CHAPTER 4

MEDICAL GEOLOGY OF FLUORIDE

The link between fluoride geochemistry in water in an area and the incidence of dental and skeletal fluorosis is a well established relationship in medical geology. While the essentiality of fluoride for human health is still being debated, its toxicity has now caused considerable concern in many lands where fluoride is found in excessive quantities in the drinking water. As in the case of some essential trace elements, the optimum range of fluoride varies within a narrow range and this causes fluoride imbalances, very often in large populations, mostly in developing countries of the tropical belt.

In the case of many trace elements, food is the principal source. Much of the fluoride entering the body however is from water and the hydrogeochemistry of fluoride in surface and groundwater is therefore of major interest.

The impact of fluoride on health is shown in Table 4.1. Several organizations throughout the world have considered fluoridating water supplies in areas where the water supplies do not provide the optimum levels of fluoride. This however, has resulted in great disagreement between those who consider fluoride as being beneficial and those who consider it as a poison (Grant, 1986; Sulton, 1988; Colquhon, 1990; Gibson, 1992; Turner et al., 1992; Pendrys, 2001).

Among the dental health concerns, dental fluorosis is the most common manifestation of excessive intake of fluoride-rich water. Children under the age of 7 are particularly vulnerable. Other factors such as nutritional deficiencies, mostly calcium and vitamin C also play minor roles in the disease.

As in the case of iodine deficiency diseases, a large population of the world is affected by fluoride toxicity in drinking water. More than 200 million people including about 70 million in India and 45 million in China (Yang et al., 2003) are prone to fluorosis. The African continent and some

parts of South America such as Mexico are also estimated to have millions of people at risk of dental and skeletal fluorosis, though the exact figures are not known.

Table 4.1. Impact of fluoride on health (WHO, 1971)

Concentration of fluoride in drinking water	Impact on health
0.0-0.5 mg/L	Limited growth and fertility, Dental caries
0.5-1.5 mg/L	Promotes dental health resulting in healthy teeth
1.5-4.0 mg/L	Prevents tooth decay
4.0-10.0 mg/L	Dental fluorosis (mottling of teeth)
>10.0 mg/L	Dental fluorosis, Skeletal fluorosis (pain in back and neck bones) Crippling fluorosis

It is worthy of note that unlike Fe in ground and surface water, fluoride does not impart any colour to the water nor does it give any kind of taste to the water. In highly underdeveloped rural areas in the tropics where drinking water is obtained directly from the ground, excessive fluoride in water may turn out to be an invisible poison. People who obtain food and water directly from their home environments for many years are particularly susceptible to diseases caused by excess fluorides in drinking water.

GEOCHEMISTRY OF FLUORIDE

Fluoride is the most electronegative and chemically reactive element of all halides. It is highly reactive with practically all organic and inorganic substances. In the natural environment it occurs as the fluoride ion F^-. It is found mostly in the silicate minerals of the earth's crust at a concentration of about 650 mg/kg (Adriano, 2001).

The geochemistry of the F^- (ionic radius 136 pm) is similar to that of the OH^- ion (ionic radius 140 pm) and there can be easy exchange between them. Extensive research has been carried out on the fluoride-hydroxyl exchange in geological materials (Gillberg, 1964; Stormer and Carmichael, 1971; Ekstrom, 1972; Munoz and Ludington, 1974). Fluorapatite $[Ca_5(PO_4)_3F]$ and hydroxylapatite $[Ca_5(PO_4)_3OH]$ are isomorphic end members in the solid solution series $Ca_5(PO_4)_3(OH,F)$. Hydroxyl apatite,

however, is the main mineral phase of enamel in human teeth, a fact often used as an argument against the non-essentiality of fluoride to humans.

As shown by Aswathanarayana et al. (1985), fluorides in the surface and the groundwater are derived from:

(a)   Leaching of the rocks rich in fluorine, e.g. granites (750 mg/kg), alkalic rocks (950 mg/kg), volcanic ash and the bentonites (750 mg/kg), phosphatic fertilizers 3.0-3.5%.
(b)   Dissolution of fluorides from volcanic gases by percolating groundwaters along faults and joints of great depth and discharging as fresh and mineral springs.
(c)   Rainwater which may acquire a small amount of fluoride from marine aerosols and continental dust.
(d)   Industrial emissions such as freons, organo-fluorine and dust in cryolite factories.
(e)   Industrial effluents.
(f)   Run-off from farms using phosphatic fertilizers extensively.

