BRITISH GEOLOGICAL SURVEY
Natural Environment Research Council

TECHNICAL REPORT

Hydrogeology Series

Technical Report WD/92/39

Relationships between Trace Elements in Water and Health, with Special Reference to Developing Countries INTERIM REPORT 1992

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This report was prepared
for the Overseas
Development Administration

Bibliographic Reference

Author, P L Smedley 1992
Relationships between Trace
Elements in Water and Health,
with Special Reference to
Developing Countries:
INTERIM REPORT 1992.
British Geological Survey
Technical Report WD/92/39

Keyworth, Nottinghamshire British Geological Survey 1992

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PREFACE

The provision of safe drinking water for communities in developing countries is an ever-increasing concern. Health problems related to drinking water are well known throughout the world but particular problems occur in developing nations less able to ameliorate and manage the quality of water supplies. Much emphasis has been placed on deterioration of water quality as a result of anthropogenic pollution (e.g. faecal and total coliforms, nitrate and other nitrogen species) but rather less on investigations of quality problems resulting from entirely natural processes of water-rock interaction. These can themselves lead to the introduction of certain trace elements and microbes in undesirable quantities into groundwater supplies. With this in mind, the Overseas Development Administration has commissioned BGS to carry out an investigation in selected developing countries of groundwater-quality problems resulting from natural geochemical processes. This review provides a background for the project which is to run over a three-year period. The first stage of subsequent investigations will be carried out in Ghana, West Africa, where vulnerability of shallow groundwater to natural pollutants is already known to be a problem in several areas. For this reason, special emphasis has been placed on Ghana in the review.

EXECUTIVE SUMMARY

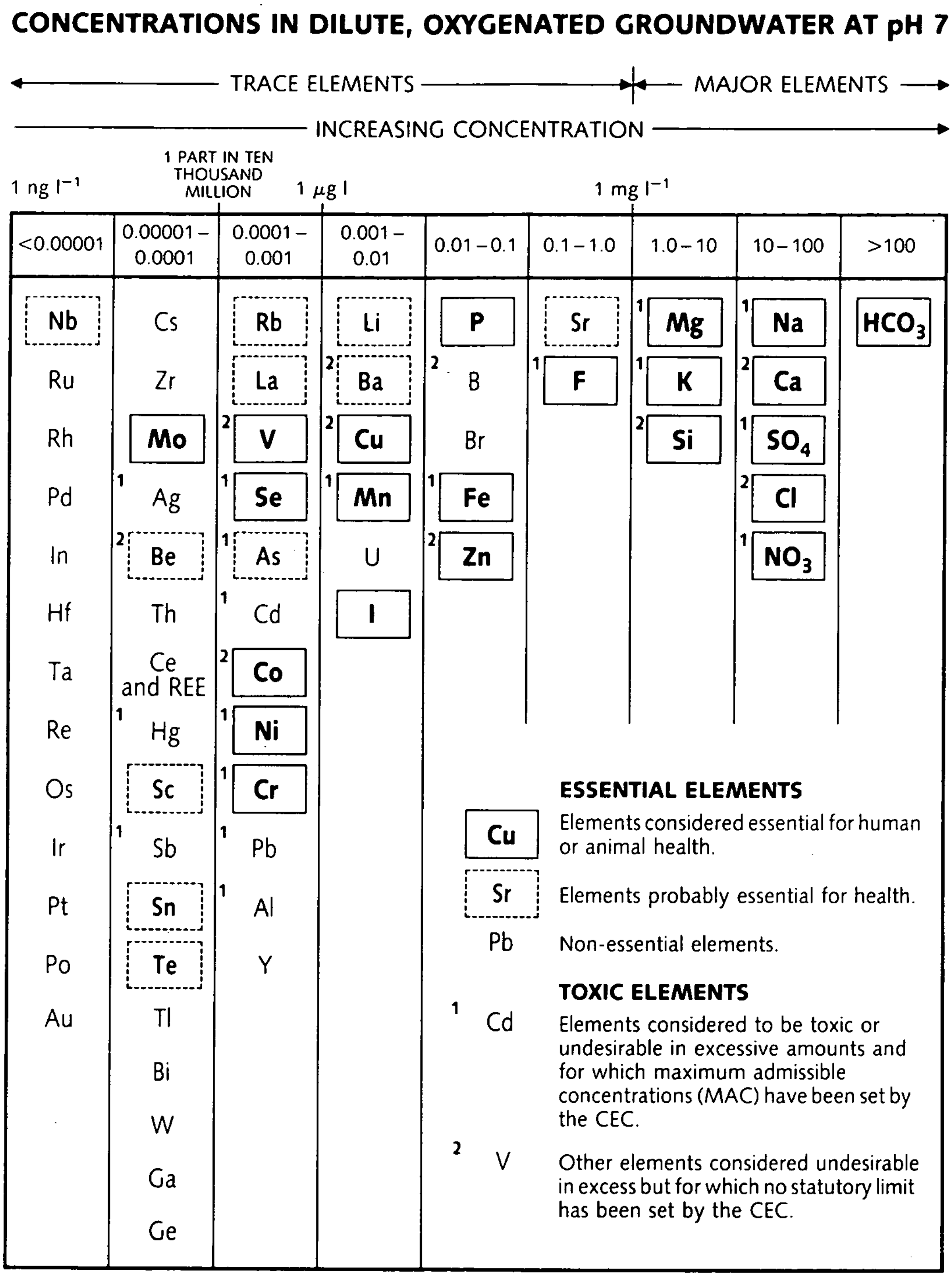
Many chemical constituents of drinking water are known to be potentially detrimental to human and animal health. Many, such as some pathogenic bacteria and nitrate, have an anthropogenic source but others may occur naturally as a result of water-rock interaction processes. The links of aluminium (Al) with Alzheimers disease, soft water with cardiac problems, iodine (I) deficiency with goitre and fluoride (F) with fluorosis or dental caries are good examples. Other problematic elements include lead (Pb), cadmium (Cd), mercury (Hg), uranium (U), arsenic (As) and selenium (Se). All these constituents are toxic if ingested in large doses but effects detrimental to health have also been observed at concentrations well within the range of natural waters. Indeed, in the case of elements such as I, Se and F, it is deficiency rather than excess which can promote a health risk.

Trace-element concentrations vary greatly according to the local physico-chemical environment. Some elements are especially mobile in acidic water (e.g. Al, Pb, Cd, Hg, Fe and Mn), some in reducing water (As, Fe and Mn), others in oxidising water (e.g. Se, U). F is found in extensional rift zones, geothermal areas and in groundwaters with low Ca concentrations. Potentially goitrous I concentrations have been detected all over the world but are most prevalent in central continental and mountainous terrains, although low I concentrations have also been observed in some limestone areas.

