Fluoride in natural waters

W Mike Edmunds[1] and Pauline L Smedley[2]

[1] *School of Geography and the Environment, Oxford University, Oxford, UK (corresponding author)*

[2] *British Geological Survey, Keyworth, Nottinghamshire, UK*

1. Introduction

The element fluorine has long been recognised to have benefits for dental health: low-fluoride intake has been linked to development of dental caries and the use of fluoride toothpastes and mouthwashes is widely advocated in mitigating dental health problems. Fluoridation of water supplies to augment naturally low fluoride concentrations is also undertaken in some countries. However, despite the benefits, optimal doses of fluoride appear to fall within a narrow range. The detrimental effects of ingestion of excessive doses of fluoride are also well documented. Chronic ingestion of high doses has been linked to the development of dental fluorosis, and in extreme cases, skeletal fluorosis. High doses have also been linked to cancer (Marshall, 1990), although the association is not well-established (Hamilton, 1992).

Drinking water is particularly sensitive in this respect because large variations in fluoride concentration exist in water supplies in different areas. Concentrations in natural waters span more than four orders of magnitude, although values typically lie in the 0.1–10 mg L^{-1} range. Where concentrations are high, drinking water can constitute the dominant source of fluorine in the human diet. Concentrations in drinking water of around 1 mg L^{-1} are often taken to be optimal. However, chronic use of drinking water with concentrations above about 1.5 mg L^{-1} is considered to be detrimental to health. The WHO (2011) guideline value for fluoride in drinking water remains at 1.5 mg L^{-1}. Many countries also use this value as a national standard for drinking water, although the standard in China is 1.0 mg L^{-1} (Table 1). The US Environmental Protection Agency (EPA) has set the primary standard (enforceable limit) at 4 mg L^{-1} for fluoride in drinking water, although the secondary standard (non-enforceable) for United States drinking water is 2 mg L^{-1}. In Tanzania, the national standard is as high as 8 mg L^{-1}, reflecting the difficulties with compliance in a country with regionally high fluoride concentrations and problems with water scarcity.

High fluoride concentrations are most often associated with groundwaters as these accumulate fluoride from rock dissolution as well as geothermal sources. Many high-fluoride groundwater provinces have been recognised in various parts of the world, particularly northern China, India, Sri Lanka, Mexico, western USA, Argentina and many countries in Africa. Fluoride removal by water treatment is carried out in some countries. However, as many of the high-groundwater provinces occur in developing countries, fluoride removal practices vary widely and many high-fluoride water sources are used without treatment. As a result, large populations throughout parts of the developing world suffer the effects of chronic endemic fluorosis. Estimates are not well-established, but more than 200 million people worldwide are thought to be drinking water with fluoride in excess of the WHO guideline value. This includes around 66 million in India (Majumdar, 2011), 45 million people in China (Wuyi et al., 2002) and some 5 million in Mexico (Diaz-Barriga et al., 1997). The population at risk in Africa is unknown but is also likely to be tens of millions.

Despite the clear evidence for health problems related to fluoride in drinking water and the links between fluoride occurrence and geology, there have been few reviews on the hydrogeochemistry of fluoride. This chapter addresses the hydrogeochemical aspects of fluoride in water, particularly groundwater, and outlines the links with health impacts. The chapter characterises the typical ranges of concentrations of fluoride found in water bodies, along with their distribution, speciation and mechanisms of mobilisation. The principles of fluoride behaviour are also illustrated with case studies from Canada, East Africa, Ghana, India, Sri Lanka and the UK.

2. History of fluoride research and links with health

Chemists first intimated the potential for an association between fluorine and health in the 19th century from its variable presence in bones and teeth. In the latter part of that century, fluorine was recommended for administration to pregnant women in the interests of dental health. In 1892, it was suggested that the high incidence of dental caries in England was due to deficiency of fluoride in the diet. However it was not until the first quarter of the 20th century that a clear association between fluorine in water supplies and dental health was established by medical scientists. The earliest studies in Europe and North America were aided by the fact that populations were less mobile than today and water supplies in rural areas were generally from wells or springs.

The first studies on fluorosis in the United States were carried out in the 1930s (Dean and Elvove, 1937). These established high fluoride concentrations in drinking water as a likely factor in fluorosis disease and led to the adoption (US Public Health Service, 1943, 1946) of an initial upper limit for fluoride in US drinking-water supplies of 1.0 mg L^{-1}, which was later revised to 1.5 mg L^{-1}. In Britain, the earliest studies (1922) were conducted on school children in Maldon, Essex, where an association was established between mottled teeth and fluoride in Chalk groundwater at concentrations of 4.5–5.5 mg L^{-1} (Ainsworth, 1933; Hoather, 1953) (see also Chapter 28, this volume).

The recognition early in the 20th century that certain areas of the USA, UK, and elsewhere had clearly defined patterns of dental caries and dental fluorosis prompted closer examination of the association with the geology and the underlying groundwater supplies. In the early studies, a strong link between caries and low-fluoride water emerged and this led, as early as 1945, to the fluoridation of fluoride-deficient water supplies in Grand Rapids, Michigan (Maier, 1950). Fluoridation of some British water supplies was also initiated in the 1950s although the policy has not been adopted widely: today around 10% of the population of England & Wales is supplied with fluoridated water. The requirement for water companies to fluoridate is stipulated by the regional health authority.

There has been much debate over the alleged benefits of fluoridation of drinking-water supplies (Hamilton, 1992) and the issue is still strongly contentious (Connett, 2007). One of the reasons is that many of the scientific studies are considered to be incomplete or flawed (Marshall, 1990). Studies of water fluoridation also yield conflicting results (Hamilton, 1992). Some conclude that the evidence for caries prevention favours fluoridation as an effective policy (Yeung, 2008). On the other hand, large reductions in the incidence of tooth decay over the last few decades have occurred in many developed countries (Diesendorf, 1986; Pizzo et al., 2007), whether or not water fluoridation has been adopted. The reductions have been linked to the large increases in use of fluoride toothpastes and mouthwashes which have increased fluoride intake, together with educational programmes and health promotion campaigns. This undermines the case for fluoridation, at least in industrialised nations (Pizzo et al., 2007). Some studies have even suggested that fluoridation has been detrimental to health (Zan-dao and Yan, 2002).

The significance of water-derived fluoride in developed nations has become further obscured since the Second World War as a result of greater variety in diets and the increased mobility of populations. A number of other foodstuffs, including tea, have also been established as key sources of additional fluoride. Today, these sources are augmented to a small extent by exposure from anthropogenic sources such as industrial emissions. Nevertheless, it is clear that exposure to fluoride from drinking water and food remains an important factor.

Despite the uncertain consequences of fluoride in drinking water at low concentrations (0.7 mg L^{-1} or less), the chronic effects of exposure to excessive fluoride in drinking water are well-established. The most common symptom is dental fluorosis (‘mottled enamel’), a condition involving interaction of fluoride with tooth enamel, which involves staining or blackening, weakening and possible eventual loss of teeth. With higher exposure to fluoride, skeletal fluorosis can result. This manifests in the early stages as osteosclerosis, involving hardening and calcifying of bones and causes pain, stiffness and irregular bone growth. At its worst, the condition results in severe bone deformation and debilitation. Long-term exposure to fluoride in drinking water at concentrations above about 1.5 mg L^{-1} can result in dental fluorosis (Table 2), while values above 4 mg L^{-1} can result in skeletal fluorosis and above about 10 mg L^{-1}, crippling fluorosis can result (Dissanayake, 1991). Recent studies have suggested that in arid areas with consumption of large quantities of water, lower concentrations should be appropriate (<1 mg L^{-1}) (Viswanathan et al., 2009). Young children are at greatest risk as the fluoride affects the development of growing teeth and bones. Once developed, the symptoms of fluorosis are irreversible. However, nutrition is also an important factor in the onset of fluorosis disease. Dietary deficiencies in calcium and vitamin C are recognised as important exacerbating factors. Links between high fluoride and other health problems, including birth defects (Hamilton, 1992) and cancer (Eyre et al., 2009) are less clearly defined.

3. The hydrogeochemical cycle of fluorine

3.1. Atmospheric and surface water inputs

The hydrogeochemical cycle of fluorine is illustrated in Figure 1. The cycle involves transfer of fluorine to the atmosphere by volcanic emissions, evaporation, marine aerosols, and industrial pollution. Wet and dry deposition transfer fluorine to the biosphere and geosphere. In the geosphere, uptake and release of fluorine are controlled by various water-rock interactions and by inputs from anthropogenic sources.

Rainfall constitutes an important component of the cycle. Fluorine sources in rainfall include marine aerosols, volcanic emissions, and anthropogenic introduction of chlorofluorocarbons (CFCs) and industrial emissions. Industrial aerosols are especially produced from coal burning, brick making and aluminium smelting (Fuge and Andrews, 1988) and fluorine exposure is also linked to domestic coal burning (Finkelman et al., 1999). Fluoride can substitute to a minor extent for OH^- in minerals, including clay minerals, and this is released (as is the OH^- by dehydroxylation) upon heating in industrial processes. Fluoride concentrations in rainfall are low and accurate data are sparse as a result of analytical difficulties. If marine aerosols contribute to rainfall compositions in their seawater proportions, rainfall in coastal areas with 10 mg L^{-1} Cl should have 0.68 μg L^{-1} F. In many continental areas where rainfall Cl concentrations are near or below 1 mg L^{-1}, fluoride inputs to streams and groundwaters from rainfall should be at or below 0.1 μg L^{-1}. In fact, rainfall fluoride concentrations tend to be higher than these estimates, implying that some fractionation favours greater uptake of the more volatile fluoride at the sea surface or that the ratio is increased by atmospheric fluoride inputs.

The concentrations of fluoride in pristine rainfall are difficult to assess since human impacts are likely to dominate in most areas. Comparative studies at inland and coastal sites in Virginia, USA, found median values of 4 and 9 μg L^{-1} respectively (Table 3) and marine aerosol inputs were considered to be small (Barnard and Nordstrom, 1982). Higher concentrations, in the range <20–80 μg L^{-1} (average 30 μg l^{-1}), have been found in rainfall from Anuradhapura, central Sri Lanka. Such values are likely to reflect a large contribution from marine aerosols. Neal (1989) reported typical fluoride concentrations in rainfall from Wales of 20–70 μg l^{-1}, reflecting in part marine influences. Occasional higher values up to 220 μg l^{-1} were interpreted as increased atmospheric inputs, presumably of anthropogenic origins. Saether and Andreassen (1989) found concentrations in Norwegian precipitation up to 253 μg l^{-1}, with values typically of 13–25 μg l^{-1}. They used the correlation between sulphate and fluoride to suggest that anthropogenic contributions amount to as much as 98% of the total fluoride, derived principally from industrial aerosols.

Concentrations of fluoride in surface waters are generally much higher than in rainfall, though still typically in the $\mu g\ L^{-1}$ range. Stream flow in upland areas of Wales has concentrations in the range 30–70 $\mu g\ L^{-1}$ (Neal et al., 1997). In the Bengal Basin, the Ganges-Brahmaputra river system has mean fluoride concentrations in the range 66–154 $\mu g\ L^{-1}$ (Datta et al., 2000) and rivers from southern Ghana have concentrations of around 30–140 $\mu g\ l^{-1}$ (Table 3, Botchway et al., 1996). In most cases, concentrations in surface waters are less than 300 $\mu g\ L^{-1}$.

Despite these generally low concentrations, fluoride in surface waters can be much higher in geothermal areas. Many alkaline lakes in the East African Rift Valley for example have concentrations of the order of tens to hundreds of mg L^{-1} (up to 1980 mg L^{-1}; Table 4).

3.2. Mineral sources of fluoride

Fluorine is more abundant in the earth's crust (625 mg kg^{-1}) than its sister halogen element chlorine (130 mg kg^{-1}). Chloride is highly mobile in the aqueous environment and most is found in the oceans. By contrast, fluorine is mostly retained in minerals. Fluorine is the lightest of the halogen elements and is also the most electronegative. It has an ionic radius very similar to that of OH^- and substitutes readily in hydroxyl positions in late-formed minerals in igneous rocks. It is mobile under high-temperature conditions and being a light, volatile element it is found along with boron and to a lesser extent chloride in hydrothermal solutions. Thus, concentrations of fluoride are generally localised in their geological occurrence. Most is found in acidic igneous rocks, mineralised veins and sedimentary formations where biogeochemical reactions have taken place.

Fluorine occurs in primary minerals, especially biotites and amphiboles (Figure 2), where it substitutes for hydroxyl positions in the mineral structure. An example is biotite:

$K_2(Mg,Fe)_4(Fe,Al)_2[Si_6Al_2O_{20}](OH)_2(\mathbf{F},Cl)_2$

On weathering, the fluorine tends to be released preferentially from these minerals. Where biotites and amphiboles are abundant, as for example in granite, these form a major source of fluoride in water bodies.

Other high-temperature fluorine minerals such as topaz are less soluble. Apatite ($Ca_5(Cl,\mathbf{F},OH)(PO_4)_3$), which may form at both high and low temperatures, is another important source of fluorine (Figure 2). Substituted apatites with high fluorine are more soluble than purer (high-temperature) apatites. Fluorite ($Ca\mathbf{F}_2$) is the main fluorine mineral, which occurs in localised secondary hydrothermal vein deposits and as a relatively rare authigenic mineral in sediments.

In marine sediments, fluorine is concentrated both by adsorption onto clays and also by biogeochemical processes involving the removal of phosphorus. Limestones may contain localised concentrations of fluorapatite, especially francolite. Most sandstones contain very low concentrations of fluorine and hence the fluoride in resident groundwaters may also be low see also Chapter 2, this volume).

3.3. Sources and reactions in soils

Typical concentrations of fluoride in soils are around 20–500 mg kg^{-1} (Kabata-Pendias and Pendias, 1984). Similar values of 200–400 mg kg^{-1} were given by Fuge and Andrews (1988), although higher concentrations were found in soils from mineralised areas of the UK. Concentrations up to 3700 mg kg^{-1} were reported in Welsh soils, up to 20,000 mg kg^{-1} in Pennine soils of the English Midlands and up to 3300 mg kg^{-1} in soils from Cornwall, all associated with hydrothermal mineralisation, including the presence of fluorite. Some plant species in the areas of mineralisation have also increased concentrations of fluoride which are potentially detrimental to humans and grazing animals (Fuge and Andrews, 1988).

Typically, only a small amount of the element present naturally in soils (e.g. <10 mg kg^{-1}) is easily soluble, the remainder residing within a variety of minerals (Pickering, 1985). Fluoride concentrations have been found in the range 24–1220 mg kg^{-1} (26 samples) in Argentine soils, the water-soluble fraction being in the range 0.53–8.33 mg kg^{-1}. The soluble fraction in these may be higher than typical because of the fine grain-size of the loess-derived soils (Lavado and Reinaudi, 1979). Easily soluble fluoride has also been reported in sodic loess-derived soils from Israel and China (Fuhong and Shuquin, 1988; Kafri et al., 1989).

Of the anthropogenic inputs to soils, high fluoride concentrations are found in phosphate fertilisers (8500–38,000 mg kg^{-1}) (Kabata-Pendias and Pendias, 1984) and sewage sludge (80–1950 mg kg^{-1}) (Rea, 1979). Contributions from these can increase the concentrations in agricultural soils considerably.