Fluorine is associated with many types of mineral deposits (Boyle, 1974) and hence it is a good indicator of mineral deposits (Lalonde, 1976). The geochemical dispersion haloes of fluorine from mineral deposits are often detected in ground and surface waters, stream sediments and soils. The higher concentrations of fluoride in water and soil are therefore often the result of the occurrence of mineral deposits in the vicinity. The fluorine chemistry of granitic material is relevant to economic prospecting in granitic terrains since fluorine is associated with Sn-W-Mo and REE-Zr-Ta-Be deposits, with Li-Rb-Cs pegmatites, rare-metal greisens and albitized granites and is ultimately responsible for fluorite and cryolite deposits (Bailey, 1977; Correns, 1956).

Fluorine is located in:

(a) F^- rich minerals such fluorite, apatite
(b)   Replacement of OH^- and O^{2-} ions in muscovite (mean 0.1-0.3%), biotite (mean ~0.7%), hornblende (mean ~0.2%) and sphene (range 0.1-1.0%)
(c)   Solid and fluid inclusions-micas and feldspars, fluid inclusions in quartz
(d)   Rock glasses-obsidians and pitchstones.

A list of fluoride-bearing minerals with formulae, fluoride contents and distribution in various granitic materials is given in Table 4.2. It is worthy of note that from among 150 fluoride-bearing minerals listed by Strunz (1970), 63 are silicates, 43 halides and 24 phosphates. In magmatic rocks, only topaz and fluorite contain fluorine as an essential part of the composition.

Geochemistry of Fluoride in Weathering and Solution

As mentioned in Chapter 2, rock and mineral weathering in the tropical climate is intense. Fluoride with its tendency to enter the aqueous medium is therefore leached out from the fluoride-bearing minerals. The geochemical pathways of fluoride in such a physico-chemical environment is strongly influenced by processes involving adsorption-desorption and dissolution-precipitation reactions. It is important therefore to realise that the degree of weathering and the leachable fluoride in a terrain is of greater significance in the fluoride concentration of water than the mere presence of fluoride-bearing minerals in soils and rocks. Some rocks, bearing minerals such as Ca-Mg carbonate act as good sinks for fluoride (Christensen and Dharmagunawardena, 1986). The leachability of fluoride from the carbonate concretions is controlled by (a) pH of the draining solutions (b) alkalinity (c) dissolved CO_2 and the pCO_2 in the soil.

Ramesam and Rajagopalan (1985) studied the fluoride geochemistry in the natural hard rock areas in Peninsular India and summarised a mechanism of fluoride pathways in arid and semi-arid areas as shown in Figure 4.1.
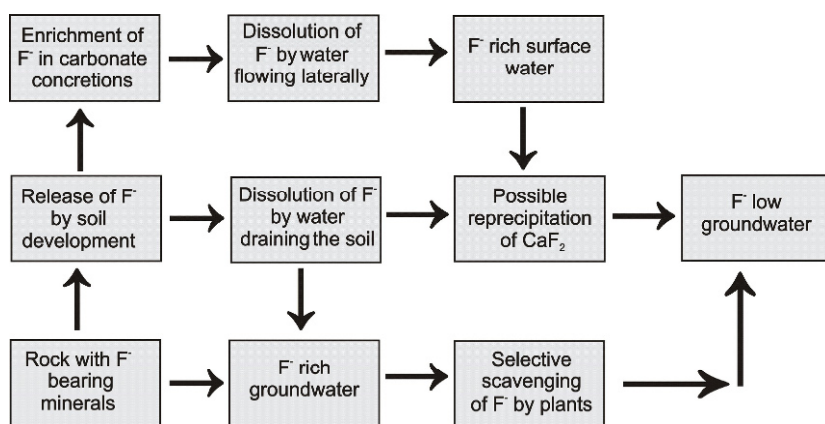

Fig. 4.1. Mechanism for fluoride ingestion in arid and semi-arid areas (modified after Ramesam and Rajagopalan, 1985)