Many shallow groundwaters are vulnerable to geochemical processes which can produce potentially harmful drinking-water supplies. However, those in hard-rock low-carbonate aquifers which have little or no acid-buffering capacity can be most vulnerable with respect to parameters such as pH, soft water and low Ca (hence high F concentrations). Moreover, hard-rock terrains cover an appreciable part of the developing world and therefore investigations of selected areas have significance and application elsewhere. Ghana has been selected as a suitable area for a first investigation of the relationships between trace elements and human health. Here, Precambrian metamorphic rocks and granite comprise about 45% of the land area and incidences of acid water as well as high levels of Fe, F, Pb and some low I concentrations have been found. Pollution from anthropogenic sources is also known to be a problem.

1. INTRODUCTION

At a UN-ESCAP Expert Group Meeting on groundwater quality in the Asia and Pacific region held at Bangkok in 1991, it emerged that the main concern for these nations is no longer the lack of water resources, but the lack of good quality water resources. This is not surprising given that about 80% of illnesses in developing countries are related to poor water quality (Tebbutt, 1983). The spread of water-borne diseases due to anthropogenic pollution remains the most important cause of illness and mortality in the developing world. However, water quality relates not only to direct health effects but also to user acceptability. Most complaints concerning quality relate to organoleptic parameters such as taste, odour and turbidity which may not in themselves be detrimental to human health but nonetheless lead to rejection of such sources. The two most important natural water quality problems in developing countries are excesses of iron and salinity. Whilst ingestion of dissolved iron does not present any known health risks, the metallic taste, discolouration and smell that it can impart to groundwater if present in high concentrations (1 mg l^{-1} or greater) leads to its abandonment in favour of alternative (surface water) sources which are frequently polluted with faecal and other bacteria. Other chemical constituents relevant to human and animal health include As, Pb, Al, I, F, Mn, Se, Cd, CN, U and Th (see also Figure 1). Many of these are present in groundwater as a result of natural geochemical processes but may be enhanced by human activity (industry, mining, agriculture and urbanisation) over geochemically-sensitive terrain. Clearly it is desirable to find groundwater sources with optimal levels of these constituents but if water of better quality is not available, suitable remediation measures need to be taken. This report presents a review of current knowledge of the effects of some of these constituents on human health as well as an outline of the geochemical processes that control them. Reference is made to some specific areas in the developing world where trace elements present a health risk but an overall lack of reliable data for many of the elements listed above prevents detailed analysis of the scale of the problem.



<0.00001	0.00001 – 0.0001	0.0001 – 0.001	0.001 – 0.01	0.01 – 0.1	0.1 – 1.0	1.0 – 10	10 – 100	>100
Nb	Cs	Rb	Li	P	Sr	[1] Mg	[1] Na	HCO_3
Ru	Zr	La	[2] Ba	[2] B	[1] F	[1] K	[2] Ca	
Rh	Mo	[2] V	[2] Cu	Br		[2] Si	[1] SO_4	
Pd	[1] Ag	[1] Se	[1] Mn	[1] Fe			[2] Cl	
In	[2] Be	[1] As	U	[2] Zn			[1] NO_3	
Hf	Th	[1] Cd	I					
Ta	Ce and REE	[2] Co						
Re	[1] Hg	[1] Ni						
Os	Sc	[1] Cr						
Ir	[1] Sb	[1] Pb						
Pt	Sn	[1] Al						
Po	Te	Y						
Au	Tl							
	Bi							
	W							
	Ga							
	Ge							

ESSENTIAL ELEMENTS

Cu	Elements considered essential for human or animal health.
Sr	Elements probably essential for health.
Pb	Non-essential elements.

TOXIC ELEMENTS

[1] Cd	Elements considered to be toxic or undesirable in excessive amounts and for which maximum admissible concentrations (MAC) have been set by the CEC.
[2] V	Other elements considered undesirable in excess but for which no statutory limit has been set by the CEC.

Figure 1. Concentration ranges of trace elements in groundwater and their significance to health and environmental protection (from Edmunds et al., 1989).

2. RELATIONSHIPS BETWEEN WATER QUALITY AND HUMAN HEALTH

2.1 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. Lacey (1981) for example found a decrease of about 8% in male cardiovascular mortality rate per 100 mg l^{-1} hardness in the range up to 170 mg l^{-1} in a study of some UK urban water supplies. 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. Since water hardness also affects solubility of other trace metals such as Pb and Cu, it may have additional indirect health consequences (Underwood, 1979). Day and Powell-Jackson (1972) also suggested that a link exists between water hardness and the occurrence of endemic goitre in village communities in Nepal.

2.2 Acid Water

The production of acid groundwater may result either from natural processes such as flow through carbonate-poor rocks (e.g. granite) or pyrite oxidation, or from anthropogenic pollution (e.g. acid rain). Acid water is not in itself thought to be a health risk but since many minerals are more soluble in acid water, toxic trace metals (e.g. Al, Pb, Cd, Hg) may be present in higher concentrations.

Acid groundwaters are common in many parts of Africa, Asia and South America as granitic basement rocks with little acid-buffering capacity comprise much of the area. High trace metal contents of such waters are likely to occur as a result. Acidic water is, for example, documented in south-western Ghana (Figure 2); Langanegger (1991) found that 76% of groundwater samples from Ghana had pH <7, 45% being below 6.5.

2.2.1 Aluminium (Al)

The WHO maximum admissible concentration for Al in drinking water is 0.2 mg l^{-1}. Al is a major element in alumino-silicate minerals and is therefore a common constituent of most rocks. However, it is usually only found in high concentrations in water with $pH < 5.5$ (Hem, 1985). The occurrence of high Al in drinking water has recently been linked to the development of Alzheimers disease. Martyn et al. (1989) found that the risk of Alzheimers disease was 1.5 times greater in parts of England and Wales where the mean Al concentration is greater than 0.11 mg l^{-1}. Most studies related to Al toxicity have been carried out in the developed world in relation to acidification by acid rain. However, some high-Al problems have recently been reported in developing countries (e.g. Davies, 1992).