The amount of fluoride adsorbed by soils varies with soil type, soil pH, salinity and fluoride concentration (Fuhong and Shuquin, 1988; Lavado and Reinaudi, 1979). Adsorption is favoured in slightly acidic conditions and uptake by acid soils can be up to ten times that of alkaline soils. Fluoride adsorption releases OH^-, though the release is non-stoichiometric. Wenzel and Blum (1992) noted that, while minimum mobility occurs at pH 6.0–6.5, it is increased at pH <6 as a result of the formation of $[AlF]^{2+}$ and $[AlF_2]^+$ complexes in solution. Fine-grained soils also generally retain fluoride better than sandy types. Adsorption is favoured strongly by the presence of freshly precipitated $Fe(OH)_3$ or $Al(OH)_3$. Clay minerals are also effective adsorbents (Wuyi et al., 2002) as is soil organic matter (Fuge and Andrews, 1988). In soil profiles containing mainly sand and with little clay, iron or aluminium, up to half of the infiltrating fluoride in water may pass through the soil profile (Pickering, 1985). Where continued loading of fluoride occurs from anthropogenic sources, it is likely that the soil-retention capacities may be exceeded and fluoride will percolate to the water table. In most cases however, soils act as a sink rather than a source of fluoride and water reaching the water table is likely to have low fluoride concentrations and be dominated by atmospheric concentrations. Nevertheless, low fluoride concentrations afforded by retention in soils may be offset by evapotranspiration at the soil surface. This may increase fluoride concentrations reaching the water table by up to five times in temperate climates and 10–100 times under semi-arid conditions.

3.4. Fluoride in solution

Fluorine occurrence in natural waters is closely related to its abundance in the local minerals and rocks. It is also strongly associated with mineral solubility and in this regard the mineral fluorite, being least soluble and with favourable dissolution kinetics at low temperature, exerts the main control on aqueous concentrations in the natural environment. An upper limit on fluoride activities in aqueous solution is controlled by the solubility product, $K_{fluorite}$:

$$CaF_2 = Ca^{2+} + 2F^- \qquad (1)$$

$$K_{fluorite} = (Ca^{2+}).(F^-)^2 = 10^{-10.57} \text{ at } 25^{\circ}\text{C} \qquad (2)$$

$$or,\ \log K_{fluorite} = (Ca^{2+}) + 2\log(F^-) = -0.57 \qquad (3).$$

This is an important relationship since it shows that in the presence of fluorite, concentrations of fluoride are directly proportional to Ca^{2+} concentrations. For example, in the presence of 10^{-3} M Ca at 25ºC, dissolved F^- should be limited to 3.1 mg L^{-1}. It is therefore likely to be the absence of Ca in solution that allows higher concentrations of fluoride to be stable in solution, although precipitation of carbonates has also been linked to loss of fluoride from solution (Reddy et al., 2010; Turner et al., 2005). Low-Ca groundwater conditions arise in volcanic regions dominated by alkaline volcanic rocks (e.g. Ashley and Burley, 1994; Kilham and Hecky, 1973) and also in conditions where cation exchange occurs naturally (e.g. Handa, 1975). Here, removal of Ca^{2+} is achieved by exchange with Na^+ from clay minerals. In both cases, the waters are typically of Na-HCO_3 type. Cation exchange occurs in soils and in groundwaters along flow gradients in response to changing chemistry (Edmunds and Walton, 1983) and in zones of saline intrusion.

The solubility of fluorite (Eq. 2) is temperature-dependent. Fluorite solubility decreases with temperature and this is reflected with a change in the equilibrium constant. For example the value of $K_{fluorite}$ changes from $10^{-10.57}$ at 25ºC to $10^{-10.8}$ at 10ºC. Further, the equilibrium constant is affected by the salt content of the waters (the ionic strength) with the solubility increasing with salinity, providing the waters are below saturation with respect to calcite.

Reaction times with aquifer minerals are also important in controlling fluoride concentration. High fluoride concentrations can occur in groundwaters which have long residence times in the host aquifers, probably as a result of diagenetic reactions. Surface waters usually have low concentrations, as do most shallow groundwaters from open wells as they represent young, recently infiltrated, rainwater. Deeper (older) groundwaters from boreholes are therefore most likely to contain high concentrations of fluoride. Exceptions occur in active volcanic areas where surface water and shallow groundwaters are affected by hydrothermal inputs.

High fluoride concentrations are also a feature of arid climatic conditions (Fuhong and Shuquin, 1988; Handa, 1975; Smedley et al., 2002). Here, groundwater infiltration and flow rates are slow, allowing prolonged reaction times between water and rocks. Fluoride concentrations are lower in the humid tropics because of high rainfall inputs and their diluting effect on groundwater chemical composition.

Table 4 shows the chemical compositions of a range of typical high-fluoride groundwaters from various parts of the world. The data illustrate the dominance of Na over Ca in most, though not all, waters and the high concentrations of HCO_3 that typify high-fluoride waters. The table also gives the likely dominant species, calculated using PHREEQC (Parkhurst and Appelo, 1999). Free F^- is overwhelmingly the dominant form in most natural waters with minor additional amounts of complexes with major cations (Ca, Na, Mg). However, the speciation is strongly pH-dependent. In acidic conditions, strong complexing with H^+ and Al^{3+} can occur (Deng et al., 2011). At pH 3.5, HF^0 is likely to be the dominant species (Hem, 1985). Fluorine also readily forms complexes with B, Be, V, U, Fe^{3+} and Si and these may enhance fluorine mobilisation if present in solution in significant quantity. The formation of complexes may have ramifications for human health for example in aluminium-bearing waters, where the total fluorine may be much higher than the measured ionic fluoride. Thus aluminium fluoride may stabilise the fluoride as a complex ion, but if these complexes are broken down during metabolism they could release both F^- and potentially toxic Al.

Table 4 gives the saturation indices for fluorite for each of the waters. Fluorite solubility is likely to control the upper limits of fluoride concentrations in most natural waters. The table shows that most are at or near saturation with respect to fluorite, although a couple of samples are significantly oversaturated ($SI_{fluorite} > 0.5$). This presumably reflects the slower kinetics of precipitation of fluorite compared with its dissolution or discrepancies related to mineral purity or grain size.

3.5. Fluoride distributions in groundwater

One of the best ways to understand the controls on the concentrations of fluoride in groundwaters is to examine its distribution according to geology, depth, salinity and other controlling parameters. Several studies have been made which take large populations of data and examine them statistically, as in Alberta, Canada (Hitchon, 1995), India (Gupta et al., 1999), Germany (Queste et al., 2001) and the UK (Edmunds et al., 1989). A statistical summary of fluorine distributions in sedimentary basins, and other aquifers in various parts of the world, is included in Table 3.

In Britain, an inter-comparison of fluoride in 13 representative major aquifers was made alongside other trace elements by Edmunds et al. (1989). These results are summarised in Figure 3 as a cumulative-frequency plot. A clear distinction is seen between groundwaters in sandstones and those in carbonate aquifers. A very narrow range of concentrations is found in all Triassic sandstones and median values do not exceed 150 μg L^{-1}. For most of the sandstone groundwaters, the fluoride concentrations do not significantly exceed the rainfall input concentrations after allowing for evapotranspiration. The only aquifer to deviate from the general trend is the Moray Sandstone in Scotland in which fluorite is recorded as a cementing phase associated with vein mineralization and may also be associated with occurrence of phosphate minerals (Edmunds et al., 1989). Median concentrations in limestones lie between 0.6 and 1.5 μg L^{-1}, the higher values found in fine-grained chalk. Although rainfall concentrations provide a contribution, the main source of the fluoride here is biogenic and closely related to phosphate-enriched horizons. The highest fluoride concentrations in British groundwaters are found in confined carbonate aquifers where the combination of a geological source of fluorine (CaF_2), residence time and some calcium depletion due to Na-Ca exchange leads to fluoride concentrations controlled by fluorite mineral solubility. In the majority of British groundwaters, fluorite solubility is not achieved.

4. High-fluoride groundwater provinces

Although the concentrations of fluoride are likely to be higher in groundwater than in other water bodies as a result of water-rock interaction, the concentrations in most groundwaters are below the upper concentrations considered detrimental to health, as shown by the British studies in Section 5. However, aquifers with high groundwater fluoride concentrations have been recognised in a number of regions across the world. The distribution of documented cases where fluoride occurs substantially in wells at concentrations >1.5 mg L^{-1} is shown in Figure 4. Endemic fluorosis is a problem in many, though not all, of these regions. High-fluoride groundwaters are found in many parts of the developing world in particular, and many millions of people rely on groundwater with concentrations above the WHO guideline value for their normal drinking-water supply. Worst-affected areas are arid parts of China, India, Sri Lanka, West Africa (Ghana, Ivory Coast, Senegal), North Africa (Libya, Sudan, Tunisia), South Africa, the East African Rift Valley (Kenya, Uganda, Tanzania, Ethiopia, Rwanda), northern Mexico and central Argentina (Figure 4). Problems have also been reported in parts of Pakistan. In the early 1980s, it was estimated that around 260 million people in 30 countries worldwide were drinking water with more than 1 mg L^{-1} of fluoride (Smet, 1990). In India alone, endemic fluorosis is a major problem in 17 out of the country's 22 states.

High-fluoride groundwaters are typically of Na-HCO_3 type with relatively low Ca concentrations (<20 mg L^{-1} or so), and with neutral to alkaline pH values (around 7–9). Fluoride problems are largely found in groundwater from basement aquifers, particularly granites, where fluorine-rich minerals are abundant; in active volcanic zones where fluorine is derived from the volcanic rocks and geothermal sources, and groundwaters in some sediments, particularly in arid areas.

4.1. Basement aquifers

Fluoride problems have been found in crystalline basement rocks, particularly those of granitic composition from several areas across the world (Table 3). Granitic rocks contain a relatively large proportion of high-fluorine minerals such as micas, apatite and amphiboles. Fluorite is also an occasional accessory mineral in these rocks.

Basement aquifers in large parts of southern Asia are known to suffer from severe fluoride and fluorosis problems. In India, the worst-affected states are Rajasthan, Andhra Pradesh, Uttar Pradesh, Tamil Nadu and Karnataka (Handa, 1975; Maithani et al., 1998; Rao, 2002; Reddy et al., 2010; Suma Latha et al., 1999). Fluorosis has also been reported in Assam (Chakraborti et al., 2000; Kotoky et al., 2008). In Pakistan, high fluoride concentrations have also been reported in Sindh Province (Rafique et al., 2009) (Table 3). In Sri Lanka, the Dry Zone in the eastern and north-central parts of the country has groundwater with high concentrations up to 10 mg L^{-1}, and associated dental and possibly skeletal fluorosis. In the Wet Zone in the west, groundwater fluoride concentrations are low, probably as a result of intensive rainfall and long-term leaching of fluorine from rocks (Dissanayake, 1991). Here, the incidence of dental caries is reported to be high.

Several countries in Africa also have high groundwater fluoride concentrations in basements areas, including parts of Cameroon, Ghana, Ethiopia, Malawi, Senegal, Tanzania and South Africa (e.g. Fantong et al., 2010; McCaffrey, 1998; Tekle-Haimanot et al., 2006; Travi, 1993).

4.2. Volcanic areas and geothermal sources

High fluoride concentrations have been reported in geothermal sources and active volcanic belts in the western USA (Nordstrom and Jenne, 1977), Iceland, Taiwan, Tibet, New Zealand, the former Soviet Union (Ellis and Mahon, 1977), France, Algeria and Tunisia (Travi, 1993) and the East African Rift Valley (Ayenew, 2008). The most common types of geothermal water are alkali-chloride solutions with near-neutral pH values. In these, fluoride concentrations are typically in the range 1–10 mg L^{-1} (Ellis and Mahon, 1977) and the waters also commonly have increased concentrations of Si and B, as well as often high As, NH_3 and H_2S. Under acidic conditions, concentrations in geothermal sources can reach more than 1000 mg L^{-1} (Ellis, 1973), with dissolved fluoride in the form of HF, HF_2^- and SiF_6^{2-}.

In New Zealand, fluoride concentrations in deep waters have been reported in the range 1–12 mg L^{-1} with maximum concentrations being influenced by subsurface temperature and the solubility of fluorite (Mahon, 1964). The main volcanic province with high fluoride waters, the East African Rift Valley, is outlined as a case study below.

4.3. Sedimentary aquifers

Some sedimentary aquifers also have groundwaters with high fluoride concentrations, particularly in arid and semi-arid regions. In La Pampa Province of central Argentina, high-pH (>8), HCO_3-rich groundwaters have concentrations of dissolved fluoride up to 29 mg L^{-1} (Smedley et al., 2002). The concentrations of fluoride are positively correlated with pH and HCO_3 and suggest that the fluoride was mobilised at high pH from F-bearing minerals present in the sediments. These contain rhyolitic volcanic ash. Fluoride concentrations were highly variable, but highest concentrations were found in groundwater from shallow depths (top 20 m). High-fluoride groundwaters are also observed in Quaternary sediment aquifers from arid regions of China. Here, soil salinity and pH have been highlighted as key factors in fluoride accumulation in groundwater (Fuhong and Shuquin, 1988).

A number of large sedimentary basins have notable increases in fluoride concentration with increasing groundwater residence time. As groundwaters flow downgradient in a typical sedimentary aquifer, Na for Ca exchange takes place and groundwaters evolve from Ca-HCO_3 to Na-HCO_3 types. Under low-Ca conditions in old groundwaters, fluoride can be maintained at relatively high concentrations unlimited by the precipitation of CaF_2. Fluoride concentrations therefore often show an increase in groundwaters down the flow line and with increasing depth as a result of increasing residence time (Edmunds and Walton, 1983; Travi, 1993). A case study of the English Lincolnshire Limestone is given in Section 5.

Edmunds (1994) reported fluoride concentrations up to 3.6 mg L^{-1} in old groundwaters from the Upper Sirte Basin of Libya and up to 6.2 mg L^{-1} in groundwaters from the Cretaceous Nubian Sandstone of Sudan (Table 3). The concentrations were variable in each aquifer but were found to be higher in marine sediments than in freshwater sediments, reflecting the overall higher concentrations of fluorine in the sediments themselves. Despite the high dissolved concentrations, most were undersaturated with respect to fluorite as a result of low dissolved Ca concentrations.

Groundwater from Cretaceous to Tertiary aquifers of western Senegal has fluoride concentrations ranging between <0.01–13 mg L^{-1} (Travi, 1993). The sediments form part of an 8000 m thick sequence forming a sedimentary basin, which overlies Precambrian basement. In the aquifers, fluoride concentrations generally increase in the direction of groundwater flow. The source of the dissolved fluoride is taken to be phosphatic horizons (containing fluorapatite), particularly in argillaceous deposits. In the Maastrichtian aquifer, fluoride concentrations range between 1.1–5.0 mg L^{-1} with increases corresponding to a facies change from sandy to more argillaceous deposits (Travi, 1993). The high concentrations are present in groundwater up to 30,000 years old.

