})(\text{PO}_4)_3$ ) and topaz ( $\text{Al}_2(\text{SiO}_4)(\text{OH},\text{F})_2$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

**Table 2.4.** Impact of fluoride in drinking water on health (from Dissanayake, 1991).

Concentration of fluoride (mg l <sup>-1</sup> )	Impact on health
Nil	Limited growth and fertility
0.0-0.5	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

volcanic glasses), geothermal fluids and granitic rocks. Thermal, high-pH waters may 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 stabilised (ca. pH 3.5; Hem 1985). Fluorine readily forms complexes with Al, Be, Fe<sup>3+</sup>,



**Figure 2.3.** Fluoride concentration in groundwaters from Rajasthan, India showing fluorite solubility control (from Handa, 1975).

**Table 2.5.** Fluoride concentrations in some Tanzanian waters (from Bugaisa, 1971).

Locality	F (mg l <sup>-1</sup> )
Shinyanga	3.0
Bahi swamp	26.6
Bahi depression	123
WDD Yard, Arusha	3.5
Wembere, Singida	26.5
Wembere	27.0–34.0
Mbutu, W. Wembere, Nzega	34.0
North Chubi	80.0
Ikasi, Dodoma	25.0
Oldonya Narok	11.0
Igombe, Tabora	2.9

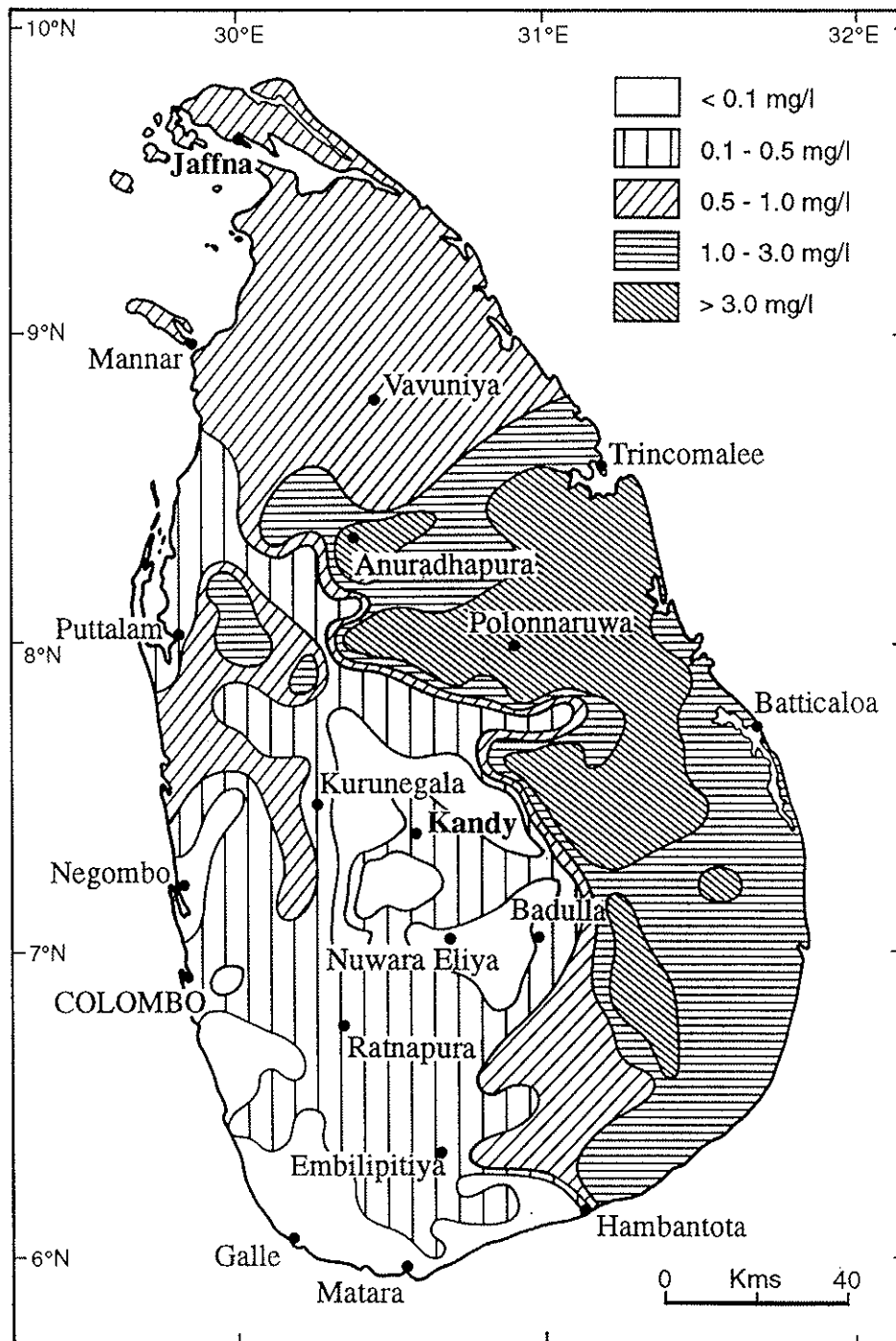
B and Si. Concentrations of F in water are limited by fluorite solubility, such that in the presence of  $10^{-3}$  M Ca, F should be limited to  $3.1 \text{ mg l}^{-1}$ . It is therefore the absence of Ca in solution which allows higher concentrations of F to be stable. Figure 2.3 shows the negative correlation observed between Ca and F in groundwaters from Rajasthan, India (from Handa, 1975). High F concentrations may therefore be expected in groundwater in Ca-poor aquifers and in areas where F-rich minerals are common. Fluoride concentration will also increase in groundwaters where cation exchange of Ca for Na takes place (Handa, 1975).