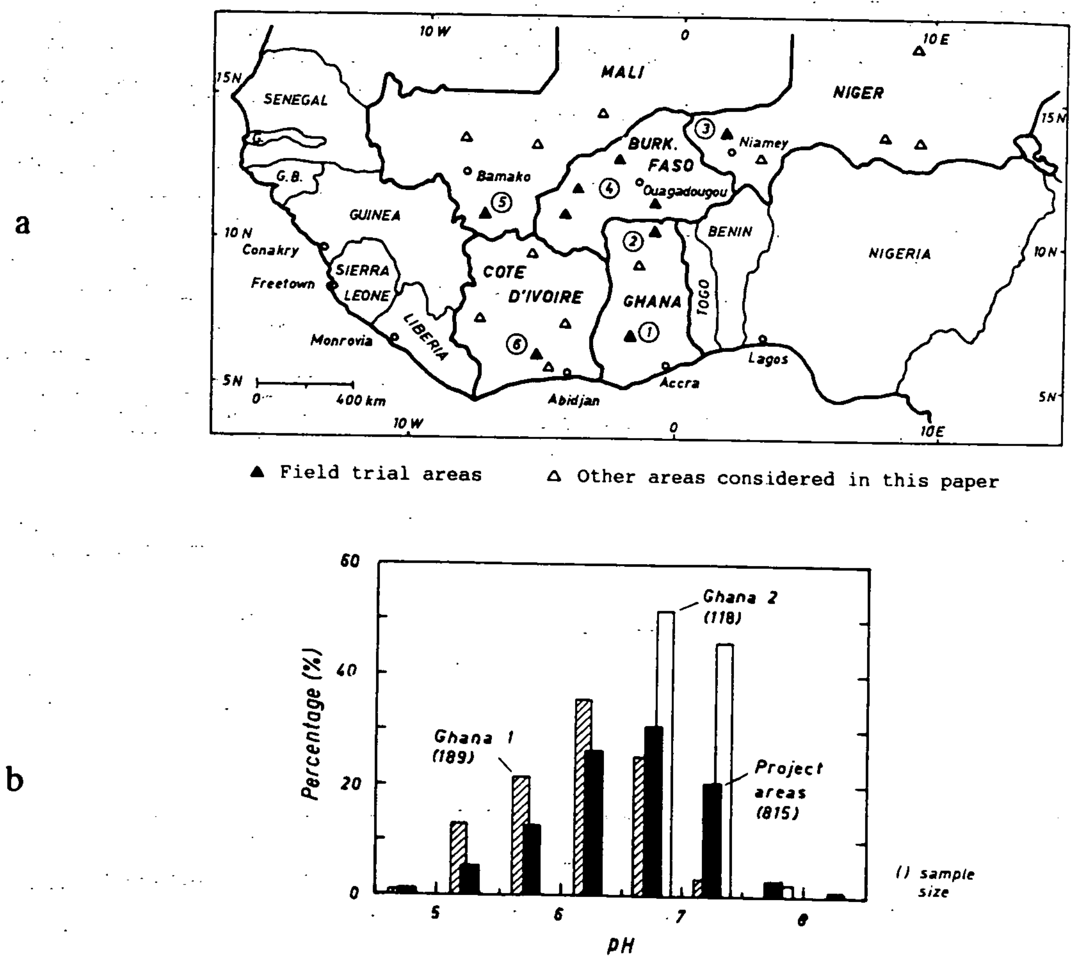


Figure 2. a. Map of groundwater-quality study areas considered by Langanegger (1991) in West Africa.

b. Distribution of pH in two of the study areas in Ghana.

Aluminium in drinking water forms only a small part of the total daily intake but because it is usually uncomplexed, 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 more harmful source than food (Martyn et al., 1989).

2.2.2 Beryllium (Be)

Relatively little is known about the epidemiology of Be and of its concentration in drinking water and the environment. However, it is known to be toxic at industrial exposure levels (Griffiths et al., 1977). Beryllium is known to be quite insoluble in water, being present in beryl and bertrandite ($Be_4Si_2O_7(OH)_2$) and concentrated in residual deposits of silicic volcanic rocks (Brookins, 1988). It is especially mobilised in acidic conditions, being present as dissolved Be^{2+} at pH < 5.5 (Edmunds and Trafford, 1992) but as insoluble BeO at higher pH (Brookins, 1988). No WHO guide level has been set for Be in drinking water.

2.2.3 Lead (Pb)

Lead is present as a major element in galena (PbS) and is a common constituent in hydrothermal mineral veins. Its average crustal abundance is 16 ppm. Pb is also produced from smelting, motor vehicle exhaust fumes and from corrosion of lead pipework. Pb solubility is controlled principally by $PbCO_3$, such that 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 $\mu g\ l^{-1}$, to 10 $\mu g\ l^{-1}$, the limit having been imposed as a result of its acute toxicity. It is also a cumulative poison, initiating tiredness, irritability, anaemia, behavioural changes and impairment of intellectual functions in affected patients (Tebbutt, 1983). Lead poisoning is likely to be a greater problem in industrialised nations where environmental Pb levels are higher, but Pb poisoning has also been recognised elsewhere. Ramnarong (1991) for example cites a case in Rayong Province, Thailand, where 5 out of 10 patients died in 1979. Water from the local well was found to contain 53.5 mg l^{-1} Pb and soils contained 0.13-4.92 mg kg^{-1} as a result of pollution from leachate derived from a local refuse dump. Pelig-Ba et al. (1991) also reported high natural Pb (and Cr) concentrations (Pb around 0.15 mg l^{-1}) in acid water from granitic terrains in Ghana.

2.2.4 Cadmium (Cd)

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 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 and 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 hypertensions (Mielke et al., 1991; Robards and Worsford, 1991). There is also evidence that increased Cd intakes 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 by inhalation. Drinking water should have lower Cd concentrations unless water sources are affected by volcanic exhalations, landfill leachate and mine waters. Evidence of endemic Cd poisoning was for example found in Toyonia Prefecture, Japan, which resulted from consumption of rice grown in irrigation water from local mining effluent (Robards and Worsfold, 1991).

The WHO limit for Cd in drinking water is 5 μg 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 $CdCO_3$ (Hem, 1985) and the element 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.

2.2.5 Mercury (Hg)

The only mineral containing Hg in large quantities is cinnabar (HgS), which occurs principally in hydrothermal mineral veins and in areas of volcanic activity. Hg in the environment is greatly increased by industrial operations such as battery manufacture, fossil fuel combustion, seed dressing, metal smelting and cement production (Tebbutt, 1983). Intake from food is in the range 10-12 μg per day, probably much greater than that from drinking water. There is also evidence that methyl mercury (the main species found in fish) is potentially more toxic than inorganic forms of the element (e.g. Underwood, 1979). Little is known about concentrations of Hg in water in developing countries. The WHO recommended limit for Hg is 1 μg l^{-1}.