Table 4.2. Fluoride-rich minerals associated with granitic materials (after Bailey 1977)

Name	Formula	F (wt.%)
Fluorite	CaF_2	47.81-48.80
Cryolite	Na_3AlF_6	53.48-54.37
Fluocerite	CeF_3	19.49-28.71
Yttrofluorite	$(Ca,Y)(F,O)_2$	41.64-45.54
Gagarinite	$NaCaYF_6$	33.0-36.0
Bastnasite	$Ce(CO_3)F$	6.23-9.94
Synchisite	$CeCa(CO_3)_2F$	5.04-5.82
Parisite	$Ce_2Ca(CO_3)_3F_2$	5.74-7.47
Pyrochlore	$NaCaNb_2O_5F$	2.63-4.31
Microlite	$(Ca,Na)_2Ta_2O_6(O,OH,F)$	0.58-8.08
Amblygonite	$LiAl(PO_4)$	0.57-11.71
Apatite	$Ca_5(PO_4)_3(F,ClOH)$	1.35-3.77
Herderite	$Ca(BePO_4)(F,OH)$	0.87-11.32
Muscovite	$KAl_2(AlSi_3O_{10})(OH,F)_2$	0.02-2.95
Biotite	$K(Mg,Fe)_3(AlSi_3O_{10})(OH)_2$	0.08-3.5
Lepidolite	$KLi(Fe,Mg)Al(AlSi_4O_{10})(F,OH)$	0.62-9.19
Zinnwaldite	$KLiFe^{2+}Al(AlSi_3O_{10})(F,OH)_2$	1.28-9.15
Polylithionite	$KLi_2Al(Si_4O_{10})(F,OH)_2$	3.00-7.73
Tainiolite	$KLiMg_2(Si_4O_{10})F_2$	5.36-8.56
Holmquistite	$Li_2(Mg,Fe^{2+})_3(Al,Fe^{3+})_2(Si_2O_{22})(OH,F)_2$	0.14-2.55
Hornblende	$NaCa_2(Mg,Fe,Al)_5(Si,Al)_8O_{22}(OH,F)_2$	0.01-2.9
Riebeckite	$Na_2Fe_3^{2+}Fe_2^{3+}(Si_4O_{11})_2(OH,F)_2$	0.30-3.31
Arfvedsonite	$Na_3Fe_4^{2+}Fe^{3+}(Si_4O_{11})_2(OH,F)_2$	2.05-2.95
Ferrohastingsite	$NaCaFe_4^{2+}(Al,Fe^{3+})(Si_6Al_2O_{22})(OH,F)_2$	0.02-1.20
Spodumene	$LiAl(SiO_3)_2$	0.02-0.55
Astrophylite	$(K,Na)_2(Fe^{2+},Mn)_4(TiSi_4O_{14})(OH)_2$	0.70-0.86
Wohlerite	$NaCa_2(Zr,Nb)O(Si_2,O_7)F$	2.80-2.98
Tourmaline	$Na(Mg,Fe)_3Al_6(BO_3)_3(Si_6O_{18})(OH)_4$	0.07-1.27
Sphene	$CaTiSiO_5$	0.28-1.36
Topaz	$Al_2SiO_4(OH,F)_2$	13.01-20.43
Yttrobrithiolite	$(Ce,Y)_3C_2(SiO_4)_3OH$	0.50-1.48

This relationship shows that the concentrations of fluoride are directly proportional to Ca^{2+} concentrations. The absence of calcium in solution allows higher concentration of fluoride to be stable in solution. In areas of alkaline volcanic rocks and in high cation exchange conditions, notably in the presence of clay minerals, such a situation may prevail.

The soil-water and the rock-water interaction and the residence time of fluoride are two important factors in the concentration of fluoride in water. The geochemical environments of surface dug wells and those in the

deeper bore holes are different. Whereas the shallow dug wells tend to have lower fluoride concentrations due to leaching and rapid groundwater circulation and lower residence times, the water-rock interaction in the deep bore holes is enhanced by longer residence times. Hence it is quite common to observe higher fluoride concentrations in water obtained from deep wells (Figure 4.2).