In the sequence of Cretaceous to Quaternary sediments of western Tunisia, Travi (1993) recorded fluoride concentrations between 0.1–2.3 mg L^{-1}. Highest concentrations were found in groundwaters from the Cretaceous 'Complexe Terminal' aquifer (average 1.7 mg L^{-1}). The Tunisian sediments are also phosphatic, although the relationships between phosphate occurrence and dissolved fluoride concentrations were found to be less clear than observed in Senegal.

5. Case studies to illustrate high-fluoride groundwater systems

A number of aquifers have been selected as case studies to illustrate the different geochemical controls on fluoride mobilisation most clearly and where possible associated health problems may also be explained.

5.1. Rajasthan, India – Pre-Cambrian basement aquifer

The distribution of fluoride in India has been reviewed by Handa (1975). He recognised Rajasthan as the state most seriously affected by high fluoride, although other high-fluoride areas were also recognised in the country. The distribution of fluoride in Rajasthan (11 districts) was also reviewed by Gupta et al. (1993). Although there are many accounts of the incidence of dental and skeletal fluorosis in the province, it is difficult to find studies linking to regional geology. However, studies in Sirohi district (one of the administrative districts of Rajasthan) seem typical of the rather complex geology of the region (Maithani et al., 1998) and illustrate the nature of the fluoride occurrence.

Rajasthan has an arid climate with low but highly variable annual rainfall. In Sirohi district, fluoride concentrations up to 16 mg L^{-1} have been found in groundwater from dug wells and boreholes at depths between 25–75 m during geochemical exploration for uranium (Maithani et al., 1998). The aquifer comprises Proterozoic metasediments with intrusions of granite and rhyolite. Significant fluorite mineralisation associated with the granites and volcanic rocks is also reported from the adjacent Jalore district (Figure 5). This geological setting seems typical of much of Rajasthan where a mixed assemblage of basement rocks outcrops as islands between a highly weathered series of younger Quaternary sediments. The association of fluoride-endemic areas with the bedrock geology is often obscure and it is unclear whether anomalies are related to primary bedrock or secondary enrichment in the sediments.

In the 150 km^2 studied by Maithani et al. (1998), 117 samples were collected and over 75% of these contained groundwater with a fluoride concentration in excess of 1.5 mg L^{-1}. A good correlation with the bedrock geology is observed, with highest concentrations being found in association with the granites, acid volcanic rocks and basic dykes (Figure 5). These dykes act as barriers, which slow down groundwater flow and permit prolonged contact times to raise concentrations of groundwater fluoride. Low-fluoride areas in the east (<1.5 mg L^{-1}) are associated with carbonate rocks and higher calcium may inhibit an excess of fluoride. It is not clear from the study to what extent the alluvium acts as a source (or a conduit) for the fluoride-bearing water and no groundwater flow data are shown.

Handa (1975) recognised a negative relationship between calcium and fluoride in the groundwaters of the Sirohi region (Figure 6). Groundwaters from both bedrock and alluvium showed the relationship. The findings demonstrated the solubility control of fluorite on the fluoride concentrations.

The ill-effects of high fluoride on human health, including dental fluorosis and a few cases of skeletal fluorosis, were observed in villages in the high-fluoride region of Sirohi, although complete medical statistics have not been reported (Handa, 1975; Maithani et al., 1998). Although the Maithani et al. (1998) study indicates a strong association between geology and groundwater-fluoride occurrence, a full appraisal of the situation is limited by the absence of hydrogeological information, especially water levels and flow data. Additional hydrochemical data would also assist identification of the causes of high and low fluoride.

5.2. Northern Ghana – alkaline granitic basement

The Bolgatanga area in the Upper East Region of northern Ghana demonstrates the often-strong influence of geology, specifically certain types of granite, on fluoride concentrations in groundwater. The region experiences maximum temperatures in the range 20–40ºC and average annual rainfall around 1000 mm (Murray, 1960). The climate is semi-arid, largely as a result of northeasterly harmattan (dry, desert) winds, which affect the region from December to March. Geology comprises crystalline basement rocks, including Upper Birimian (Precambrian) rocks of mixed meta-igneous and meta-sedimentary origin. Intruded into these are a suite of coarse granites, the Bongo Granite suite, and associated minor intrusions, the ages of which are unknown. The Bongo Granite comprises typically a pink microcline-hornblende-granite with interstitial quartz, plagioclase and biotite (Figure 2). The granite is slightly alkaline, with the amphibole appearing to be in the hornblende-arfvedsonite range (Murray, 1960). Accessory mineral phases include abundant sphene as well as magnetite, apatite, zircon, rutile and more rarely fluorite. The Bongo Granite has been found to contain up to 0.2 % fluorine (Smedley et al., 1995). The Tongo Granite just to the south of the study area (Figure 7) is similar in composition (Murray, 1960). To the east of the study area (Sekoti district), a north-south tract of granodiorite has been classed together with other hornblende-biotite granodiorites (Figure 7 and Murray, 1960). However, in outcrop the rock type forms rounded tors resembling those of the Bongo Granite and some workers have grouped the Sekoti Granodiorite with the Bongo suite. The Sekoti Granodiorite comprises mainly plagioclase and quartz with biotite, often replacing amphibole, and accessory apatite and sphene (Murray, 1960).

Groundwater is abstracted for drinking water mostly from shallow hand-pumped boreholes (typically 30–50 m deep), although some traditional shallow hand-dug wells also occur with depths of less than 10 m. Surveys of groundwater quality (Apambire et al., 1997; Smedley et al., 1995) indicate clearly that highest fluoride concentrations occur in groundwater from the Bongo area in the west, with values reaching up to 3.8 mg L^{-1}, and from Sekoti district in the east, with values reaching up to 3.2 mg L^{-1} (Figure 7). The higher concentrations from any given rock type are generally found in borehole waters. Water from shallow hand-dug wells typically (but not always) has very low fluoride concentrations (<0.4 mg L^{-1}) as these have had much shorter reaction times with the host rocks. They also circulate within the superficial weathered overburden layer rather than the fractured granite at greater depth. From this association, it is possible that shallower groundwaters in such fluoride-vulnerable zones are safer sources of drinking water with respect to fluoride than deeper sources. However, the potential for bacterial contamination is increased in such open, shallow wells.

Villagers in some parts of the Bolgatanga area suffer from dental fluorosis as a result of the high concentrations of dissolved fluoride. The problem is particularly prevalent in Bongo and Sekoti districts, although the numbers of people affected and the regional extent is not known in detail. The fluorosis is particularly prevalent among children. There is to date no evidence of skeletal fluorosis in the region.

5.3. The English Lincolnshire Limestone – downgradient evolution

A common situation in many aquifers is to encounter increasing fluoride concentrations in the groundwaters down the flow gradient. This situation arises initially as a result of continuous dissolution of fluoride from minerals in the carbonate aquifers, up to the limit of fluorite solubility, followed by ion-exchange reactions involving removal of calcium. The phenomenon is particularly well-illustrated in the Jurassic Lincolnshire Limestone aquifer of eastern England (Edmunds, 1973; Edmunds and Walton, 1983).

The gently-dipping oolitic Lincolnshire Limestone is typically 30 m thick and downgradient becomes confined beneath clays and marls. Groundwater flow is predominantly through fractures, although there is also an intergranular porosity (13–18%). The unaltered limestone at depth is grey-green in colour due to the presence of Fe^{2+}. However, oxidation of the limestone on a geological timescale has produced an orange-brown oxidised zone through groundwater action. This is also reflected in an oxidation-reduction ‘barrier’ in the groundwaters, with aerobic groundwaters near to outcrop and reducing waters (with some dissolved iron) at depth.

Fluoride concentrations in the limestone at outcrop are quite low (up to 0.2 mg L^{-1}). The relationship between fluoride and other major ions and iodide is shown in Figure 8. The groundwaters are essentially of calcium-bicarbonate type and are saturated with calcite, buffering the concentrations of Ca and HCO_3 over the first 12 km of the flow line and producing ‘hard’ water. Thereafter, the profile shows distinctive ion exchange, with Ca^{2+} being replaced by $2Na^{+}$. This produces a ‘soft’, sodium-bicarbonate groundwater (with a high pH, up to 8.5) and increased bicarbonate concentrations. In these waters, the Ca^{2+} falls to as low as 1 mg L^{-1}, yet the groundwater adjusts under the new physicochemical conditions to maintain saturation with calcite.

It can be seen that the fluoride concentration increases progressively across the aquifer and this increase starts in the calcite-buffered part of the aquifer. The progressive decrease in concentration of Ca^{2+} allows the continuing rise in fluoride concentrations to a maximum of 5.6 mg L^{-1}. The fluoride increase is not controlled by the increase in salinity down-gradient in the aquifer; an increase in chloride concentration only begins some 17 km from outcrop. It is interesting to see that the other halogen measured in this study, iodide, follows the chloride behaviour and not the water-rock interaction pathway shown clearly by fluoride. The source of fluoride in this case is thought to be traces of phosphate minerals in the impure limestone.

This situation was utilised by the water engineers in the 1950s, noting “by a fortunate geological accident, it is possible to obtain in the geographical centre of the district a pure un-aggressive water which has in effect been softened, fluoridated and transported free of charge by nature” (Lamont, 1958). Today, most of the public water supply in the region is derived from the unconfined and semi-confined sections of the aquifer with lower natural concentrations of fluoride. There are additional water-supply problems in the Lincolnshire Limestone with the need to manage the high nitrate concentrations from agricultural chemicals although nature again assists the management of this problem in the confined aquifer as nitrate is reduced naturally through redox reactions.

5.4. Sri Lanka – climatic and geological controls

Sri Lanka consists of over 90% metamorphic rocks of Precambrian age. These include metasedimentary and metavolcanic rocks, gneisses and granitoids. Within these are abundant fluorine-bearing minerals such as micas, hornblende and apatite, as well as less common fluorite, tourmaline, sphene and topaz. As a result, large parts of Sri Lanka can be considered a fluorine province. Concentrations of fluoride up to 10 mg L^{-1} have been recorded in the groundwater and the incidence of dental fluorosis among children is high (Dissanayake, 1991). Groundwater compositions across the island indicate that fluoride problems have a strong geographical control linked to both geology and climate.

Dissanayake (1991) compiled a hydrogeochemical atlas for Sri Lanka, based on the results of analyses of 1970 water samples from shallow wells. It can be seen from the fluoride map produced (Figure 9) that high concentrations lie in the eastern and north central regions of the country. The central hill country and the south-west coastal regions have relatively low fluoride concentrations. Although rocks containing fluoride-rich minerals underlie almost the whole country (except the Jaffna Peninsula), areas with mean annual rainfall above 500 mm experience few fluoride problems. In these wetter areas, there is a tendency for the soluble ions, including F^-, to be leached out under the effects of high rainfall. Indeed, the Wet Zone of Sri Lanka is found to have quite high incidence of dental caries, presumably related to fluoride deficiency. In the Dry Zone, evaporation brings the soluble ions to the surface by capillary action. Despite these generalities, the precise composition of the rock types needs to be considered since even in the Dry Zone, fluoride concentrations vary considerably. In particular, within the Dry Zone the high concentrations coincide with rocks rich in mafic minerals such as hornblende- and biotite-gneisses, charnockites, marble and calc-gneisses (Dissanayake, 1991).

The high-fluoride groundwaters of Sri Lanka have many characteristics in common with high-fluoride aquifers elsewhere. In an investigation of groundwater chemistry in Anuradhapura, north central Sri Lanka, groundwaters were found to have typically near-neutral pH values (6.0–7.9), with high alkalinity (alkalinity as HCO_3 up to 713 mg L^{-1}; BGS, unpublished data; 123 samples). Groundwater from many wells also has relatively high salinity (SEC up to 3850 µS cm^{-1}, average 1260 µS cm^{-1}), the high salinity values reflecting the importance of water-rock reactions and evapotranspiration in the semi-arid climatic conditions.

The excess or deficiency of fluoride in groundwater is of special concern in Sri Lanka since 75–80% of the population depend on wells without treatment. Unlike high iron for example, fluoride has no taste and a high percentage of the population who suffer from dental fluorosis were unaware of the problem until the later stages of the disease. The use of fluoride toothpaste has alleviated the condition for those suffering from dental caries, but by 1991 at least, no preventative measures were taken against fluorosis. As a result of the studies (Dissanayake, 1991), it was recommended that very detailed maps showing the concentrations of fluoride in groundwater should be made, followed up by rural-water-supply schemes to avoid the use of high-fluoride groundwater. The development of relatively inexpensive defluoridation techniques was also recommended, coupled with rural education programmes.

5.5. The East African Rift Valley – the alkaline volcanic province

Some of the highest concentrations of fluoride ever recorded have been found in water from the East African Rift Valley. The Rift extends through Eritrea, Djibouti, Ethiopia, Kenya, Tanzania, Uganda, Rwanda, Burundi and Malawi and excessive fluoride concentrations have been found in groundwaters, hot springs, alkaline lakes and some river systems in all these countries (Table 3). The region has well-documented cases of severe dental and skeletal fluorosis (Ayenew, 2008; Bugaisa, 1971; Gaciri and Davies, 1993; Nanyaro et al., 1984).

The anomalous fluoride concentrations have been linked to a number of sources and processes. However, they are in large part related to the development of hyper-alkaline volcanic rocks in the rift zone, including nepheline and carbonatite magmas and associated ash deposits. These are capable of accumulating large concentrations of fluoride in melts and volatile fractions. Hence, water bodies in the rift zone can accumulate fluoride directly as a result of weathering of these rocks, as well as from high-fluoride geothermal solutions. The fine-grained and friable ashes are likely to be particularly reactive. Weathering of the silicate minerals in the lavas and ashes by silicate hydrolysis reactions produces Na-HCO_3-rich groundwaters (Ayenew, 2008; Jones et al., 1977), which are relatively depleted in Ca and Mg. Hence, high concentrations of fluoride can occur as the solubility of fluorite (CaF_2) is not a limiting factor. Ultimately, villiaumite (NaF) should limit the dissolved concentrations, although as this mineral is very soluble, fluoride can reach very high concentrations before this limit is achieved.

In the area of Mount Meru, a Neogene volcano in northern Tanzania, Nanyaro et al. (1984) reported fluoride concentrations of 12–76 mg L^{-1} in rivers draining the volcano's slopes (Table 3) and 15–63 mg L^{-1} in associated springs. They attributed the high concentrations to weathering of fluorine-rich alkaline igneous rocks and to contributions from fumaroles and gases as well as to the re-dissolution of fluorine-rich trona ($Na_2CO_3.NaHCO_3.2H_2O$), which occurs as a seasonal encrustation in low-lying river valleys and lake margins as a result of extreme evaporation. The river water chemistry varies significantly seasonally as a result of dilution following periods of heavy rainfall.

In perhaps the most extensive survey of water sources in the East African Rift, Tekle-Haimanot et al. (2006) outlined the distributions of fluoride in surface water and groundwater sampled nationally in Ethiopia. From 1438 samples, they found 24.2% exceeded the WHO guideline value with 50% of deep wells and 90% of hot spring samples exceeding the WHO guideline value. Areas along the Awash River were the most affected. Here, the sugar plantations attracted large settler communities and long-term use of deep borehole water has resulted in development of high rates of both dental and skeletal fluorosis (Tekle-Haimanot et al., 2006).