2.2.6 Iron (Fe) and Manganese (Mn)

Whilst these elements have no known toxicological effects, indeed Fe is a necessary element in the production of haemoglobin, water with high concentrations may be unpalatable due to taste, odour, discolouration and staining of laundry and food (Gale and Smedley, 1989). The solubility of Fe and Mn is greater at low pH and acid water may contain several mg l^{-1} of Fe and Mn. Both elements are also more soluble under reducing conditions, although the solubility is limited by sulphide (for a fuller account of the mobility of Fe in groundwater, see Gale and Smedley, 1989).

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. Fe problems are reported for example in parts of India (e.g. Smedley, 1991), Bangladesh (Mawla, 1991), Malawi (Lewis, 1986), Ghana (UN, 1988; Pelig-Ba et al., 1991), Thailand (Ramnarong, 1991) and Sri Lanka, Malaysia, Vietnam and Indonesia (Lawrence and Foster, 1991). Most Fe problems probably relate to dissolution of Fe-bearing minerals under acid and/or reducing conditions but the problem may be exacerbated by corrosion of ferrous casing, pumps and pipework in supply boreholes.

2.3 Arsenic (As)

The crustal average As concentration is 2 ppm (Tebbutt, 1983). Arsenic occurs as a trace element in many rocks and minerals but is especially chalcophile, being present as a major element in sulphide minerals such as orpiment (As_2S_3), arsenopyrite (FeAsS), realgar (AsS) and enargite (Cu_3AsS_4). It is therefore more abundant in hydrothermal sulphide-bearing mineral veins, volcanic deposits, geothermal systems and reducing sediments than in sandstone, limestone, igneous rocks and their metamorphic equivalents. (Table 1 from Welch et al., 1988). Coal may contain about 2000 ppm As (Onishi, 1969) and phosphorite may also be enriched (Table 1).

Environmental levels have increased greatly in recent years (e.g. threefold in ocean water; Ferguson and Gavis, 1972) as a result of pollution from industry and agriculture. Arsenic is commonly used in insecticides, herbicides, crop desiccants, wood preservatives, pharmaceuticals, metallurgical additives and glass (Matisoff et al., 1982) but is also released as a result of smelting, fossil fuel combustion, soil erosion and mining operations (Ferguson and Gavis, 1972; Belzile, 1988).

Arsenic is toxic and carcinogenic. Chronic exposure can produce lung and skin cancer, hyperpigmentation, keratosis and peripheral vascular disorders (Matisoff et al., 1982), although toxicity to humans 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 oxidised 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). Arsenite is reputed to be about 60 times more toxic than arsenate (Ferguson and Gavis, 1972).

Table 1. Arsenic concentrations in rocks (from Welch et al., 1988 and references therein).

Rock type	As (ppm)
Igneous	
Peridotite, dunite, serpentinite	0.3-15.8
Basalt	0.18-113
Gabbro	0.06-28
Latite, andesite, trachyte	0.5-5.8
Diorite, granodiorite, syenite	0.09-13.4
Rhyolite	3.2-5.4
Granite	0.18-15
Metamorphic	
Quartzite	2.2-7.6
Slate/phyllite	0.5-143
Schist/gneiss	0-18.5
Sedimentary	
Nearshore shale/clay	4.0-25
Offshore shale/clay	3.0-490
Carbonate	0.1-20.1
Phosphorite	0.4-188
Sandstone	0.6-9
Freshwater shale	3.0-12
Freshwater clay	3.0-10

Arsenic intake by humans is probably greater from food (e.g. seafood) and inhalation than from drinking water but the latter represents by far the greatest hazard as the species present in water are more toxic than those organically bound in flesh (Ferguson and Gavis, 1972). The WHO recommended limit for As in drinking water is 50 $\mu g\ l^{-1}$ but a reduction to 15 $\mu g\ l^{-1}$ is under consideration.

Arsenic species in aqueous systems consist principally of arsenite ($H_nAsO_3^{3-n}$) and arsenate ($H_nAsO_4^{3-n}$) oxyanions. The reduced forms are mainly responsible for chronic arsenosis. Under reducing conditions in the presence of sulphide, As is largely insoluble and is precipitated as orpiment, realgar or arsenopyrite, although at low pH the aqueous species $HAsS_2$ may be present.

In organic-rich waters, biomethylation of As may take place with the production of species such as methane arsenic acid ($CH_3AsO(OH)_2$), dimethylarsenic acid ($(CH_3)_2AsOOH$), dimethylarsine ($(CH_3)_2AsH$) and trimethylarsine ($(CH_3)_3As$).

Arsenic is strongly sorbed onto, or co-precipitated with, ferric hydroxide ($Fe(OH)_3$), 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 $Fe(OH)_3$ is more soluble at low Eh. Many studies of groundwater and sediments have detected correlations between As concentration and both $Fe(OH)_3$ and Eh (e.g. Matisoff et al., 1982; Belzile, 1988; Varsányi et al., 1991). Arsenic is also readily sorbed onto aluminium hydroxide ($Al(OH)_3$), except at low pH where Al is more stable in dissolved ionic form.

Not many analyses of As are published for groundwater in developing countries. The few that are reported suggest that high concentrations are associated with mining operations. Ramnarong et al. (1991) for example, note the occurrence of endemic Bowens disease (a form of skin cancer) in Ron Phiburn district, southern Thailand, as a result of high As concentrations derived from arsenopyrite in effluent from local tin mines. Chronic arsenosis has also been reported from similar sources in Taiwan (Tseng et al., 1968) and the southern Andes (Henriquez and Gischler, 1980). In mining areas and especially under reducing conditions, dissolved As concentrations may therefore be relatively high, possibly greater than the WHO recommended limit.

2.4 Selenium (Se)

Trace levels of Se are essential in the diet of humans and animals (e.g. Oldfield, 1972) and Se deficiency may promote a health problem. Muscular degeneration, impeded growth, fertility disorders, anaemia and liver disease may result (Låg, 1984; Peereboom, 1985). However, at high concentrations of 10 mg per day or greater, other problems such as gastro-intestinal ailments, skin discoloration and tooth decay may occur (Tebbutt, 1983). Se toxicity in American Indians has been reported by Beath (1962). There are conflicting reports over the role of Se in the development of cancer, some suggesting that the element is a carcinogen, others claiming that it acts as an anti-cancer agent (e.g NAS, 1976; Underwood, 1979). The WHO recommended limit for Se in drinking water is 10 μg l^{-1} but concentrations in natural water rarely exceed 1 μg l^{-1} (Hem, 1985).