Climatic effects, notably evaporation of surface water due to the prevailing high ambient temperature, also affect the relative fluoride concentration in the water. In many arid regions of the world, this situation arises while in regions where there is intense rainfall, leaching of fluoride takes place easily resulting in its lower concentrations.

Fluoride concentrations in natural water vary widely depending on the geochemistry of the rainfall, soils, rocks and minerals in the immediate environment. Recently, Edmunds and Smedley (2004), reviewed the fluoride concentrations in natural water from different geological situations (Table 4.3) and it is observed that some areas such as Lake Magadi in Tanzania have fluoride concentrations as high as 1980 mg/L while in some other regions (e.g. UK chalk regions) it is lower than 0.1 mg/L.

Table 4.3. Average fluoride ranges of different types of waters (summarised from Edmunds and Smedley, 2004)

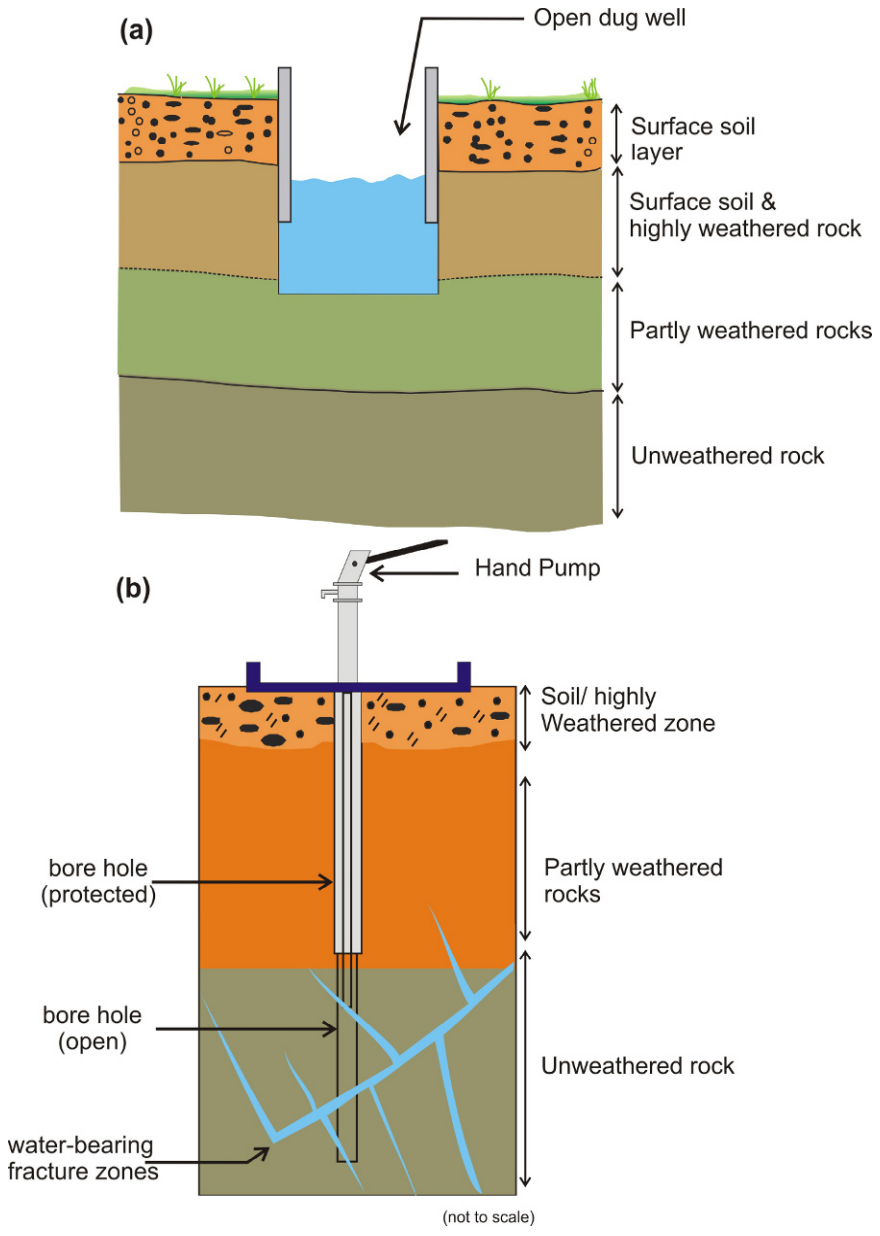| Source	Range of F^- (mg/L)
Rainfall	0.013 to 0.096
Surface waters (rivers)	0.06 to 0.18
Surface waters in high fluoride regions	0.6 to 1281
Soil water	0.02 to 0.30
Geothermal springs	0.4 to 330
Groundwater crystalline basement rocks	<0.02 to 20
Groundwater volcanic rocks	2.1 to 250
Groundwater sediments and sedimentary basins	<0.1 to 29