In a study of the Wonji/Shoa and Metahara areas of the Awash Valley in Ethiopia, Ashley and Burley (1994) found concentrations up to 26 mg L^{-1} in groundwater from volcanic rocks of the Pliocene to Recent Aden Volcanic Series and up to 4.3 mg L^{-1} in recent alluvium overlying the volcanic rocks. They concluded that the fluoride originated from the volcanic rocks and that high concentrations in solution were maintained by the dominance of Na ions over Ca in the groundwaters. Concentrations diminished slightly in the overlying alluvium as a result of increased groundwater Ca concentrations following likely reaction with carbonate minerals in the sediments.

Alkaline and crater lakes in the East African Rift have some of the highest recorded dissolved fluoride concentrations. In their survey, Tekle-Haimanot et al. (2006) observed highest fluoride values in the Rift Valley lakes Shala (264 mg L^{-1}) and Abijata (202 mg L^{-1}). In Lake Magadi in Kenya, Jones et al. (1977) reported concentrations up to 1980 mg L^{-1} in surface brines (Table 3). The lake waters have evolved towards saline compositions, in some cases with dissolved solids in excess of 300 g L^{-1}, principally by surface evaporative concentration in the low-lying lake basin, which has acted as an evaporating pan for the lake waters. Elevated concentrations of fluoride are also achieved by very low Ca concentrations, following precipitation of carbonate minerals. The lake waters appear to be largely saturated with respect to fluorite and the mineral is an abundant accessory authigenic phase in many of the Magadi lake sediments (Jones et al., 1977). Jones et al. (1977) reported extremely high fluoride concentrations (up to 2170 mg L^{-1}) in saline groundwaters from boreholes in Magadi lake sediments. The occurrence of fluoride in the natural waters of Kenya is also further explored by Gaciri and Davies (1993) and Wambu and Muthakia (2011).

Nanyaro et al. (1984) found concentrations of 60–690 mg L^{-1} in alkaline lakes and ponds of the Momella Lakes Group (Mount Meru area) in Tanzania (Table 3). The lake waters are also brackish and the most alkaline and saline compositions are found in the largest lakes of the group. Evaporation is also considered a major factor in the development of the extreme fluoride enrichments and the higher concentrations in the larger lakes of the group may be related to a smaller influence of dilution from runoff during wet periods and the long history of evolution of the lakes (Nanyaro et al., 1984). Also in Tanzania, concentrations up to 72 mg L^{-1} have been reported for Lake Natron (Table 3). Ashley and Burley (1994) also found 36 mg L^{-1} fluoride in Lake Besaka in the Awash Valley of Ethiopia. Variable concentrations were obtained for lake waters from East Africa by Kilham and Hecky (1973). The highest concentrations (up to 437 mg L^{-1} reported for Lake Tulusia in the Momella Group and up to 437 mg L^{-1} in Lake Magadi) were found in lake waters of Na-HCO_3 (low Cl) composition. Kilham and Hecky (1973) postulated that the fluoride most likely originates from weathering of volcanic rocks and/or from geothermal solutions in the rift system. As with other lakes in the Rift, the maintenance of high dissolved concentrations is possible because they have low Ca concentrations resulting from loss of Ca by precipitation of travertine in local streams and springs.

It is an unfortunate fact that this region of anomalously high fluoride concentrations, like many arid areas, also suffers from significant problems with water scarcity. The arid climate, combined with often poor coverage by, or poor maintenance of, abstraction boreholes in many of the affected countries means that the emphasis is usually on water availability and that drinking-water quality is of lower priority.

5.6. Gaspé Peninsula, Canada – depth control where glacial deposits overlie bedrock

Increasing fluoride concentrations are found with depth in groundwaters in many parts of the world. Such areas may represent increasing reaction times and decreasing circulation rates, or alternatively a change in geology. One such area is the Gaspé Peninsula in Canada, where Quaternary glacial till overlies older bedrock. This is likely to be a widespread geological occurrence in North America, Europe and northern Asia and this example serves as a type area for other glacial terrain.

A farming community relying on shallow wells for water supply occupies the town of Maria in the Gaspé Peninsula of Quebec, Canada. The community has only recently suffered from cases of chronic skeletal fluorosis, resulting from fluoride concentrations in the water supplies up to 28 mg L^{-1} (Boyle and Chagnon, 1995). The area is situated on a flat coastal plain covered by colluvial, alluvial and glacial sediments, varying in thickness from 10 to 30 m. The coastal plain is underlain by Carboniferous sediments comprising conglomerates, sandstones, mudstones and commonly containing calcareous cements. High-fluoride waters occur throughout the region and there is a clear correlation between fluoride concentrations and depth. Thus, almost all the wells completed in the Carboniferous sediments contain excessive fluoride; the mean concentration in water from the overlying sediments was around 0.1 mg L^{-1}, compared to 10.9 mg L^{-1} in the bedrock. The high fluoride concentrations are explained by the high cation-exchange capacities of the sediments, which give rise to softening of the groundwaters and exchange of Ca^{2+} for $2Na^{+}$, in a similar way to the Lincolnshire Limestone described above. Tritium analyses of groundwater also suggest that the groundwaters in this low-lying area have long residence times.

Farmers relied originally on shallow dug wells, but were advised in the 1970s to deepen these to increase yields (to satisfy the same demands as the townspeople who were supplied by mains water). Two cases of skeletal fluorosis drew attention to the potentially widespread nature of the problem, with the affected individuals only having been exposed to the fluoride-rich water for a period of 6 years. This study draws attention to the need for water-quality as well as water-quantity assessments during groundwater investigations, as well as an awareness of the geochemical properties of the sediments and a consideration of groundwater residence times.

6. Remediation of high-fluoride groundwater

As a means of combating the fluoride problem, several methods of water treatment using various media have been tested and a number are in use in various parts of the world. Some of the common methods are listed in Table 5 and reviews have been published by Heidweiller (1990) and Mohapatra et al. (2009). Most low-technology methods rely on precipitation or flocculation, or adsorption/ion-exchange processes. Probably the best-known and most established method is the Nalgonda technique (Nawlakhe and Bulusu, 1989), named after the Nalgonda District in Andhra Pradesh, India where the technique has been developed and is in use today. The technique uses a combination of alum (or aluminium chloride) and lime (or sodium aluminate), together with bleaching powder, which are added to high-fluoride water, stirred and left to settle. Fluoride is subsequently removed by flocculation, sedimentation and filtration. The method can be used at a domestic scale (in buckets) or community scale (fill-and-draw type defluoridation plants; Nawlakhe and Bulusu, 1989). It has moderate costs and uses materials which are usually easily available. It is therefore preferred for small defluoridation units used exclusively for drinking water. Aluminium polychloride sulphate has been found to have technical advantages over alum as use of alum results in increased concentrations of SO_4 and suspended particles in the treated water (N'dao et al., 1992).

Other precipitation methods include the use of gypsum, dolomite or calcium chloride. Most methods tested are capable in principle of reducing fluoride in treated water to a concentration below the WHO guideline value. Vanderdonck and Van Kesteren (1993) reported that the calcium chloride method is capable of reducing fluoride concentrations up to 20 mg L^{-1} to acceptable concentrations.

The most common ion-exchange removal methods tested are activated carbon, activated alumina (Barbier and Mazounie, 1984), ion-exchange resins (e.g. Defluoron 2), plant carbon, clay minerals (Chaturvedi et al., 1988), clay pots, crushed bone or bone char (Rao et al., 2009). Activated alumina and bone materials are among the most effective appropriate-technology removal methods (with highest removal capacity, Table 5). These also have drawbacks however: activated alumina may not always be available or affordable and bone products are not readily acceptable in some cultures (Tekle-Haimanot et al., 2006). Use of fired clay-pot shards has proved a promising approach in some developing countries (Moges et al., 1996). The use of fly ash has also been tested favourably for fluoride removal (Chaturvedi et al., 1990), although the concentrations of other solutes in the water after treatment with fly ash need to be ascertained. Some success has also been demonstrated experimentally using aluminium-rich volcanic soils (Ando soils) from the East African Rift of Kenya (Zevenbergen et al., 1996), although field testing of the technique has not been reported.

Other highly efficient methods of removal include electro-dialysis, reverse osmosis and nanofiltration (Banasiak and Schaefer, 2009; Richards et al., 2010; Schneiter and Middlebrooks, 1983). These methods tend to involve higher technology and higher costs (Table 5) and are therefore less suitable for many applications in developing countries.

Most methods designed for village-scale fluoride removal have drawbacks in terms of removal efficiency, cost, local availability of materials, chemistry of resultant treated water and disposal of treatment chemicals. Local circumstances will dictate which methods, if any, are the most appropriate. In addition, many of the defluoridation methods have only been tested at pilot scale or in the laboratory. In practice, remediation techniques such as those outlined above often meet with disappointing success when put into operation. Success rates depend on efficacy, user acceptance, ease of maintenance, and degree of community participation, availability and cost of raw materials. An additional problem lies with monitoring. In most rural communities, it will be almost impossible to monitor the initial fluoride concentrations so that dosing can be accurate. It is also not practicable at village level to chemically monitor the progress of treatment schemes, such as knowing when to recycle or replace the media involved in the treatment.

As an example of problems with the water treatment approach, defluoridation schemes have been in operation in Wonji, Ethiopia since 1962. In the past, these principally involved bone char, but most recently a resin-activated-alumina adsorption method has been used (Kloos and Tekle-Haimanot, 1999). Only two of twelve plants were still in operation in 1997 and in the years of operation, only four of the plants consistently reduced fluoride below 1.5 mg L^{-1}. The major problems encountered included efficiencies in the operation of the plant, lack of spare parts and materials and lack of community involvement. The affected areas are currently served by a piped water scheme, but in more remote areas, interest in defluoridation continues.

Given the potential drawbacks of water treatment, alternative fluoride mitigation approaches could prove more effective, such as careful borehole siting (Ayenew, 2008), groundwater management and use of alternative sources such as rainwater harvesting. It should be borne in mind that the main issue is for the provision of rather small amounts of water for drinking purposes so rainwater harvesting from roof collection or augmenting aquifer recharge provides a straightforward and low-cost solution.

Factors worth considering in borehole siting are local geology and variations in groundwater fluoride concentration with depth. Groundwater management includes consideration of optimum pumping rates, especially where there exists the possibility of mixing of groundwater with deep fluoride-rich groundwater (e.g. old groundwater or hydrothermal solutions), which would be increasingly drawn upwards at high pumping rates (Carrillo-Rivera et al., 2002). Possibilities for enhanced recharge of low-fluoride surface water to aquifers could also give benefits to shallow groundwater quality. Examples include the charco dams of Tanzania. A fully-fledged artificial recharge scheme would offer similar benefits. Considerations with rainwater harvesting include availability of rainfall in arid and semi-arid areas that tend to be worst-affected by fluoride problems, and in maintenance of clean storage facilities for the water supply.

In view of the site-specific nature of each incidence of high fluoride and also the problems of applying remediation, especially in small communities, the supply of small quantities of imported low-fluoride water should also be considered. This could be achieved by importation of water in bottles or tankers to central distribution points and may prove cost-effective, since the high-fluoride source can still be used for sanitation and possibly also for most forms of agriculture.

In low-rainfall areas with fluoride problems, it is important to assess the hydrogeological situation very carefully. The generation of high-fluoride groundwaters usually requires considerable residence times in the aquifer, for reasons outlined in the preceding sections. Thus, it is likely that younger, shallow groundwaters, for example those recharged rapidly below wadis or stream channels, may have lower fluoride concentrations than the bulk groundwater. They may be exploitable as a resource overlying older groundwater. Exploitation may require ‘skimming’ the shallow water table rather than abstraction from deeper penetrating boreholes. The harvesting of rainwater, either directly in cisterns or by collection in small recharge dams, offers a potentially attractive alternative solution.

7. Conclusions

This review has summarised the occurrence of fluorine in natural water and the environment and outlined its behaviour in terms of the hydrogeochemical cycle. The principal sources of fluoride in rainfall are marine aerosols, volcanic emissions and anthropogenic inputs. Concentrations in rain typically lie in the range 0.02–0.2 mg L^{-1} with pristine and continental rains lying at the lower end of the range. Surface waters generally also reflect these sources and concentrations in most are low, except where affected by extensive evapotranspiration or geothermal inputs. Surface waters rarely have fluoride concentrations sufficiently high to be detrimental to health and if fluoride-related health problems exist, they are more likely to be linked to deficiency.

Groundwaters are generally more vulnerable to the build up of fluoride and although concentrations in these are also mostly low (<1 mg L^{-1}), a number of conditions can give rise to detrimentally high concentrations. Geology plays a key role in defining fluoride concentrations. Areas with potentially high-fluoride groundwater include crystalline basement rocks, especially those of granitic composition. These contain relatively high concentrations of fluorine-bearing minerals (e.g. apatite, mica, hornblende, occasionally fluorite) and have low calcium concentrations. Such areas occur over large parts of India, Sri Lanka and Africa for example. The active volcanic province of the East African Rift Valley is also an anomalous area with high fluoride concentrations on a regional scale. High concentrations result from both weathering of volcanic rocks and geothermal inputs. In groundwaters from the East African Rift, fluoride concentrations in excess of 1 mg L^{-1} are common, while concentrations up to several hundred mg L^{-1} have been recorded in some hot springs, and concentrations in excess of 1000 mg L^{-1} have been found in some alkaline lakes. Some sedimentary aquifers also contain high-fluoride groundwaters, especially where calcium concentrations are low and Na-HCO_3 waters dominate. These can occur under arid conditions and in aquifers affected by ion exchange.

The influence of low recharge on dissolved fluoride concentrations in groundwater is also clear from documented studies. The tendency for fluoride accumulation in groundwater from arid and semi-arid areas is well-illustrated from crystalline basement aquifers of India and Sri Lanka and many sedimentary aquifers. The accumulations under arid conditions are the result of rock weathering, evapotranspiration and low recharge. Excessive groundwater fluoride concentrations are relatively rare in tropical and even temperate regions.

Groundwaters in a number of aquifers display progressive increases in fluoride along flow lines and demonstrate the importance of residence time and their position in the flow and reaction sequence. The phenomenon has been demonstrated in the English Lincolnshire Limestone aquifer where dissolved fluoride concentrations increase progressively from 0.11 mg L^{-1} in the unconfined aquifer to 5.6 mg L^{-1} in the deep confined aquifer in response to time-dependent mineral dissolution and ion-exchange reactions. In many aquifers, the evolution of groundwater down the flow gradient has taken place over centuries or millennia, with water being abstracted having had significant opportunity for equilibration with host aquifer minerals. The accumulation of fluoride in water is ultimately limited by mineral solubility. In groundwaters where calcium is abundant, fluoride concentrations are limited by saturation with the mineral fluorite. In cases where calcium concentrations are low, or where calcium is removed by ion exchange, fluoride may build up to excessive and dangerous concentrations.