The geochemistry of Se is similar to that of sulphur. It naturally occurs in four oxidation states: 2-, 0, 4+ and 6+. In its 2- state, Se occurs as H_2Se, a highly toxic and reactive gas which readily oxidises in the presence of oxygen. In elemental form (Se^0), Se is insoluble and therefore non-toxic. The element occurs in the 4+ oxidation state as inorganic selenite (SeO_3^{2-}) which is highly toxic. However, under reducing and acidic conditions, selenite is readily reduced to elemental Se (NAS, 1976; Howard, 1977). Oxidising and alkaline conditions favour the stability of the 6+ form, selenate (SeO_4^{2-}), which is highly soluble. Se mobility should therefore be greater in oxidising 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 and Rice, 1989). It may also form the mineral ferroselite ($FeSe_2$) 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 high incidence in China of 'Keshan disease', a chronic endemic cardiomyopathy thought to be related to Se deficiency. 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).

2.5 Fluorine (F)

A large 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 0.7 mg l^{-1} total F, dental caries may result, whilst at higher concentrations (>2 mg l^{-1}), dental fluorosis involving the development of yellow, brown or black staining of the permanent teeth, or skeletal fluorosis (> 4 mg l^{-1}) may occur (e.g. Rajagopal and Tobin, 1991). The effects are incurable. High F concentrations in drinking water have also been linked with cancer (Marshall, 1990). The health effects of fluoride in drinking water are summarised in Table 2.

In the USA and Europe during the 1950s, it was found that introduction of F to toothpaste and fluoridation of public water supplies to a concentration of about 1 mg l^{-1} reduced the incidence of dental caries by more than 50%. However, the benefits of water fluoridation in recent years have been much less pronounced, probably as a result of long-term use of F toothpastes, increased dietary F, improved dental health education and reduced sugar intake (Diesendorf, 1986). The WHO recommended limit for F in drinking water is 1.5 mg l^{-1}.

The average crustal abundance of F is 300 ppm (Tebbutt, 1983). Fluorite (CaF_2) is the most common F-bearing mineral but it is also present in apatite ($Ca_5(Cl,F,OH)(PO_4)_3$) and in trace quantities in amphibole, mica and pyroxene. F occurrence is commonly associated with volcanic activity, (being especially high in volcanic glasses) and geothermal activity. Thermal, high-pH waters have particularly high concentrations.

The principal form of F in water is as free dissolved F^- but at low pH the species HF^0 may be stabilised (at pH 3.5, this may be the dominant species; Hem, 1985). F readily forms complexes with Al, Be, Fe^{3+}, B and Si. Concentrations of F in water are limited by fluorite

Table 2. Impact of fluoride in drinking water on health (from Dissanayake, 1991).

Concentration of fluoride ($mg\ l^{-1}$)	**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

solubility, such that in the presence of 10^{-3} M Ca, F should be limited to 3.1 mg l^{-1} (Hem, 1985). It is therefore the absence of Ca in solution which allows higher concentrations of F

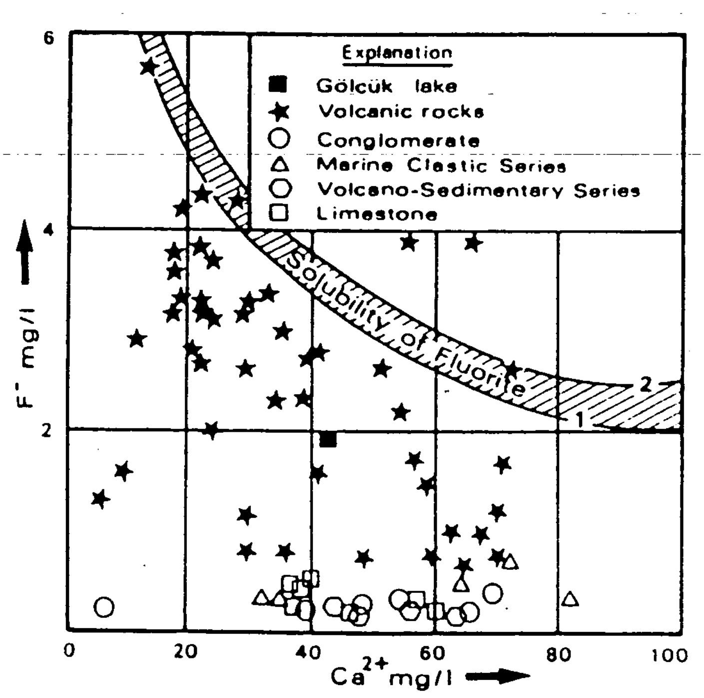
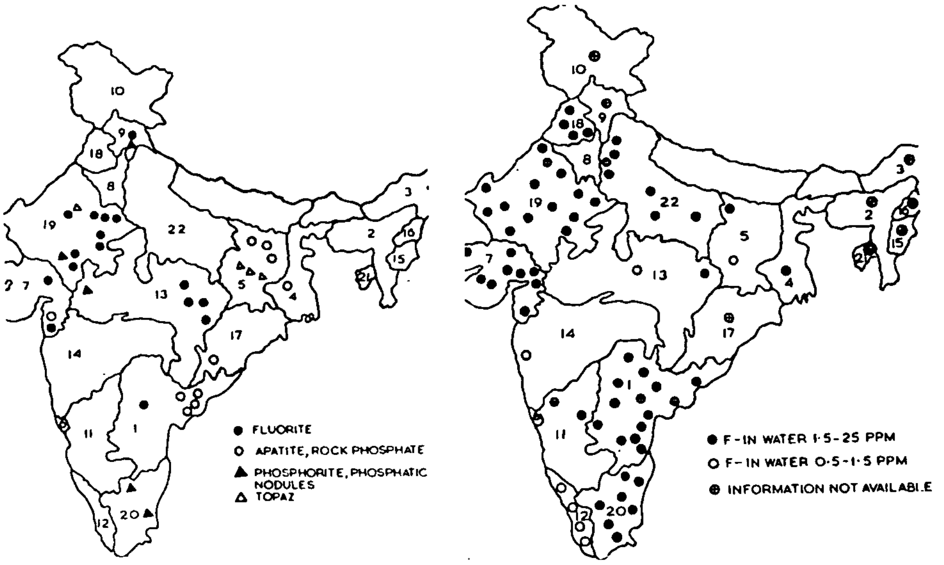


Figure 3. Variation of F with Ca in groundwaters from volcanic and related rocks in Turkey. F concentration is limited by fluorite solubility (from Pekdeger et al., 1991).



1. Andhra Pradesh 2. Assam 3. Arunachal Pradesh 4. Bengal
5. Bihar 6. Goa 7. Gujart 8. Haryana 9. Himachal Pradesh
10. Jammu & Kashmir 11. Karnataka 12. Kerala 13. Madhya
Pradesh 14. Maharashtra 15. Manipur 16. Nagaland 17. Orissa 18. Punjab 19. Rajasthan 20. Tamil Nadu 21. Tripura
22. Uttar Pradesh

Figure 4. Distribution of F-bearing minerals and endemic fluorosis in India (from Teotia et al., 1981).

to be stable (Figure 3). High F concentrations may therefore be expected in groundwater in Ca-poor aquifers and in areas where F minerals are common. F concentration will also increase in groundwaters where cation exchange of Ca for Na takes place, the process being potentially important in carbonate rocks.