Fig. 4.2. Groundwater regimes in (a) shallow dug well, (b) deep well

Fluoride in Soils

Fluoride in soils is found in the range 20-500 mg/kg (Kabata-Pendias and Pendias, 1984) and its mobility is influenced mainly by pH and complexation with aluminium and calcium (Pickering, 1985). The soil type, salinity and fluoride concentration are also important in the amount of fluoride adsorbed by soil. Acidic conditions favour the fluoride adsorption markedly. Barrow and Ellis (1986) reported that the maximum adsorption of fluoride to soil was at pH 5.5. In acidic soils when the pH is lower than 6, much of the fluoride complexes with either Al or Fe. In the case of alkaline soils at pH >6.5, it is almost completely fixed in soils as calcium fluoride, provided sufficient calcium carbonate is available (Brewer, 1966).

Clay minerals, $Fe(OH)_3$, $Al(OH)_3$ and fine-grained soils adsorb fluoride relatively easily, by displacing hydroxides on the clay surface. It is best adsorbed at a pH range of 3-4 and decreases above 6.5 (Savenko, 2001).

Fluorine is immobile in soil and in soil profiles the fluoride content decreases with increasing distance from the parent rock. Soils therefore act as good sinks for fluoride. Fluoride retention in soil is generally correlated with soil aluminium and it leaches out simultaneously with the leaching of Al, Fe and organic material in the soil (Polomski et al., 1982). In some soils, notably the sandy acidic soils, leaching out of fluoride can be greatly reduced by the addition of lime or gypsum which precipitates fluorite. In the case of calcareous soils with low flow rates of water, the adsorption of fluoride from the water phase is an important step in the geochemical pathway of fluoride in soils. At high flow rates however, this exchange is limited (Flühler et al., 1982).

In agricultural soils where there is a high input of phosphate fertilizer, the fluoride contents may increase significantly phosphate fertilizers (8500-38000 mg/kg) (Kabata-Pendias and Pendias, 1984) and sewage sludges (80-1950 mg/kg) (Rea, 1979), have high fluoride contents.

Fluoride in Sediments

Fluorine is an abundant halogen in sedimentary rocks with fluorite, apatite, mica, illite, and montmorillonite being the main fluorine-bearing minerals (Deshmukh et al., 1995). As shown in Table 4.4, shales, volcano-clastics and bentonites are among the most fluoride-rich sedimentary rocks. Shales in particular, due to their high clay content retain larger concentrations of

fluoride. It has been observed that out of the total fluorine content of the clays associated with clastic rocks, 80-90% is found in the mica group of minerals while the rest is adsorbed on clay minerals montmorillonite, illite and kaolinite. The average fluorine content of sedimentary micas and illite is more than 1.5 times the average fluorine content of igneous rocks.

Table 4.4. The average fluorine content in different sedimentary rocks (Fleischer and Robinson, 1963)

Rocks	Range in mg/kg	Average in mg/kg
Limestone	Up to 1210	220
Dolomite	110-400	260
Sandstone and Greywacke	10-1100	200
Shale	10-7600	940
Volcanic ashes and Bentonites	100-2900	750
Oceanic sediments	100-1600	730

Kau et al. (1998) compared the experimental sorption isotherms of fluoride for aluminosilicate clays. It was observed that bentonite is a far superior fluoride sorbent than kaolinite quantitatively even though the mechanism of sorption may be the same. Factors that influenced fluoride sorption included solution pH, clay surface area, aluminium content and the presence of certain exchangeable cations capable of forming fluoride precipitates.