Given these key controls on fluoride occurrence and distribution, it is possible to anticipate broadly where areas of regionally high fluoride concentrations are likely to exist. Such an understanding of the fluoride occurrence is important for the management of the fluoride-related epidemiological problems. Water-supply programmes in potentially high-fluoride areas should have geological and hydrological guidance, including chemical analyses and geological maps. High fluoride incidence may not be universal within a given area and remediation strategies may include identification of areas of distinct geology, residence time or selective recharge where fluoride concentrations are locally lower. Nevertheless, even taking into account all available hydrogeological information, groundwater fluoride concentrations are frequently so variable on a local scale that prediction of concentrations in individual wells is difficult. Hence, for the purposes of compliance, testing of each well used for drinking water should be undertaken in fluoride-prone areas. Testing can be achieved effectively either in the field or laboratory by ion-selective electrodes, colorimetry or ion chromatography. Chemical and other forms of intervention and treatment should generally be a last resort, especially since their monitoring in rural communities is virtually impossible.

8. References

Ainsworth, N.J., 1933. Mottled teeth. British Dental Journal 55, 233-250.

Apambire, W.B., Boyle, D.R., Michel, F.A., 1997. Geochemistry, genesis, and health implications of fluoriferous groundwaters in the upper regions of Ghana. Environ. Geol. 33, 13-24.

Ashley, P.P., Burley, M.J., 1994. Controls on the occurrence of fluoride in groundwater in the Rift Valley of Ethiopia., in: Nash, H., McCall, G.J.H. (Eds.), Groundwater Quality. Chapman & Hall, London, pp. 45-54.

Ayenew, T., 2008. The distribution and hydrogeological controls of fluoride in the groundwater of central Ethiopian rift and adjacent highlands. Environ. Geol. 54, 1313-1324.

Banasiak, L.J., Schaefer, A.I., 2009. Removal of boron, fluoride and nitrate by electrodialysis in the presence of organic matter. Journal of Membrane Science 334, 101-109.

Banks, D., Frengstad, B., Midtgard, A.K., Krog, J.R., Strand, T., 1998. The chemistry of Norwegian groundwaters: I. The distribution of radon, major and minor elements in 1604 crystalline bedrock groundwaters. The Science of the Total Environment 222, 71-91.

Barbier, J.P., Mazounie, P., 1984. Methods of reducing high fluoride content in drinking water: fluoride removal methods - filtration through activated alumina: a recommended technique. Water Supply 2, 3-4.

Bårdsen, A., Bjorvatn, K., Selvig, K.A., 1996. Variability in fluoride content of subsurface water reservoirs. Acta Odont. Scand. 54, 343-347.

Barnard, W.R., Nordstrom, D.K., 1982. Fluoride in precipitation - II. Implication for the geochemical cycling of fluorine. Atmos. Environ. 16, 105-111.

Botchway, C.A., Ansa-Asare, O.D., Antwi, L.A.K., 1996. Natural fluoride and trace metal levels of ground and surface waters in the greater Accra region of Ghana. West African Journal of Medicine 15, 204-209.

Boyle, D.R., Chagnon, M., 1995. An incidence of skeletal fluorosis associated with groundwaters of the maritime Carboniferous basin, Gaspé region, Quebec, Canada. Environ. Geochem. Health 17, 5-12.

Bugaisa, S.L., 1971. Significance of fluorine in Tanzania drinking water, in: Tschannerl, G. (Ed.), Proceedings of a Conference on Rural Water Supply in East Africa. Bureau of resource assessment and land use planning, Dar Es Salaam, Dar Es Salaam, pp. 107-113.

Carrillo-Rivera, J.J., Cardona, A., Edmunds, W.M., 2002. Use of abstraction regime and knowledge of hydrogeological conditions to control high-fluoride concentration in abstracted groundwater: San Luis Potosí basin, Mexico. Journal of Hydrology 261, 24-47.

Chakraborti, D., Chanda, C.R., Samanta, G., Chowdhury, U.K., Mukherjee, S.C., Pal, A.B., Sharma, B., Mahanta, K.J., Ahmed, H.A., Sing, B., 2000. Fluorosis in Assam, India. Current Science 78, 1421-1423.

Chaturvedi, A.K., Pathak, K.C., Singh, V.N., 1988. Fluoride removal from water by adsorption on China Clay. Applied Clay Science 3, 337-346.

Chaturvedi, A.K., Yadava, K.P., Pathak, K.C., Singh, V.N., 1990. Defluoridation of water by adsorption on fly ash. Water, Air and Soil Pollution 49, 51-61.

Connett, P., 2007. Professionals mobilize to end water fluoridation worldwide. Fluoride 40, 155-158.

Cook, J.M., Edmunds, W.M., Robins, N.S., 1991. Groundwater contributions to an acid upland lake (Loch Fleet, Scotland) and the possibilities for amelioration. Journal of Hydrology 125, 111-128.

Corbett, R.G., Manner, B.M., 1984. Fluoride in ground water of northeastern Ohio. Ground Water 22, 13-17.

Datta, D.K., Gupta, L.P., Subramanian, V., 2000. Dissolved fluoride in the Lower Ganges-Brahmaputra-Meghna River system in the Bengal Basin, Bangladesh. Environ. Geol. 39, 1163-1168.

Dean, H.T., Elvove, E., 1937. Further studies on the minimal threshold of chronic endemic dental fluorosis. Public Health Reports (Washington) 52, 1249-1264.

Deng, Y., Nordstrom, D.K., McCleskey, R.B., 2011. Fluoride geochemistry of thermal waters in Yellowstone National Park: I. Aqueous fluoride speciation. Geochimica Et Cosmochimica Acta 75, 4476-4489.

Diaz-Barriga, F., Leyva, R., Quistian, J., Loyola-Rodriguez, J.B., Pozos, A., Grimaldo, M., 1997. Endemic fluorosis in San Luis Potosi, Mexico. Fluoride 30, 219-222.

Diesendorf, 1986. The mystery of declining tooth decay. Nature 322, 125-129.

Dissanayake, C.B., 1991. The fluoride problem in the groundwater of Sri Lanka - environmental management and health. International Journal of Environmental Studies 38, 137-156.

Edmunds, W.M., 1973. Trace element variations across an oxidation-reduction barrier in a limestone aquifer, Proc. Symp. Hydrogeochem. Clarke Co. Washington, Tokyo (1970), pp. 500-526.

Edmunds, W.M., 1994. Characterization of groundwaters in semi-arid and arid zones using minor elements., in: Nash, H., McCall, G.J.H. (Eds.), Groundwater Quality. Chapman & Hall, London, pp. 19-30.

Edmunds, W.M., Cook, J.M., Darling, W.G., Kinniburgh, D.G., Miles, D.G., Bath, A.H., Morgan-Jones, M., Andrews, J.N., 1987. Baseline geochemical conditions in the Chalk aquifer, Berkshire, UK: a basis for groundwater quality management. Appl. Geochem. 2, 251-274.

Edmunds, W.M., Cook, J.M., Kinniburgh, D.G., Miles, D.G., Trafford, J.M., 1989. Trace element occurrence in British groundwaters. British Geological Survey Research Report SD/89/3, Keyworth, p. 424.

Edmunds, W.M., Walton, N., 1983. The Lincolnshire Limestone - hydrogeochemical evolution over a ten-year period. Journal of Hydrology 61, 201-211.

Ellis, A.J., 1973. Chemical processes in hydrothermal systems - a review, in: Ingerson, E. (Ed.), Proceedings of a Symposium on Hydrogeochemistry, pp. 1-26.

Ellis, A.J., Mahon, W.A.J., 1977. Chemistry and Geothermal Systems. Academic Press, New York.

Eyre, R., Feltbower, R.G., Mubwandarikwa, E., Eden, T.O.B., McNally, R.J.Q., 2009. Epidemiology of Bone Tumours in Children and Young Adults. Pediatr. Blood Cancer 53, 941-952.

Fantong, W.Y., Satake, H., Ayonghe, S.N., Suh, E.C., Adelana, S.M.A., Fantong, E.B.S., Banseka, H.S., Gwanfogbe, C.D., Woincham, L.N., Uehara, Y., Zhang, J., 2010. Geochemical provenance and spatial distribution of fluoride in groundwater of Mayo Tsanaga River Basin, Far North Region, Cameroon: implications for incidence of fluorosis and optimal consumption dose. Environ. Geochem. Health 32, 147-163.

Finkelman, R.B., Belkin, H.E., Zheng, B., 1999. Health impacts of domestic coal use in China. Proceedings of the National Academy of Sciences USA 96, 3427-3431.

Fritz, B., 1981. Etude thermodynamique et modélisation des réactions hydrothermales et diagénétiques., Sciences Géologiques. Strasbourg, Strasbourg, p. 197.

Fuge, R., Andrews, M.J., 1988. Fluorine in the UK environment. Environ. Geochem. Health 10, 96-104.

Fuhong, R., Shuquin, J., 1988. Distribution and formation of high-fluorine groundwater in China. Environmental Geology and Water Science 12, 3-10.

Gaciri, S.J., Davies, T.C., 1993. The occurrence and geochemistry of fluoride in some natural waters of Kenya. Journal of Hydrology 143, 395-412.

Goni, J., Greffard, J., Leleu, M., Monitron, L., 1973. Le fluor dans les eaux de boisson. Bureau de Recherches Géologiques et Minières, Orléans, France.

Guo, Q., Wang, Y., Liu, W., 2009. Hydrogeochemistry and environmental impact of geothermal waters from Yangyi of Tibet, China. Journal of Volcanology and Geothermal Research 180, 9-20.

Gupta, M.K., Singh, V., Rajwanshi, P., Agarwal, M., Rai, K., Srivastava, S., Srivastav, R., Dass, S., 1999. Groundwater quality assessment of Tehsil Kheragarh, Agra (India) with special reference to fluoride. Environmental Monitoring and Assessment 59, 275-285.

Gupta, S.C., Rathore, G.S., Doshi, C.S., 1993. Fluoride distribution in groundwaters of southeastern Rajasthan. Indian Journal of Environmental Health 35, 97-109.

Hamilton, M., 1992. Water fluoridation: a risk assessment perspective. Journal of Environmental Health 54, 27-32.

Handa, B.K., 1975. Geochemistry and genesis of fluoride-containing ground waters in India. Ground Water 13, 275-281.

Heidweiller, V.M.L., 1990. Fluoride removal methods, in: Frencken, J.E. (Ed.), Proceedings of a Symposium on Endemic Fluorosis in Developing Countries: Causes, Effects and Possible Solutions. NIPG-TNO, Leiden, pp. 51-85.

Hem, J.D., 1985. Study and interpretation of the chemical characteristics of natural water. USGS Water Supply Paper 2254, p. 263.

Hitchon, B., 1995. Fluorine in formation waters in Canada. Appl. Geochem. 10, 357-367.

Hoather, R.C., 1953. Fluorides in water supplies. Journal of the Royal Sanitary Institute 73, 202-223.

Jacob, B., 1975. Contribution à l'étude géochimique des eaux froides et thermominérales du Massif du Mont-Dore. Université de Paris VI, Paris, p. 205.

Jones, B.F., Eugster, H.P., Reitig, S.L., 1977. Hydrochemistry of the Lake Magadi basin, Kenya. Geochimica Cosmochimica Acta 41, 53-72.

Kabata-Pendias, A., Pendias, H., 1984. Trace Elements in Soils and Plants. CRC Press, Boca Raton, Florida.

Kafri, U., Arad, A., Halicz, L., Ganor, E., 1989. Fluorine enrichment in groundwater recharged through loess and dust deposits, southern Israel. Journal of Hydrology 110, 373-376.

Kilham, P., Hecky, R.E., 1973. Fluoride: geochemical and ecological significance in East African waters and sediments. Limnology & Oceanography 18, 932-945.

Kloos, H., Tekle-Haimanot, R., 1999. Distribution of fluoride and fluorosis in Ethiopia and prospects for control. Tropical Medicine and International Health 4, 355-364.

Kotoky, P., Barooah, P.K., Baruah, M.K., Goswami, A., Borah, G.C., Gogoi, H.M., Ahmed, F., Gogoi, A., Paul, A.B., 2008. Fluoride and endemic fluorosis in the Karbianglong district, Assam, India. Fluoride 41, 72-75.

Lamont, P., 1958. Interim report on an investigation of the chemical characteristics of the underground waters from the Lincolnshire Limestone in the area of supply, with special reference to the possibility of locating new sources yielding a more suitable water for public supplies, Spalding, Lincolnshire, UK.

Lavado, R.S., Reinaudi, N., 1979. Fluoride in salt affected soils of La Pampa (Republica Argentina). Fluoride 12, 28-32.

Mahon, W.A.J., 1964. Fluorine in the natural thermal waters of New Zealand. New Zealand Journal of Science 7, 3-28.

Maier, F.J., 1950. Fluoridation of public health supplies. Journal of the American Waterworks Association 42, 1120-1132.

Maithani, P.B., Gurjar, R., Banerjee, R., Balaji, B.K., Ramachandran, S., Singh, R., 1998. Anomalous fluoride in groundwater from western part of Sirohi district, Rajasthan, and its crippling effects on human health. Current Science 74, 773-777.

Majumdar, K.K., 2011. Health impact of supplying safe drinking water containing fluoride below permissible level on flourosis patients in a fluoride-endemic rural area of West Bengal. Indian Journal of Public Health 55, 303-308.

Marshall, E., 1990. The fluoride debate: one more time. Science 247, 276-277.

Martinez, D.E., Quiroz Londono, O.M., Massone, H.E., Palacio Buitrago, P., Lima, L., 2012. Hydrogeochemistry of fluoride in the Quequen river basin: natural pollutants distribution in the argentine pampa. Environmental Earth Sciences 65, 411-420.

McCaffrey, L.P., 1998. Distribution and causes of high fluoride groundwater in the western Bushveld area of South Africa. Cape Town.

Moges, G., Zewge, F., Socher, M., 1996. Preliminary investigations on the defluoridation of water using fired clay chips. Journal of African Earth Sciences 22, 479-482.

Mohapatra, M., Anand, S., Mishra, B.K., Giles, D.E., Singh, P., 2009. Review of fluoride removal from drinking water. Journal of Environmental Management 91, 67-77.

Murray, R.J., 1960. The Geology of the "Zuarungu" E Field Sheet. Geol. Survey Ghana Bulletin No. 25, Accra, p. 118.

N'dao, I., Lagaude, A., Travi, Y., 1992. Défluoruration expérimentale des eaux souterraines du Sénégal par le sulphate d'aluminium et le polychlorosulphate basique d'aluminium. Sciences et Techniques de l'Eau 26, 243-249.

Nanyaro, J.T., Aswathanarayana, U., Mungure, J.S., 1984. A geochemical model for the abnormal fluoride concentrations in waters in parts of northern Tanzania. Journal of African Earth Sciences 2, 129-140.

Nawlakhe, W.G., Bulusu, K.R., 1989. Nalgonda technique - a process for removal of excess fluoride from water. Water Quality Bulletin 14, 218-220.

Neal, C., 1989. Fluorine variations in Welsh streams and soil waters. The Science of the Total Environment 80, 213-223.

Neal, C., Wilkinson, J., Neal, M., Harrow, M., Wickham, H., Hill, L., Morfitt, C., 1997. The hydrochemistry of the River Severn, Plynlimon. Hydrology and Earth System Science 1, 583-617.

Nordstrom, D.K., Jenne, E.A., 1977. Fluorite solubility equilibria in selected geothermal waters. Geochimica Cosmochimica Acta 41, 175-198.

Parkhurst, D.L., Appelo, C.A.J., 1999. User's guide to PHREEQC (Version 2) - A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. Water-Resources Investigations Report 99-4259. USGS, Denver.