In many developing countries, high F concentrations have been reported in association with rifts and other volcanic zones as well as granitic (Ca-poor) basement rocks (Hadwen, 1975; Bugaisa, 1971; Kilham and Hecky, 1973; Nanyaro et al., 1984). High F concentrations are noted in the Kenyan part of the East African Rift (Ockerse, 1953; Gaciri and Davies, 1993), Tanzania (Bugaisa, 1971; Table 2.5) and in Uganda (Møller et al., 1970). Concentrations in Rift-Valley waters are often in excess of  $10 \text{ mg l}^{-1}$ .

In India, Teotia et al. (1981) noted that endemic fluorosis affects nearly 1 million people, the high concentrations of dissolved fluoride in drinking water resulting from dissolution of fluorite, apatite, phosphorite and topaz in the bedrocks. Dissanayake (1991) found concentrations of F in the Dry Zone of Sri Lanka up to  $10 \text{ mg l}^{-1}$  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 (Figure 2.4). 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 and Helmer, 1991), Ghana (UN 1988, Amoah 1990, Smedley et al., 1995b), Ivory Coast (especially in granitic areas; Akiti et al., 1990), Thailand (Ramnarong, 1991) and China (Zhaoli et al., 1989).





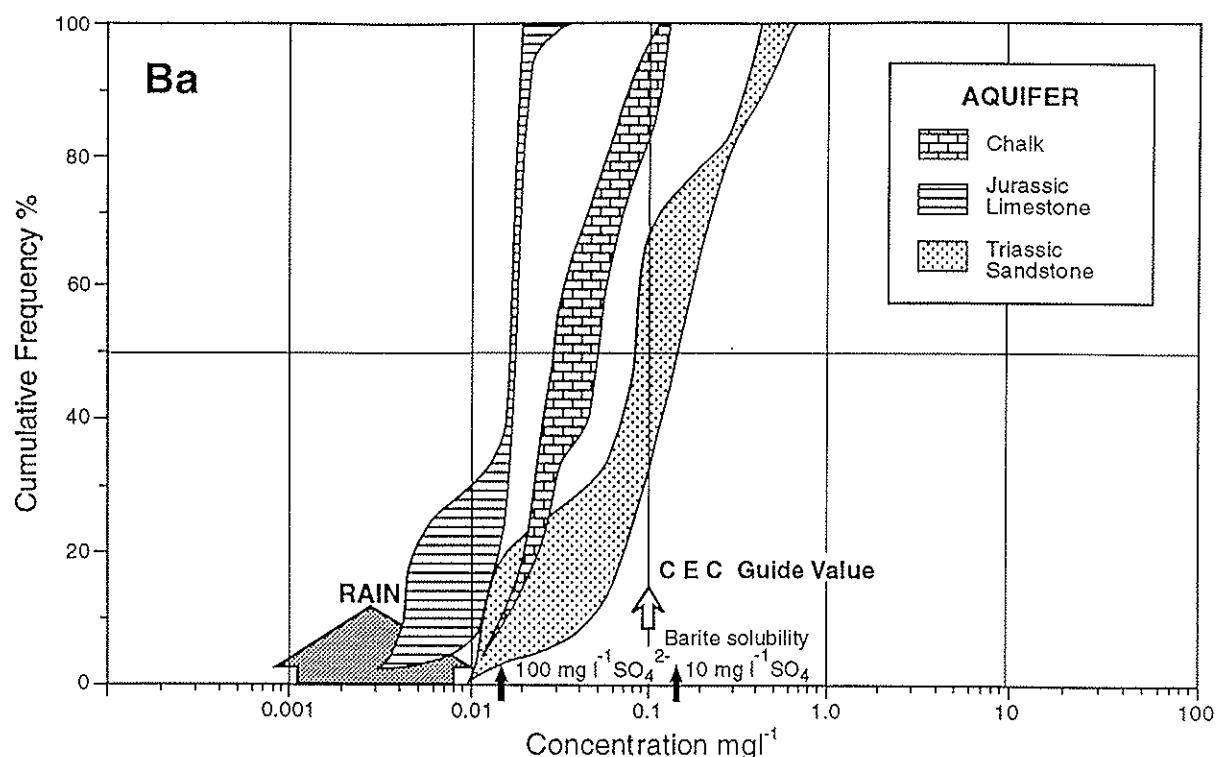
**Figure 2.4.** Distribution of F in groundwater from dug wells in Sri Lanka (from Dissanayake, 1991).

Fluoride occurrence in groundwater and its relationship with prevalence of fluorosis is discussed in more detail in Smedley et al. (1995b and 1995c, Volumes 2 and 3), where case studies of F-rich groundwater in northern Ghana and the Anuradhapura area of Sri Lanka are given.

## Barium

Barium occurs as a minor element in many rock types, although it is most abundant in acid igneous rocks. It is readily released during rock weathering but dissolved concentrations are controlled by the solubility of barite. Concentrations of Ba in natural waters should therefore be inversely proportional to  $\text{SO}_4$  concentrations. High Ba 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 WHO give a guideline maximum value for Ba in drinking waters of  $0.7 \text{ mg l}^{-1}$  (Table 2.1).