In many developing countries, high F levels have been reported in association with rift zones, volcanic rocks and granitic (Ca-poor) basement rocks. Hadwen (1975) for example, noted high F concentrations in groundwaters and especially in hot springs (20-43 mg l^{-1}) in the Ethiopian part of the East African Rift, with resultant physiological damage to local populations. Bugaisa (1971) has reported similar problems in the Tanzanian part of the Rift with concentrations up to 330 mg l^{-1} in hot springs. Some F data for Tanzanian waters are given in Table 3. Nanyaro et al. (1984) also gave data for groundwater and lakes in Tanzania and reported values for F up to 690 mg l^{-1} in some of the lake waters. In a survey conducted by Lewis (1986), about 45% of groundwaters analysed in Tanzania had F concentrations greater than 1 mg l^{-1} and 40% had less than 0.7 mg l^{-1}. High F concentrations are also noted in the Kenyan part of the Rift (Ockerse, 1953; Gaciri and Davies, 1992) and in Uganda

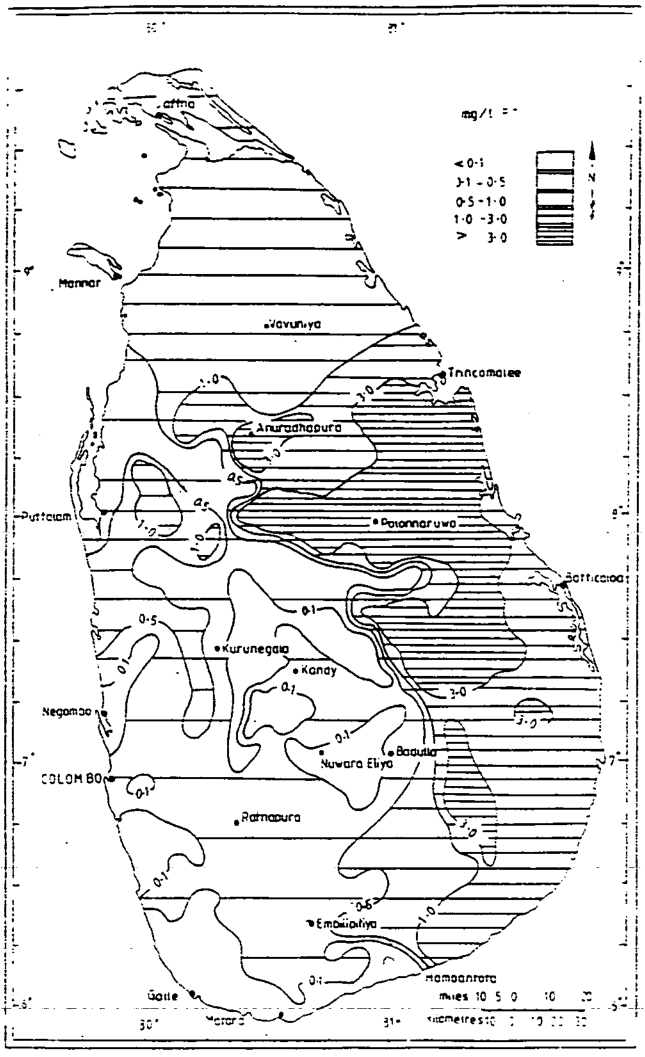


Figure 5. Distribution of fluoride in groundwater from dug wells in Sri Lanka (from Dissanayake, 1991).

(Møller et al., 1970) where incidences of dental fluorosis have been linked with concentrations of F up to 3 mg l^{-1} . Kilham and Hecky (1973) also report high F concentrations in parts of Tanzania, Kenya and Uganda.

Fluoride problems have also received much attention in Asia. Teotia et al. (1981) note that endemic fluorosis affects nearly 1 million people in India, the high concentrations of dissolved flouride in drinking water resulting from dissolution of fluorite, apatite, phosphorite and topaz

Table 3. Fluoride concentrations in some Tanzanian waters (from Bugaisa; 1971)

Locality	F (mg l^{-1})
Shinyanga	3.0
Bahi swamp	26.6
Bahi depression	123.0
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

in the bedrocks (Figure 4). Handa (1975) noted a general negative correlation between F and Ca concentration in Indian groundwater. In the Dry Zone of Sri Lanka, Dissanayake (1991) found concentrations of F up to 10 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 has resulted in low groundwater F concentrations. Here, the incidence of dental caries is reported to be high (Figure 5).

Excessive F concentrations in water have also been found in Algeria and Kenya (Tjook, 1983), South America (Lloyd and Helmer, 1991), Ghana (UN, 1988; Amoah, 1990), Senegal and The Ivory Coast (especially in granitic areas; Akiti et al., 1990), Zimbabwe and Malawi (Lewis, 1986), Thailand (Ramnarong, 1991; Table 4) and China (Zhaoli et al., 1989).

Table 4. Chemical analysis of general groundwater, contaminated groundwater and thermal water from hot springs at San Kamphaeng in Ching Mai Basin, Thailand (from Ramnarong; 1991).

Parameters	**Range of concentration (mg l^{-1})**		
	General groundwater	Contaminated groundwater	Thermal water from hot springs
Surface Temperature °C	26-37	28-37	64-102
pH	7.3-8.4	7.3-8.4	7.5-8.8
TDS	60-800	640-1160	580-920
Ca	0.4-191	4.2-28	0.1-8.3
Na	0.6-135	84-146	138-150
K	0.8-17.2	2.2-8.4	10-15
Si	9.0-52.4	8.4-14.4	80-93
Fe	0.4-48	0.05-0.78	0.1-0.2
Mg	0.16-42	2.8-16.6	0.01-0.02
F	<0.1-1.2	1.7-14.0	17.3-20.5
Cl	0.18-14.3	22-74	12-30
SO_4	0-141	0-9.2	2.5-12.3
CO_3	0-50	0-50	0-55
HCO_3	39-672	96-603	307-429

2.6 Iodine (I)

The association of I deficiency in the human diet with endemic goitre has long been recognised. Links with cretinism are also reported (e.g. Taylor, 1956). Goitre results from enlargement of the thyroid in order to compensate for I deficiency in hormone production. The condition has been recognised in areas all over the world but is particularly prevalent in mountainous areas and continental areas remote from the sea (e.g. Kelly and Sneddon, 1960).