Pickering, W.F., 1985. The mobility of soluble fluoride in soils. Environmental Pollution (Series B) 9, 281-308.

Pizzo, G., Piscopo, M.R., Pizzo, I., Giuliana, G., 2007. Community water fluoridation and caries prevention: a critical review. Clinical Oral Investigations 11, 189-193.

Queste, A., Lacombe, M., Hellmeier, W., Hillerman, F., Bortulussi, B., Kaup, M., Ott, O., Mathys, W., 2001. High concentrations of fluoride and boron in drinking water wells in the Muenster region - results of a preliminary investigation. Int. J. Hygiene Environ. Health 203, 221-224.

Rafique, T., Naseem, S., Usmani, T.H., Bashir, E., Khan, F.A., Bhanger, M.I., 2009. Geochemical factors controlling the occurrence of high fluoride groundwater in the Nagar Parkar area, Sindh, Pakistan. Journal of Hazardous Materials 171, 424-430.

Rao, A.S.M., Rajayalakshmi, K., Sastry, K.R.K., Rao, P.S., Rao, V.V.K., Rao, K.N., 1974. Incidence of fluorides in drinking water resources, in Andhra Pradesh., Fluorosis, Hyderabad, India, pp. 227-235.

Rao, N.S., 2002. Geochemistry of groundwater in parts of Guntur District, Andhra Pradesh, India. Environ. Geol. 41, 552-562.

Rao, S.M., Reddy, B.V.V., Lakshmikanth, S., Ambika, N.S., 2009. Re-use of fluoride contaminated bone char sludge in concrete. Journal of Hazardous Materials 166, 751-756.

Rea, R.E., 1979. A rapid method for the determination of fluoride in sewage sludges. Water Pollution Control 78, 139-142.

Reddy, D.V., Nagabhushanam, P., Sukhija, B.S., Reddy, A.G.S., Smedley, P.L., 2010. Fluoride dynamics in the granitic aquifer of the Wailapally watershed, Nalgonda District, India. Chemical Geology 269, 278-289.

Richards, L.A., Vuachere, M., Schaefer, A.I., 2010. Impact of pH on the removal of fluoride, nitrate and boron by nanofiltration/reverse osmosis. Desalination 261, 331-337.

Saether, O.M., Andreassen, B.T., 1989. Fluoride in precipitation in southern Norway: amounts and sources. Report 89/106. Geological Survey of Norway. Geological Survey of Norway.

Schneiter, R.W., Middlebrooks, E.J., 1983. Arsenic and fluoride removal from groundwater by reverse osmosis. Environment International 9, 289-292.

Smedley, P.L., Edmunds, W.M., Pelig-Ba, K.B., 1995. Groundwater vulnerability due to natural geochemical environment: 2: Health problems related to groundwater in the Obuasi and Bolgatanga areas, Ghana. BGS Technical Report.

Smedley, P.L., Nicolli, H.B., Macdonald, D.M.J., Barros, A.J., Tullio, J.O., 2002. Hydrogeochemistry of arsenic and other inorganic constituents in groundwaters from La Pampa, Argentina. Appl. Geochem. 17, 259-284.

Smet, J., 1990. Fluoride in drinking water, in: Frencken, J.E. (Ed.), Proc. Symposium on Endemic Fluorosis in Developing Countries: Causes, Effects and Possible Solutions. NIPG-TNO, Leiden, pp. 51-85.

Solsona, F., 1985. Water defluoridation in the Rift Valley, Ethiopia. UNICEF, Addis Ababa, p. 27.

Suma Latha, S., Anbika, S.R., Prasad, S.J., 1999. Fluoride contamination status of groundwater in Karnataka. Current Science 76, 730-734.

Tekle-Haimanot, R., Melaku, Z., Kloos, H., Reimann, C., Fantaye, W., Zerihun, L., Bjorvatn, K., 2006. The geographic distribution of fluoride in surface and groundwater in Ethiopia with an emphasis on the Rift Valley. Sci. Total Environ. 367, 182-190.

Ten Haven, H.L., Konings, R., Schoonen, M.A.A., Jansen, J.B.H., Vriend, S.P., Van der Weijden, C.H., Buitenkamp, J., 1985. Geochemical studies in the drainage basin of the Rio Vouga (Portugal). Chemical Geology 51, 225-238.

Travi, Y., 1993. Hydrogéologie et hydrochimie des aquifères du Sénégal. Sciences Géologiques, Memoire 95. Université de Paris-Sud, Paris.

Turner, B.D., Binning, P., Stipp, S.L.S., 2005. Fluoride removal by calcite: evidence for fluorite precipitation and surface adsorption. Environmental Science & Technology 39, 9561-9568.

US Public Health Service, 1943. Public Health Drinking Water Standards. Journal of the American Waterworks Association 35, 93-104.

US Public Health Service, 1946. Drinking Water Standards. Journal of the American Waterworks Association 38, 361-370.

Vanderdonck, P., Van Kesteren, X., 1993. Utilisation du chlorure de calcium. Tribune de l'Eau 562, 39-40.

Vijaya Kumar, V., Sai, C.S.T., Rao, P.L.K.M., Rao, C.S., 1991. Studies on the distribution of fluoride in drinking water sources in Medchal Block, Ranga Reddy District, Andra Pradesh, India. Journal of Fluorine Chemistry 55, 229-236.

Viswanathan, G., Jaswanth, A., Gopalakrishnan, S., Ilango, S.S., Aditya, G., 2009. Determining the optimal fluoride concentration in drinking water for fluoride endemic regions in South India. Sci. Total Environ. 407, 5298-5307.

Wambu, E.W., Muthakia, G.K., 2011. High fluoride water in the Gilgil area of Nakuru County, Kenya. Fluoride 44, 37-41.

Wenzel, W.W., Blum, W.E.H., 1992. Fluorine speciation and mobility in F-contaminated soils. Soil Sci. 153, 357-364.

WHO, 2011. Guidelines for Drinking-Water Quality, fourth edition. World Health Organization, Geneva.

Woo, N.C., Moon, J.W., Won, J.S., Hahn, J.S., Lin, X.Y., Zhao, Y.S., 2000. Water quality and pollution in the Hunchun Basin, China. Environ. Geochem. Health 22, 1-18.

Wuyi, W., Ribang L., Jian'an T., Kunli, L., Lisheng, Y., Hairong, L., Yonghua, L., 2002. Adsorption and leaching of fluoride in soils of China. Fluoride 35, 122-129.

Yeung, C.A., 2008. A systematic review of the efficacy and safety of fluoridation. Evidence-based dentistry 9, 39-43.

Zan-dao, W., Yan, W., 2002. Fluoridation in China: a clouded future. Fluoride 35, 1-4.

Zevenbergen, C., van Reeuwijk, L.P., Frapporti, G., Louws, R.J., Schuiling, R.D., 1996. A simple method for defluoridation of drinking water at village level by adsorption on Ando soil in Kenya. The Science of the Total Environment 188, 225-232.

Zubair, L., 2003. Sensitivity of Kelani streamflow in Sri Lanka to ENSO. Hydrological Processes 17, 2439-2448.

Table 1. Regulations and recommendations for fluoride in drinking water from a number of organisations or countries.

Institution/ nation	**Limit/guideline**	**Value ($\mathrm{mg\ L^{-1}}$)**	**Comment**
WHO	Guideline value (GV)	1.5	2011 guidelines, as previous
US EPA	Maximum contaminant level guideline (MCL)	4	Enforceable regulation
US EPA	Secondary standard	2	Guideline intended to protect against dental fluorosis; not enforceable
EC	Maximum admissible concentration (MAC)	1.5	1998 regulations
Canada	National standard	1.5	
India	National standard	1.5	'Acceptable' limit 1.0 $\mathrm{mg\ L^{-1}}$
China	National standard	1	
Tanzania	National standard	8	Interim standard

Table 2. Health effects of fluoride concentrations in drinking water (from Dissanayake, 1991).

Fluoride concentration range ($\mathrm{mg\ L^{-1}}$)	**Chronic health effects**
Nil	Limited growth and fertility
0.0–0.5 $\mathrm{mg\ L^{-1}}$	Dental caries
0.5–1.5 $\mathrm{mg\ L^{-1}}$	Promotes dental health, prevents tooth decay
1.5–4.0 $\mathrm{mg\ L^{-1}}$	Dental fluorosis (mottled teeth)
4–10 $\mathrm{mg\ L^{-1}}$	Dental fluorosis, skeletal fluorosis
>10 $\mathrm{mg\ L^{-1}}$	Crippling fluorosis

Table 3. Ranges of fluoride concentrations in various natural waters.

Country	Aquifer	Range of F (mg L^{-1})	Average (mg L^{-1})	No. analyses	Reference
Rainfall					
Norway		0.0–0.253	0.013–0.025		Saether and Andreassen (1989)
USA	Virginia – coastal	0.002–0.02	0.009		Barnard and Nordstrom (1982)
	Virginia – inland		0.004		
Sri Lanka	Anuradhapura	<0.02–0.08	0.03	6	BGS (unpublished data)
UK	Chilton, south-east England		0.096	24	Edmunds et al. (1987)
UK	Mid Wales	0.02–0.22	0.02		Neal (1989)
UK	Loch Fleet, Scotland	<0.05	<0.05	10	Cook et al. (1991)
Surface waters					
India	Ganges River		0.154		Datta et al. (2000)
India	Meghna River		0.066		Datta et al. (2000)
India	Brahmaputra River		0.120		Datta et al. (2000)
UK	Hafren River, Wales	0.03–0.07	0.05		Neal (1989)
Ghana	Rivers, Accra region	0.03–0.14	0.09	5	Botchway et al. (1996)
Ghana	Ponds, Accra region	0.07–0.30	0.18	5	Botchway et al. (1996)
Surface waters in high-fluoride regions					
Tanzania, Kenya, Uganda	Lakes on alkaline volcanic rocks and others	0.2–1627		200	Kilham and Hecky (1973)
Ethiopia	River Awash	0.9–1.3	1.1	2	Ashley and Burley (1994)
Ethiopia	Rift Valley lakes	1.7–264	54.3	10	Tekle-Haimanot et al. (2006)
Kenya	Streams bordering Lake Magadi	0.1–1.9	0.6	14	Jones et al. (1977)
Kenya	Lake Naivasha	1.7–1.8	1.75	2	Jones et al. (1977)
Tanzania	Lake Magadi	759–1980	1281	13	Jones et al. (1977)
Tanzania	Little Magadi Lake	668–754	711	2	Jones et al. (1977)
Tanzania	Lakes, alkaline volcanic area	60–690		9	Nanyaro et al. (1984)
Tanzania	Rivers, alkaline volcanic area	12–26		9	Nanyaro et al. (1984)
Soil water					
UK	Upland Wales	0.02–0.30	0.05		Neal (1989)
Geothermal springs					
Tanzania	Mbulu springs	up to 99			Bugaisa (1971)
Tanzania	Lake Natron thermal springs	330			Bugaisa (1971)
Kenya	Hot springs (>50ºC) bordering Lake Magadi	141–166	7	155	Jones et al. (1977)
Kenya	Warm springs (<50ºC) bordering Lake Magadi	50–146	14	82	Jones et al. (1977)
Ethiopia	Rift Valley hot springs	to over 13		20	Tekle-Haimanot et al. (2006)
Tunisia	Hot springs	up to 4			Travi (1993)
USA	Western states	0.8–30.8			Nordstrom and Jenne (1977)
USA	Wister mudpots, Salton Sea	14–15			Ellis and Mahon (1977)
USA	Yellowstone National Park	up to 50		140	Deng et al. (2011)
Iceland	Spring, Reykjavik	1.0			Ellis and Mahon (1977)
Iceland	Spring, Hveragerdi	1.1–1.9			Ellis and Mahon (1977)
Kamchatka	Spring	0.8			Ellis and Mahon (1977)
Former USSR	Spring, Makhachkala, Dagestan	0.4			Ellis and Mahon (1977)
New Zealand	Springs	0.3–8.4			Ellis and Mahon (1977)
Taiwan	Spring, Tatun	7.3			Ellis and Mahon (1977)
France	Vichy water	3.8–8.0			Goni et al. (1973)

France	Mont Dore springs	0.07–3.6			Jacob (1975)
France	Plombières springs	1.9–7.0			Fritz (1981)
China	Springs, Shixingsian, Guangdong	up to 45			Fuhong and Shuquin (1988)
Tibet, China	Yangi geothermal field	13.0–22.7	19.2	8	Guo et al. (2009)
Portugal	Rio Vouga hot springs	0.04–20.5	11.0	6	Ten Haven et al. (1985)
Groundwater: crystalline basement rocks					
Norway	Caledonian basic and ultrabasic rocks		1.89		Banks et al. (1998)
	Precambrian granite		1.69		Banks et al. (1998)
	Precambrian anorthosite, charnockite		<0.05		Banks et al. (1998)
Norway	Igneous and metamorphic rocks, Hordaland	0.02–9.48	0.30	1063	Bårdsen et al. (1996)
Cameroon	Granite	0.2–15.2			Fantong et al. (2010)
Ghana	Crystalline basement, including granite and metasediment	0.09–3.8	1.07	118	Smedley et al. (1995)
Senegal	Granitoids, pelites, schists, amphibolites	0.1–3.5			Travi (1993)
India	Crystalline basement, Andhra Pradesh	up to 20			Rao et al. (1974)
India	Crystalline basement, Nalgonda, Andra Pradesh	0.5–7.6	3.6	433	Reddy et al. (2010)
India	Archaean granites and gneisses, east and south-east Karnataka	0.80–7.4	3.5	25	Suma Latha et al. (1999)
India	Archaean banded gneiss, south-east Rajasthan	<0.1–16.2	1.28	2649	Gupta et al. (1993)
India	Archaean granite	0.3–6.9		188	Vijaya Kumar et al. (1991)
Pakistan	Nagar Parkar, Sindh Province	1.1–7.9	3.33	32	Rafique et al. (2009)
Sri Lanka	Crystalline basement, including granite and charnockite	<0.02–10			Dissanayake (1991)
South Africa	Western Bushveld Complex	0.1–10	143	3485	McCaffrey (1998)
Groundwater: volcanic rocks					
Ethiopia	Volcanic bedrock (Wonji/Shoa area)	6.1–20.0	12.9	14	Ashley and Burley (1994)
Ethiopia	Pleistocene sediment above volcanic bedrock (Wonji/Shoa)	2.1–4.6	3.4	6	Ashley and Burley (1994)
Ethiopia	Pleistocene sediment above volcanic bedrock (Metahara)	2.7–15.3	5.9	15	Ashley and Burley (1994)
Tanzania	Ngorongoro Crater & Lemagrut volcanic cone	40–140			Bugaisa (1971)
Tanzania	Kimberlites, Shinyanga	110–250			Bugaisa (1971)
Groundwater: sediments and sedimentary basins					
China	Quaternary sands, Hunchun Basin, north-east China	1.0–7.8		19	Woo et al. (2000)
Argentina	Quaternary loess, La Pampa	0.03–29	5.2	108	Smedley et al. (2002)
Argentina	Quaternary loess, Quequen Grande River Basin	0–5.7	1.84	135	Martinez et al. (2012)
India	Quaternary alluvium Agra, Uttar Pradesh	0.11–12.8	2.1	658	Gupta et al. (1999)
UK	Cretaceous Chalk, Berkshire	<0.1–2.4	0.74	22	Edmunds et al. (1989)
	Cretaceous Chalk, London Basin	0.11–5.8	1.44	21	Edmunds et al. (1989)
	Cretaceous Lower Greensand, London	<0.1–0.35	0.17	26	Edmunds et al. (1989)
	Triassic Sandstone, Shropshire	<0.1–0.17	<0.1	40	Edmunds et al. (1989)
	Triassic Sandstone, Lancashire	<0.1–0.14	0.1	16	Edmunds et al. (1989)
	Triassic Sandstone, Cumbria	<0.1–0.26	<0.1	23	Edmunds et al. (1989)
Canada	Carboniferous clastic rocks, Gaspé,	0.02–28	10.9	20	Boyle and Chagnon (1995)
	alluvial/glacial (<30m depth)		0.09	39	Boyle and Chagnon (1995)
Canada	Non-marine Upper Cretaceous	0.01–22.0	1.83	469	Hitchon (1995)

	sediments, Alberta Basin				
Germany	Cretaceous Chalk Marls	<0.01–8.9	1.28	179	Queste et al. (2001)
Libya	Miocene, Upper Sirte Basin	0.63–3.6	1.4	11	Edmunds (1994)
Sudan	Cretaceous, Nubian Sandstone (Butana area)	0.29–6.2	1.8	9	Edmunds (1994)
Senegal	Palaeocene sediments	1.5–12.5		26	Travi (1993)
Senegal	Maastrichtian sediments	1.1–5.0		32	Travi (1993)
Tunisia	Cretaceous to Quaternary sediments	0.1–2.3		59	Travi (1993)
USA	Carboniferous sediments, Ohio	0.05–5.9		255	Corbett and Manner (1984)

Table 4. Chemical compositions of a range of groundwaters with naturally high fluoride concentrations. The table also gives the modelled dominant species in the waters and fluorite saturation indices, calculated using PHREEQC..