The concentration of Ba rarely exceeds  $1 \text{ mg l}^{-1}$  in natural waters (Edmunds et al., 1989). Median concentrations in waters undersaturated with respect to barite tend to be highest in groundwaters from non-carbonate aquifers (Figure 2.5) and this reflects the lower geochemical abundance in carbonate rocks and the higher Ba concentrations in silicate minerals such as K-feldspar.



**Figure 2.5.** Barium concentrations in groundwater from UK aquifers (Chalk, Jurassic Limestone, Triassic Sandstone). The Ba concentrations in rain and in groundwaters at saturation with  $10 \text{ mg l}^{-1}$  and  $100 \text{ mg l}^{-1}$   $\text{SO}_4$  are also shown. Note that highest concentrations of Ba occur in sandstone aquifers.

### 2.3.6 Other elements

#### Lead

Lead is a cumulative poison. Chronic exposure through ingestion or inhalation can initiate tiredness, irritability, anaemia, behavioural changes and impairment of intellectual functions in affected patients (Tebbutt, 1983). Principal sources include drinking water (from oxidation of natural galena (PbS) or other sulphide minerals or by corrosion of Pb pipework), food or inhalation of air polluted by smelting operations or motor-vehicle exhaust fumes. An extensive literature exists on Pb in the environment and its health effects (e.g. Englert and Höring, 1994). 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.

The average crustal abundance of Pb is  $16 \text{ mg kg}^{-1}$ , principally in association with sulphide minerals. Solubility in water is controlled strongly by pH and alkalinity, mobility being greatest under acidic, low-alkalinity conditions. Under near-neutral pH conditions in the presence of carbonate, mobility is restricted by the precipitation of  $\text{PbCO}_3$  (cerussite; Hem, 1985).