Experiments by Kau et al. (1997) on fluoride retention by kaolin clay showed that the quantity of fluoride sorbed onto kaolin stabilizes essentially after 24 hours. Fluoride measurements after 24 hours revealed that a minimum of 95±2% of the equilibrium concentration has been achieved throughout the tested pH range (Figure 4.3).

Fluoride in Plants

Fluorine is not considered as an essential element for plants. The fluoride levels in terrestrial biota are higher in areas with high fluoride levels from natural and anthropogenic sources. Lichens, for example are used extensively as biomonitors for fluorides. Mean fluoride concentrations of 150-250 mg/kg were measured in lichens growing within 2-3 km of fluoride emission sources, compared with a background level of <1 mg fluoride/kg (Anonymous, 2002). In soil, much of fluoride is insoluble and hence less available to plants. However, since high soil fluoride concentrations or low pH, low clay and/or organic matter contents in soil can increase fluoride levels in solution, there can be greater uptake by the plant. It is of interest

to note that due to the low mobility of fluoride within the plant, the root has higher fluoride contents than the shoot.

Terrestrial plants however may accumulate inorganic fluorides from the air through stomata in the leaves. Further, small amounts may also enter the plant through the epidermis and cuticle (Underwood, 1962). The application of fluoride-bearing phosphate fertilizers however introduces a sudden influx of fluoride into the soil and the plants may accumulate more fluoride in the form of aluminium fluoride species (Steven et al., 1997).

Tea (*Camellia sinensis*) has been known to accumulate fluoride in higher concentrations (0.1-0.6 mg/100 ml, Food and Nutrition Board, 1997). It is cultivated in acidic soils in the tropical regions and is the most popular drink next to water. Aluminium accumulates profusely, with Al in tea leaves reaching levels as much as 8700-23000 mg/kg and even up to 30000 mg/kg (Matsumoto et al., 1976). However, as mentioned earlier, the complexation of the fluoride with Al paves the way for fluoride entry into the plant.
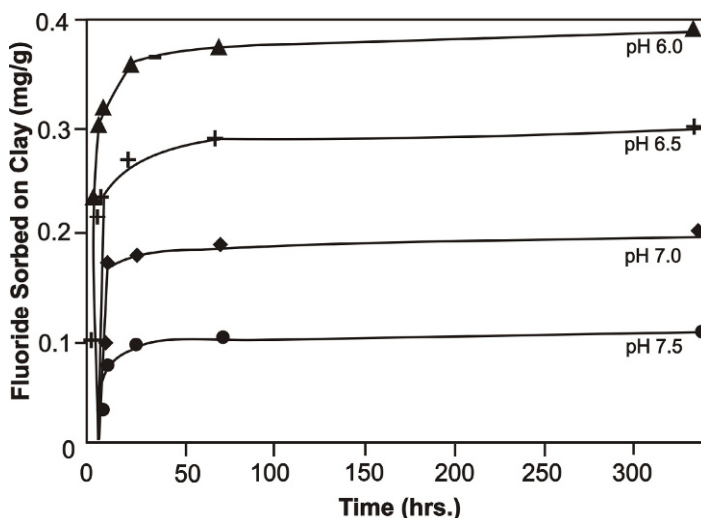

Fig. 4.3. Effect of reaction time on fluoride sorbed onto kaolinite at pH values between 6.0 and 7.5 (Kau et al., 1997)

In areas where fluorosis is endemic, notably in the Asian countries, the fluoride content of food plants grown have shown higher concentrations (Wakode et al., 1993; Kumari et al., 1995). It was observed that the fluoride intake in sorghum, wheat, rice, red gram dhal and red chillies was in

proportion to the fluoride concentration of the root zone. The average Partition Factor (F^--food/F^--soil) was of the order in dry red chillies 15.76; red gram dhal 5.3; sorghum 3.6; wheat 2.4 and rice 2.4.

From among aquatic plants, the water hyacinth (*Eichornia crissipes*) is known to take up fluoride from water. Plants that were exposed to fluoride solutions of 6-26 mg/L for 4 weeks had a fluoride uptake of 0.8 mg/kg (Rao et al., 1973).