Country	**Units**	**Ghana**	**United Kingdom**	**Sri Lanka**	**Argentina**	**Canada**	**Tanzania**
Location		Yorogu Abagabisi, Bolgatanga	Spalding, Lincolnshire	Paniyankadawala, Anuradhapura	El Cruce, La Pampa	Maria, Gaspé Peninsula	Imalanguzu, Singida
Water type		Unconfined	Confined	Unconfined	Unconfined		Unconfined
Well depth	m	26	99	Nd	16	>30	110
pH		6.63	8.32	6.96	8.1	9.2	8.86
Temperature	ºC	31.2	11	29.5			27.7
SEC		348		3840	2610	598	1360
Ca	mg L^{-1}	27.6	2.0	173	24.1	4.3	17.6
Mg	mg L^{-1}	13.7	4.1	179	22.9	0.7	1.37
Na	mg L^{-1}	18.8	540	355	616	137	332
K	mg L^{-1}	1.56	4.0	3.02	12.6	0.4	2.07
HCO_3	mg L^{-1}	146	506	516	1180	232	845
SO_4	mg L^{-1}	1.65	33	15.5	190	13.6	20.8
Cl	mg L^{-1}	5.89	490	1050	113	56.7	13.6
NO_3-N	mg L^{-1}	4.92	<0.1	9.00	45.9	nd	7.81
F	mg L^{-1}	3.6	5.6	4.4	15.8	10.9	17.5
Si	mg L^{-1}	34.4	6.0	45.0	28.1	3.5	54.2
Fe	mg L^{-1}	0.37	0.48	0.007	0.055	0.087	0.053
Al	µg L^{-1}	30	14	nd	40	67	81
Be	µg L^{-1}	1	nd	nd	83	nd	2
U	µg L^{-1}	1.3	nd	nd	71	nd	nd
B	mg L^{-1}			0.15	4.58		0.46
Charge imbalance	%	+3.8	+2.01	-0.51	-0.65	-0.06	-2.13
F^-	%	95.98	98.56	79.21	96.54	99.58	99.04
NaF	%	0.04	0.98	0.46	1.04	0.29	0.63
MgF^+	%	2.91	0.44	18.86	2.22	0.09	0.17
CaF^+	%	0.49	0.02	1.46	0.18	0.04	0.16
AlF_3	%	0.35					
AlF_2^+	%	0.18					
HF^0	%	0.04					
AlF_4^-	%	0.02					
$BF(OH)_3^-$	%				0.01		
SI_{fluorite}	log	-0.32	-1.01	+0.18	+0.75	+0.05	+0.62

Data source for Gaspé Peninsula: Boyle and Chagnon (1995)

SEC: specific electrical conductance; nd: not determined

Table 5. Popular removal methods for fluoride from drinking water.

Removal method	Capacity/ dose	Working pH	Interferences	Advantages	Disadvantages	Relative Cost
Precipitation						
Alum (aluminium sulphate)	150 mg/ mg F	Non-specific	-	Established process	Sludge produced, treated water is acidic, residual Al present	Med-high
Lime	30mg/mg F	Non-specific	-	Established process	Sludge produced, treated water is alkaline	Med-high
Alum+lime ('Nalgonda')	150 mg alum+ 7mg lime/mg F	Non-specific, optimum 6.5	-	Low-tech, established process	Sludge produced, high chemical dose, residual Al present	Med-high
Gypsum + fluorite	5 mg gypsum + <2 mg fluorite/mg F	Non-specific	-	Simple	Requires trained operators Low efficiency, high residual Ca, SO_4	Low-med
Calcium chloride	3 mg $CaCl_2$/mg F	6.5–8.0	-	Simple	Requires additional flocculent (e.g. $FeCl_3$)	Med-high
Adsorption/ion exchange						
Activated carbon	Variable	<3	Many	-	Large pH changes before and after treatment	High
Plant carbon	300 mg F/kg	7	-	Locally available	Requires soaking in potassium hydroxide	Low-med
Zeolites	100 mg F/kg	Non-specific	-		Poor capacity	High
Defluoron 2	360 g F/m^3	Non-specific	Alkalinity		Disposal of chemicals used in resin regeneration	Medium
Clay pots	80 mg F/kg	Non-specific	-	Locally available	Low capacity, slow	Low
Activated alumina	1200 g F/m^3	5.5	Alkalinity	Effective, well-established	Needs trained operators, chemicals not always available	Medium
Bone	900 g F/m^3	>7	Arsenic	Locally available	May give taste; degenerates Not universally accepted	Low
Bone char	1000 g F/m^3	>7	Arsenic	Locally available High capacity	Not universally accepted; may give adverse colour, taste	Low
Other						
Electrodialysis	High	Non-specific	Turbidity	Can remove other ions. Used for high salinity	Skilled operators High cost. Not much used	Very high
Reverse osmosis/ nanofiltration	High	Non-specific	Turbidity	Can remove other ions. Used for high salinity	Skilled operators High cost	Very high

(after Heidweiller, 1990; Richards et al., 2010; Solsona, 1985; Vanderdonck and Van Kesteren, 1993)

Figure Captions

Figure 1 Schematic diagram showing the fluorine hydrogeochemical cycle.

Figure 2 Photomicrographs of typical crystalline basement rocks showing high-fluorine minerals, on the left by plane-polarised light, polars rotated 90°; on the right by back-scattered SEM. 1: view of hornblende engulfing biotite, sphene (titanite) and euhedral apatite; granite, Bongo, Upper East Region, Ghana. 2: View of hornblende, biotite, quartz and apatite; granite, Anuradhapura, Sri Lanka.

Figure 3 Cumulative-frequency diagram showing the distribution of fluoride in groundwater from carbonate and non-carbonate aquifers in Britain (modified from Edmunds et al. 1989).

Figure 4 World map of documented high-fluoride (>1.5 mg L^{-1}) groundwaters.

Figure 5 Geological map of parts of Sirohi district, Rajasthan, India with contoured groundwater-fluoride concentrations (reproduced with permission from Maithani et al., 1998).

Figure 6 Variation of calcium with fluoride in groundwaters from the Sirohi District of Rajasthan (from data provided by Handa, 1975), along with the saturation curve for fluorite. Groundwaters from alluvium and Aravalli Hills (bedrock) are distinguished.

Figure 7 Geological map of the Bolgatanga area of Upper East Region, Ghana, showing the distribution of fluoride concentrations in groundwater. The concentrations are highest where associated with outcrops of biotite- and hornblende-bearing granite and granodiorite (from Smedley et al., 1995).

Figure 8 Profiles of changing groundwater chemistry with increasing distance from the outcrop zone of the Lincolnshire Limestone, eastern England (after Edmunds and Walton, 1983). A geological cross section across the aquifer is also shown.

Figure 9 Maps of the regional distribution of annual rainfall and fluoride concentrations in groundwater in Sri Lanka (after Dissanayake, 1991; Zubair, 2003).

Figure 1.

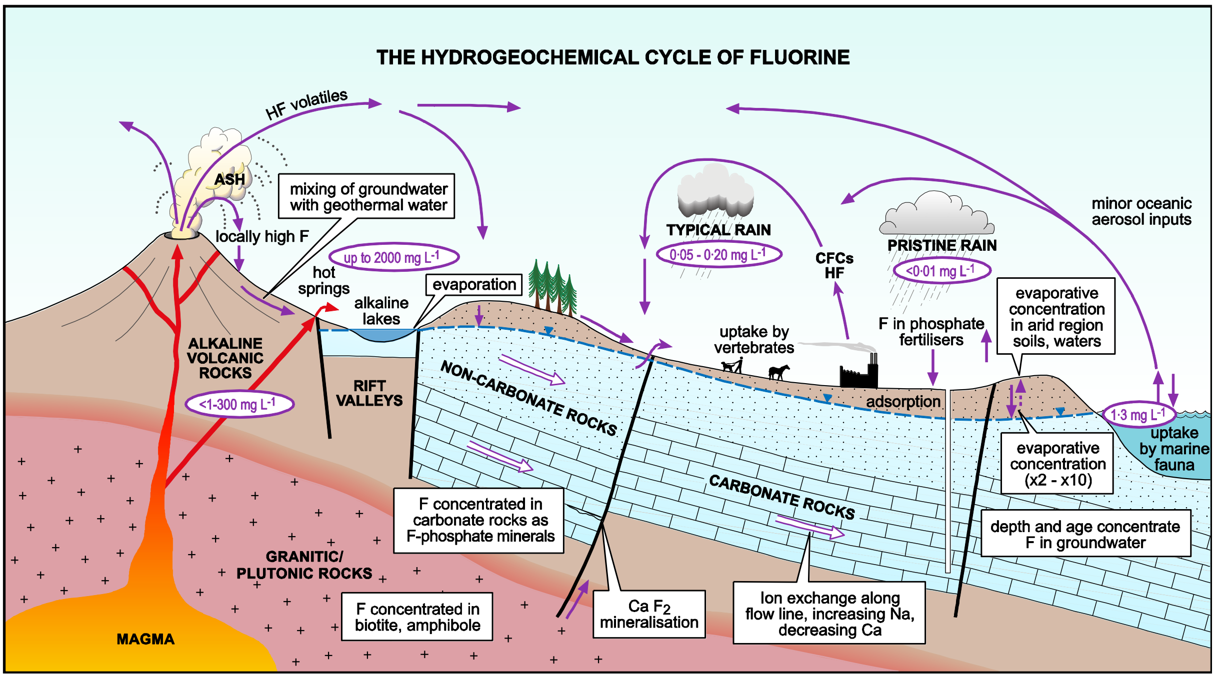


Figure 2.

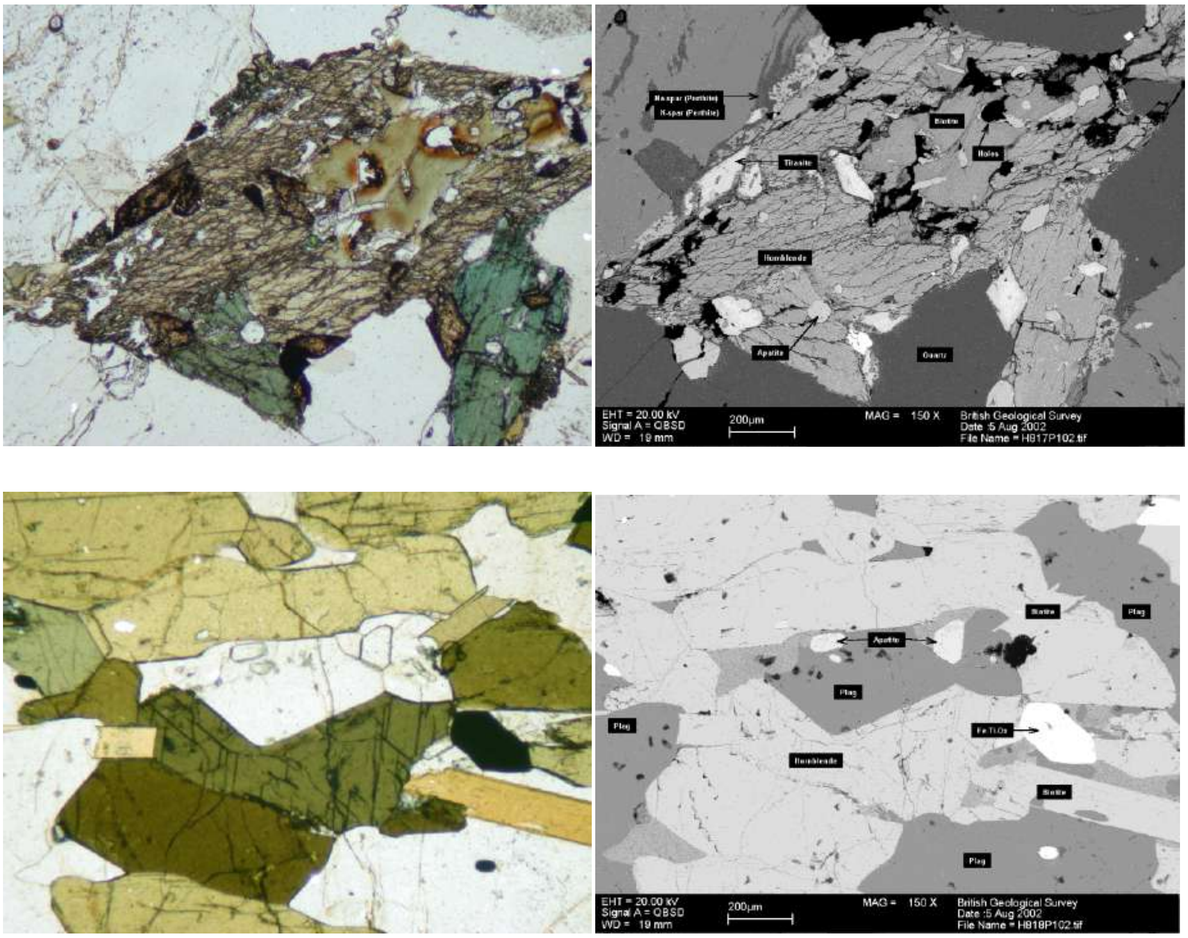


Figure 3.