The revised WHO recommended limit for Pb in drinking water is rarely exceeded, but a few exceptions have been documented. Ramnarong (1991) for example, cites a case in Thailand, where 5 out of 10 patients died in 1979. Water from the local well was found to contain  $53.5 \text{ mg l}^{-1}$  Pb and soils contained  $0.13\text{--}4.92 \text{ mg l}^{-1}$  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 pollution sources. It is usually associated with zinc ores and may be present in volcanic emissions and released from vegetation (Robards and 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, metal fabrication and finishing. It is also released during the smelting of copper ores and from sewage sludge (Nicholson et al., 1983). Cadmium is highly toxic, acute toxicity producing symptoms such as giddiness, vomiting, respiratory difficulties, cramps and loss of consciousness. Chronic exposure to the metal can lead to anaemia, anosmia (loss of sense of smell), cardiovascular diseases, hypertension, renal problems, osteomalacia and osteoporosis (Mielke et al., 1991; Robards and Worsfold, 1991; Kasuya et al., 1992). Chronic Cd poisoning of a population in Toyama Prefecture, Japan, resulting from pollution from a nearby Zn mine, has given rise to Itai-itai disease, characterised particularly by renal tubular dysfunction, decrease in bone mass and severe bone pain (Kasuya et al., 1992). 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). Cadmium 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 and minewaters. Endemic Cd poisoning observed in Toyama Prefecture resulted from consumption of rice grown in irrigation water from the local mining

effluent (Robards and 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. Cadmium may also be adsorbed 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 for 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.

### 3 CONCLUSIONS

An enormous literature exists on the topic of environmental geochemistry and health. This report does not attempt to review all aspects of the subject as many chemical elements and health problems are involved and the relationships between them are often highly complex. Other potentially harmful dissolved constituents in some groundwaters not mentioned here include U, Sb, Th, CN, Hg, Ni and Cr. However, some of the most important and well-documented associations are outlined. The most important health-impacting inorganic constituents in drinking water are considered to be F, As and I. As a result, endemic fluorosis, arsenosis and goitre affect many millions of people throughout the developing world.

It is clear that health relates not only to excesses of trace elements in drinking-water supplies, but also to deficiencies. With many elements (e.g. I, F, Se, Mn), health depends upon a delicate balance between the two. Geochemical associations are frequently complicated by the fact that drinking water is not the only dietary source of inorganic compounds. Relationships may also be masked by the effects of other elements. *In-vivo* competition between different elements can for example, either exacerbate health problems or effect some form of protection. Examples include the protective effects of Fe, Cu and Zn on Cd toxicity (Underwood, 1979), the mitigating effects of K on Na in development of hypertension, or the exacerbating effects of Ca and Mg deficiency on high Mn in relation to Guamanian amyotrophic lateral sclerosis; Foster, 1992). However, investigation of drinking water may 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. Aluminium, Be, Pb, Cd, Fe and Mn for example are preferentially mobilised under acidic conditions. Arsenic (along with Fe and Mn) may be more mobile under reducing conditions, whilst Se and U are mobilised in oxidising environments. Fluoride is most soluble 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 from 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.

From the practical point of view, some conclusions may be drawn in relation to studies connected with rural water schemes. Eradication of the effects of I deficiency is best achieved in vulnerable areas by the administration of dietary I supplements. This is an effective method if the disorder is identified sufficiently early, but education is still lacking in many developing countries and this needs to be stepped up if reduction of the prevalence of endemic goitre is to be achieved. The problem of As in water, which is mainly related to sulphide oxidation, can be minimised by preventing mineral oxidation through good aquifer-

or mine-management practice (e.g. avoiding overabstraction of groundwater or aeration of mine workings and tailings). Fluoride, the other area of major concern, is difficult to manage, although groundwater with shorter residence times in F-rich aquifers should in general be more likely to contain lower fluoride concentrations. Those responsible for development schemes must be aware of the geochemical provinces likely to give rise to problems. Furthermore, there is a tendency in many aid schemes to specify a blanket borehole depth and design, regardless of local geochemical and environmental conditions and to complete boreholes to that specification. As far as Fe and Mn are concerned, if concentrations are too high, villagers will abandon the offending water sources. In the case of F and As, the health impact is more intangible and their consequences are often realised too late. It is therefore most important that when large wellfields are planned, a pilot investigation of the water quality is carried out first.

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 clinical studies and it is recognised 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 data bases are an essential component in epidemiological studies.

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