Iodine is not a major element in any minerals and does not enter readily into the crystal lattice (Table 5). It is however chalcophile and may be found in higher concentrations in association with organic carbon (e.g. Fuge and Johnson, 1986). Fe and Al oxides may also contain sorbed I (Whitehead, 1984).

Table 5. Concentrations of I in some rocks (mean values; taken from Fuge and Johnson, 1986). * Soil I content varies according to type (especially organic content) and to distance from the coast.

Rock type	I (ppm)
Granite	0.25
Gabbro	0.32
Basalt	0.27
Rhyolite	0.20
Schist	0.36
Gneiss	2.3
Metaquartzite	0.6
Carbonate	2.7
Shale	2.3
Sandstone	0.8
Recent sediments	5-200
Soil*	5

The principal natural source of I is seawater (mean value 58 μg l^{-1}; Fuge and Johnson, 1986), but additional sources are formation waters, fluid inclusions and volcanic emanations. The geochemical cycle of I involves volatilisation to atmospheric I (as iodine gas, I_2 or as methyl iodide, CH_3I), 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). I in rainfall over coastal areas is therefore generally higher (1.5-2.5 μg l^{-1}; Whitehead, 1984) than over inland areas (1 μg l^{-1} or less; Fuge, 1989).

Soils (especially shallow soils) generally have higher concentrations of I than their parent rocks, presumably owing to the addition of I from rainfall (Fuge and Johnson, 1986). Whitehead (1979) found a range of 0.5-98.2 ppm (dry weight) in surface soils from the UK, the highest being in fen peat and the lowest in podzolic sands poor in organic carbon.

Iodine concentrations in the environment are increased by man's activities. I is used in herbicides (ioxynil, ioxynil octanoate), fungicides (e.g. benodanil), sterilants for dairy

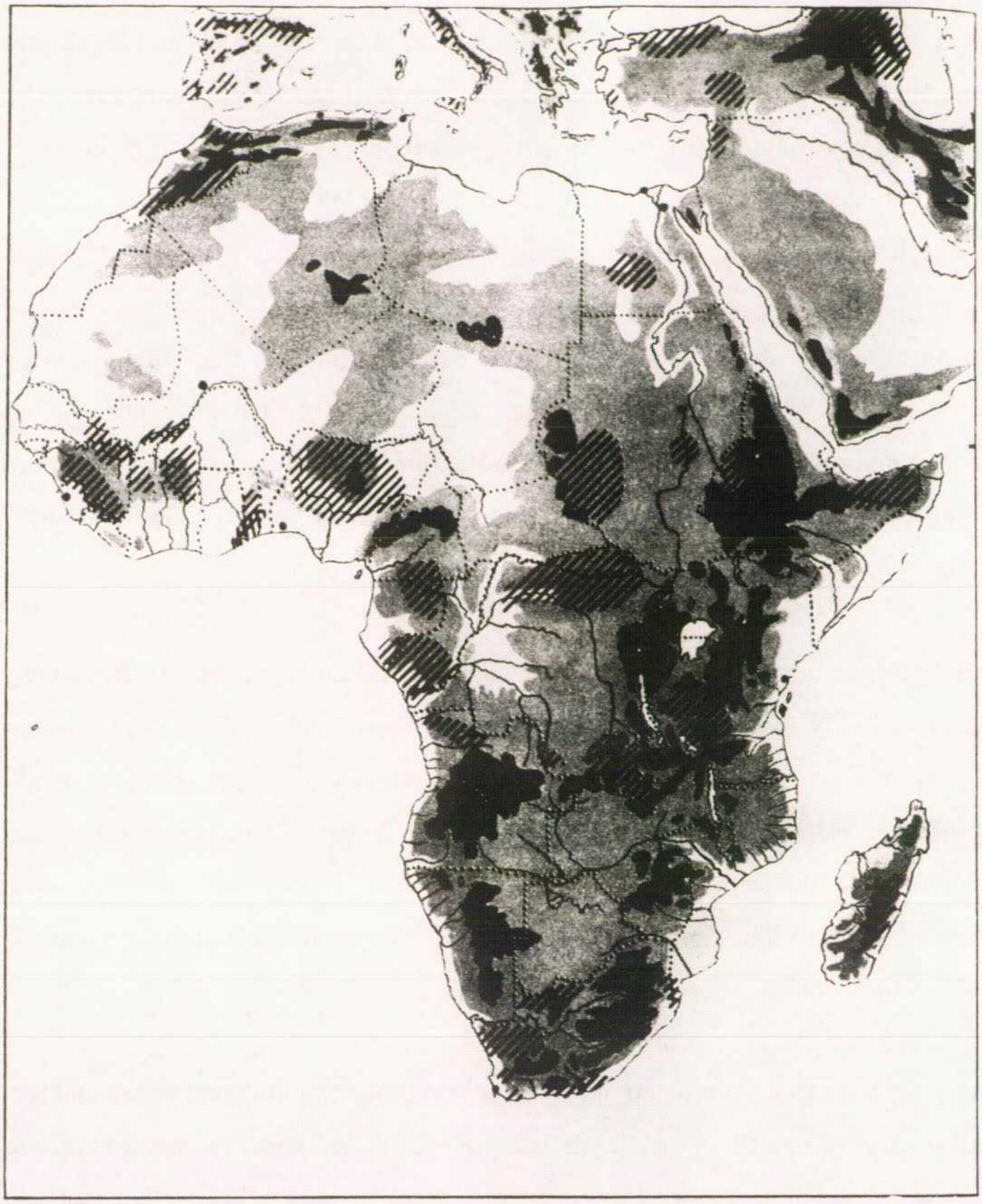


Figure 6. Topographic map of Africa showing (hatched areas) the recorded occurrence of endemic goitre (after Kelly and Sneddon, 1960).

situation was found in Darfur Province, Sudan, where goitre affected 18.5% of the population. The area is more than 500 miles from the sea, the soil poor, rock types are volcanic or Precambrian basement, food was restricted to local produce, consumption of meat and milk was low, water was from local wells and salt from lakeshore salt deposits rather than sea water (Kambal et al., 1969).

equipment, iodophor detergents, table-salt production, pharmaceuticals and bread making. It is enhanced in some soils by addition of seaweed as a fertiliser (Whitehead, 1984) and is also produced in the environment from fossil fuel combustion, car exhausts and from sewage. Tap water in London, for example, is observed to have a higher than average I concentration (7.7 μg l^{-1}), thought to be related to the fact that the water is heavily recycled (Fuge, 1989).