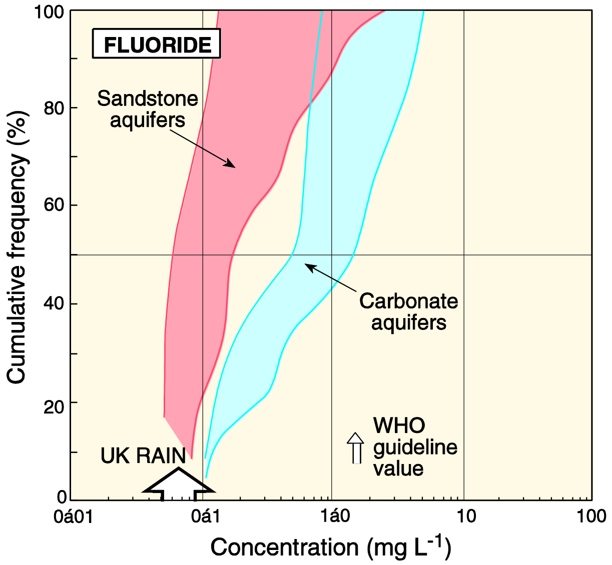


Figure 4.

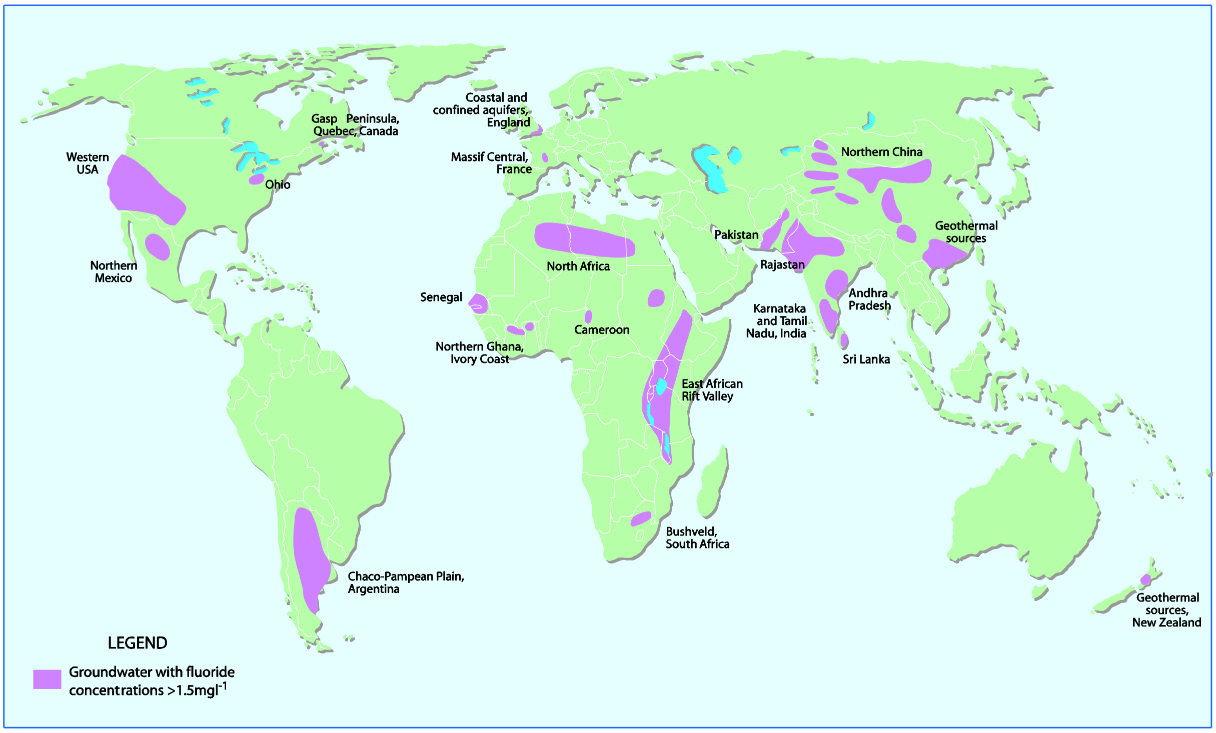


Figure 5.

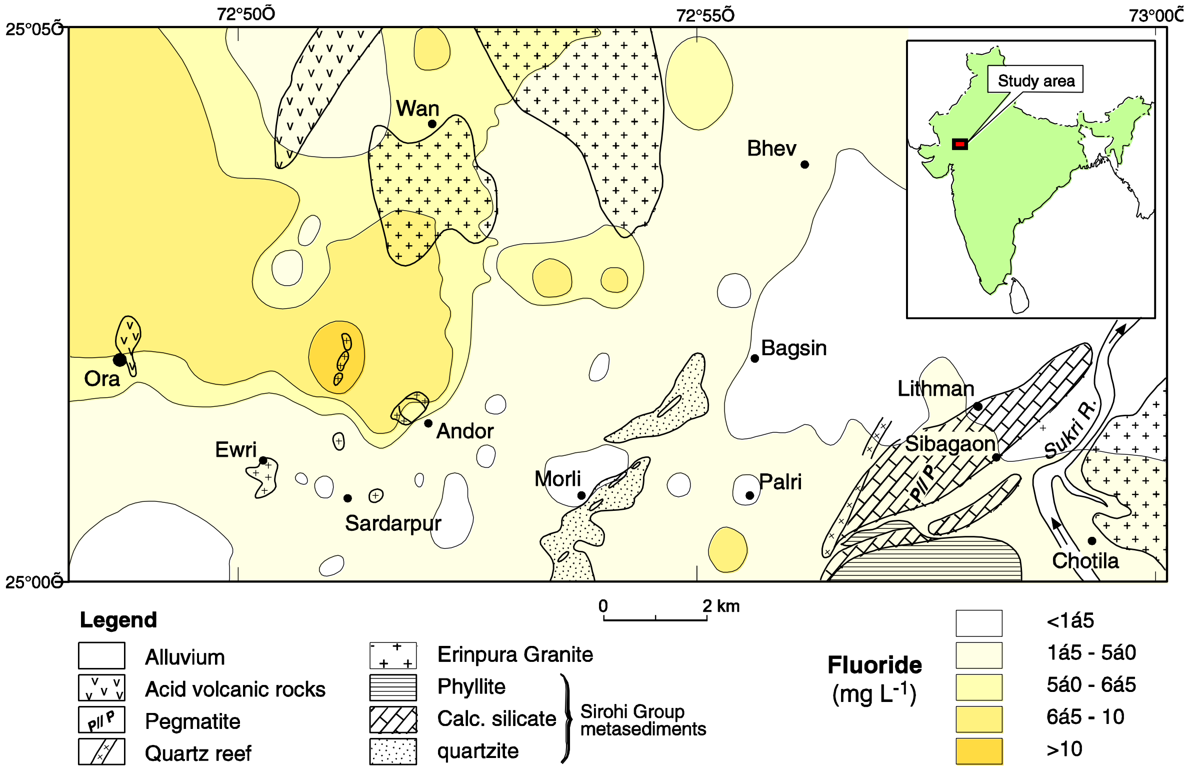


Figure 6.

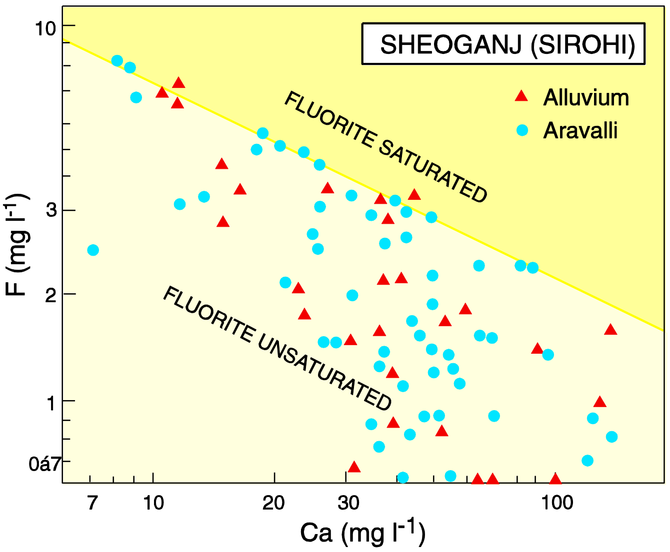


Figure 7.

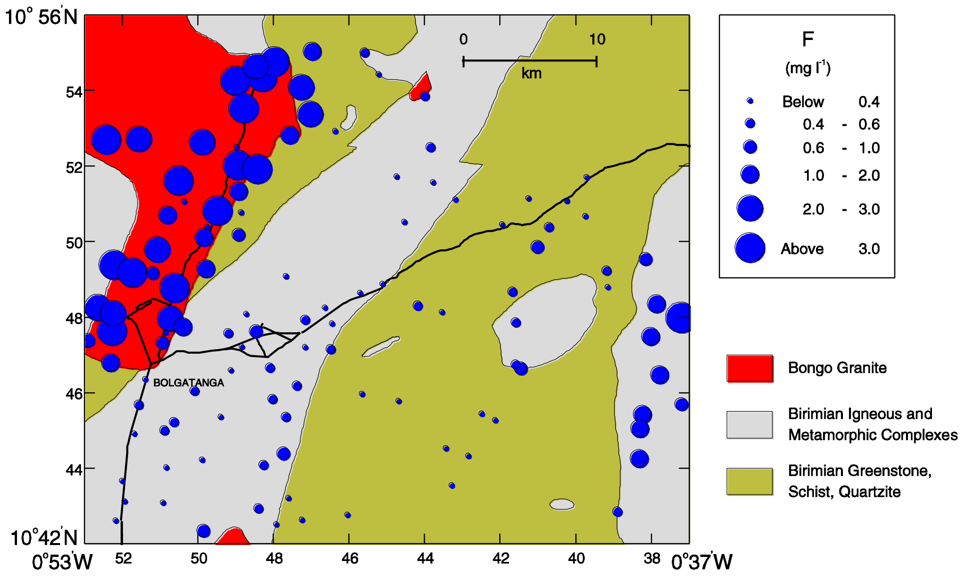


Figure 8.

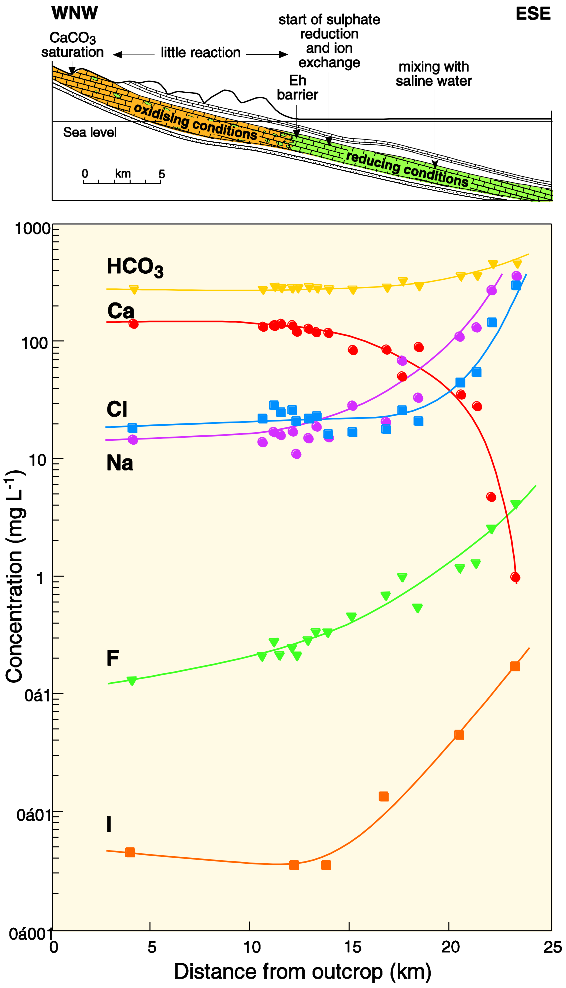
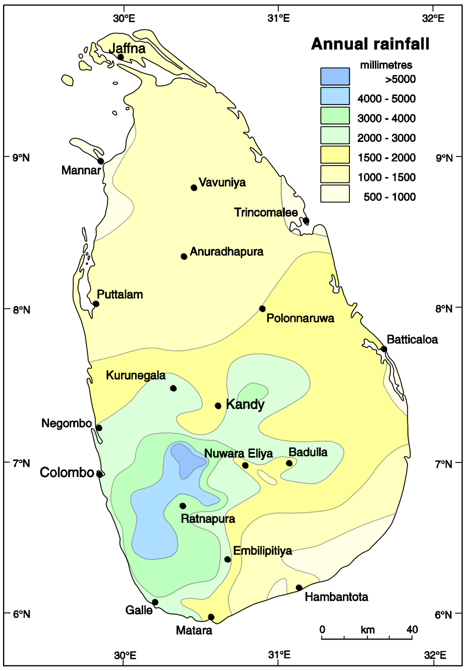
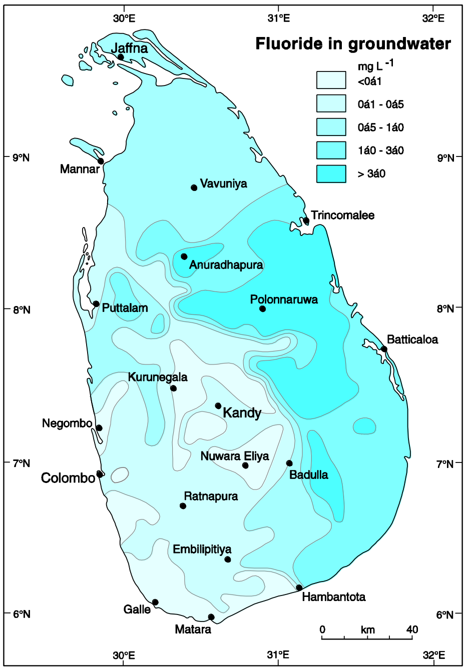

WNW
ESE
CaCO3 saturation
little reaction
start of sulphate reduction and ion exchange
Eh barrier
mixing with saline water
oxidising conditions
reducing conditions
Sea level
0 km 5
HCO3
Ca
Cl
Na
F
I
Concentration (mg L-1)
1000
100
10
1
0á1
0á01
0á001
0
5
10
15
20
25
Distance from outcrop (km)

Figure 9.


Annual rainfall
millimetres
>5000
4000 - 5000
3000 - 4000
2000 - 3000
1500 - 2000
1000 - 1500
500 - 1000
30°E
31°E
32°E
9°N
8°N
7°N
6°N
Jaffna
Mannar
Vavuniya
Trincomalee
Anuradhapura
Puttalam
Polonnaruwa
Batticaloa
Kurunegala
Kandy
Negombo
Nuwara Eliya
Badulla
Colombo
Ratnapura
Embilipitiya
Hambantota
Galle
Matara
0 km 40


Fluoride in groundwater
mg L -1
<0á1
0á1 - 0á5
0á5 - 1á0
1á0 - 3á0
> 3á0
30°E
31°E
32°E
9°N
8°N
7°N
6°N
Jaffna
Mannar
Vavuniya
Trincomalee
Anuradhapura
Puttalam
Polonnaruwa
Batticaloa
Kurunegala
Kandy
Negombo
Nuwara Eliya
Badulla
Colombo
Ratnapura
Embilipitiya
Hambantota
Galle
Matara
0 km 40