In rivers and groundwater, I speciation depends upon local redox conditions but generally tends to be present as iodide (I^-) rather than as iodate (IO_3^-). Total I concentrations range between 0.01 and about 70 μg l^{-1} depending on location, topography and rainfall pattern (mean river water content 5 μg l^{-1}; Fuge and Johnson, 1986; Fuge, 1989). Some I may also be organically bound.

The daily I requirement for the human diet is about 100-200 μg (Fuge, 1987). Only about 20% of this is likely to come from drinking water, the remaining 80% being derived from food. Dairy products are especially enriched in I, as is iodised salt where it is available. Since drinking water is such a minor I source, links between concentrations in water and occurrence of endemic goitre must be relatively dubious. 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.

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 (see for example Figure 6). However, since the predominant source of I in water is from seawater, it is not surprising that central continental areas, mountainous regions and high rainfall areas away from the oceans are those most prone to endemic goitre occurrence (Fuge, 1987). Goitre has been particularly noted in Alpine, Himalayan and Andean regions. Day and Powell-Jackson (1972) for example, reported I concentrations of less than 1 μg l^{-1} in goitrous areas of Nepal.

North Africa is also apparently prone to endemic goitre: Coble et al. (1968) found that in Egyptian oases, drinking water with concentrations of 7-18 μg l^{-1} was associated with goitre whilst concentrations of 44-100 μg l^{-1} did not apparently produce the condition. A similar

Endemic goitre linked to I deficiency has also been reported in Israel (Rosenthal and Mates, 1986), Sri Lanka (Mahadeva et al., 1968), Nigeria (Wilson, 1953; Fuge and Johnson, 1986) and northern Ghana (Kelly and Sneddon, 1960; Pelig-Ba, pers. commun., 1992). In addition, I deficiency may be caused by high dissolved Ca concentrations. Goitre has been observed in limestone areas (e.g. Fuge, 1989) and has been linked to water hardness (e.g. Day and Powell-Jackson, 1972). It has been suggested that high Ca can suppress I solubility in water.

3. CONCLUSIONS

Not all elements relevant to human health have been considered in detail in this report. Other potentially harmful dissolved constituents in groundwater include U, Th, CN, 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, Zn, Cu). 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. For example, 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). However, 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, Hg, Fe and Mn are preferentially mobilised under acidic conditions, As (along with Fe and Mn) is more soluble under reducing conditions and Se and U are more mobile in oxidising environments. F 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. I is expected to be highest in central continental areas, mountain belts and high rainfall areas remote from the sea. It is therefore clearly difficult to locate suitable study areas for further research based on all the elements discussed in this report and their relationship to health. The approach best adopted is to locate one or more geochemical provinces on the basis of extreme conditions

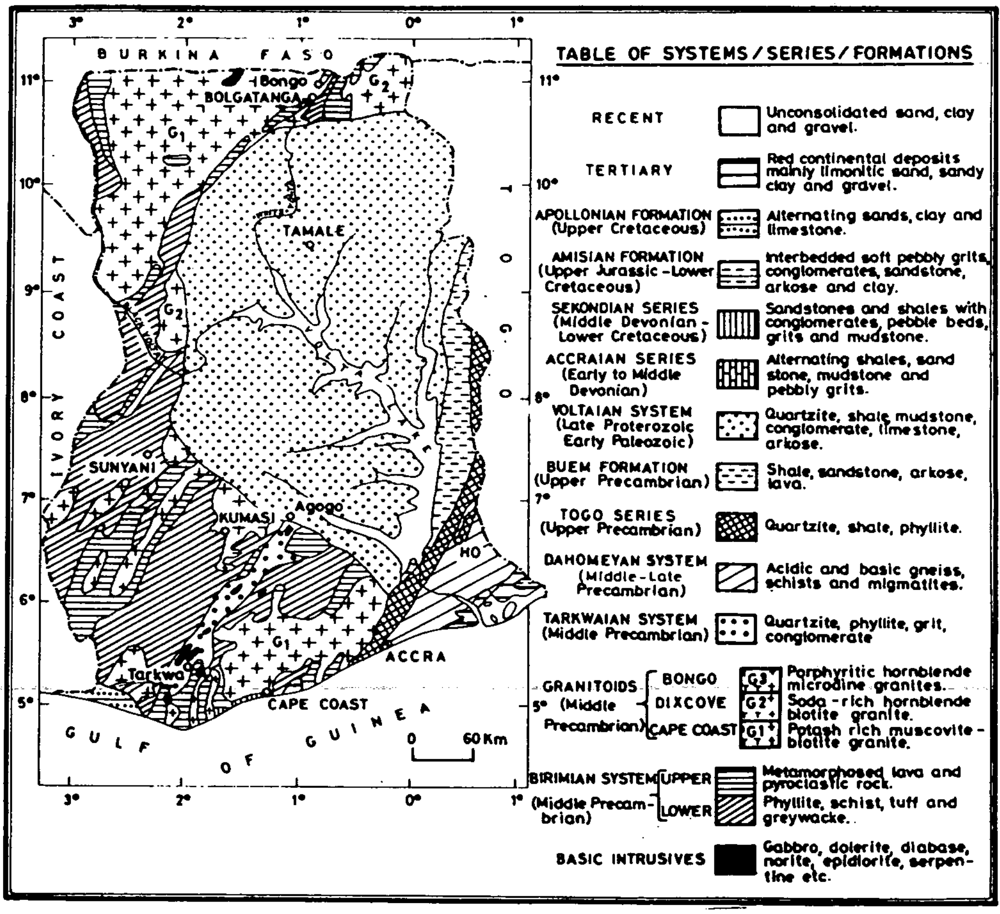


Figure 7. Geological map of Ghana (from Kesse, 1985).

(e.g. low pH or known Ca-deficient bedrock) or to locate regions where one or more key elements are known to occur in excess (e.g. Fe, F) or where a deficiency is already known to produce health problems (e.g. I, Se). Other elements may also be deficient or excessive in the same regions such as Al, Be associated with low pH.

Hard-rock terrains in developing countries are a suitable place to investigate trace element behaviour since carbonate-poor basement rocks are likely to contain relatively low Ca concentrations and may therefore have elevated F levels and comprise soft water. Granitic basement rocks may also contain acidic water and abundant hydrothermal mineral veins. Furthermore, basement rocks comprise a large part of Africa, Asia and South America and therefore investigations of trace element behaviour in such terrains are likely to have direct relevance for much of the developing world.

One country which is well-suited to further investigation is Ghana, where much of the geology comprises Precambrian metamorphic and granitic rocks (Gill, 1969) and where incidences of high Pb and Cr (Pelig-Ba et al., 1991), Fe, Mn, and F and low I have already been reported. The existing network of several thousand wells and boreholes will enable study on a regional basis.

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