FLUORIDES AND HEALTH

As mentioned earlier, the range of fluoride tolerance and toxicity is narrow. Deviation from the optimal levels therefore results in dental health effects such as caries and fluorosis. The beneficial and detrimental effects of fluoride are mainly on the tooth enamel and bone. While the prevalence of dental caries is inversely related to the concentration of fluoride in drinking water, the prevalence of dental fluorosis is strongly associated with the concentration of fluoride, with a positive dose-response relationship. In the case of skeletal fluorosis, apart from a high intake of fluoride-rich water, other factors such as nutritional status and diet, climate (related to fluid intake) concomitant exposure to other substances and intake of fluoride from sources other than drinking water are believed to play an important role in the development of this disease (WHO, 2002). Other diseases such as cancer, respiratory, hepatic, renal and haematopoietic disorders attributed to fluorides have not been proved beyond doubt.

Bioavailability of Fluoride

Figure 4.4 illustrates the fate of fluoride ingested with food. In areas where the natural fluoride levels are low the total daily adult intake will be <1 mg while for those living in areas with a higher water fluoride intake, the total daily fluoride intake will be about 2 mg/day.

As shown in Figure 4.4 the fluoride ingested is absorbed by the stomach and in greater quantities by the small intestine. In the stomach, when the pH is low, highly diffusible hydrogen fluoride forms (pKa = 3.4) and this results in high absorption (Whitford and Pashley, 1984). In the small intestine fluoride is absorbed as the free ion (F^-) by diffusion via membrane channels and is non-pH dependent (Nopakun and Messer, 1990). When

fluoride is ingested with little or no food, fluoride absorption is much higher in the stomach, some times as much as 100% (Ophang, 1990).
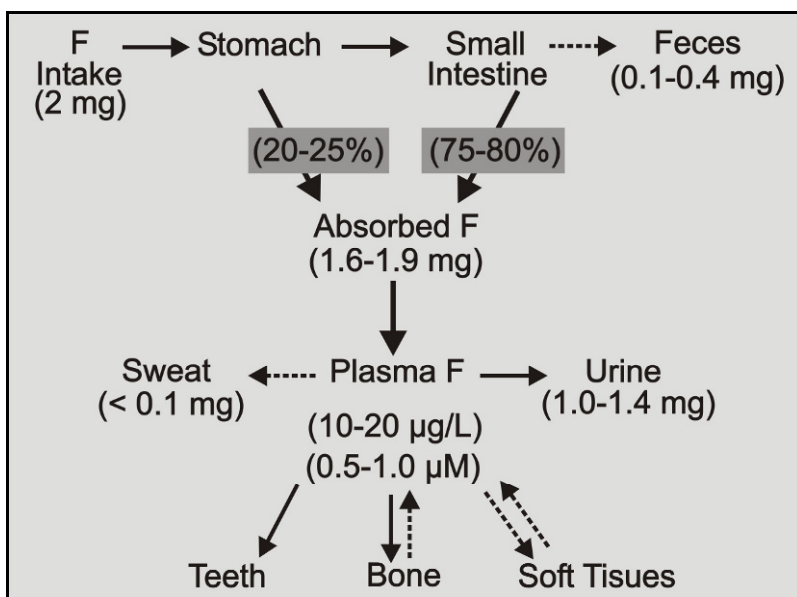

Fig. 4.4. Fate of fluoride ingested with food in adult. Dashed arrows denote a minor pathway (Cerklewski, 1997a)

Under normal fluoride intakes and rate of absorption, the plasma fluoride concentration is known to range from 10-20 µg/L or 0.5-1.0 µM (Ekstrand, 1978). In the adult body over 95% of total fluoride is in the bones and teeth and these remove the plasma fluoride rapidly by ion exchange with hydroxyl ions, citrate and carbonate. Soft tissues on the other hand do not accumulate fluoride. Forbes (1990) has noted that the total body fluoride estimated to be about 2.6 g is second only to the trace element iron. It is during the period of rapid development of bones and teeth that fluoride is taken up quickly. As in the case of bone, the outer layer of surface enamel contains higher fluoride- about 3000 µg/g as against 100 µg/g at the deeper dentine-enamel junction (Ten Cate and Featherstone, 1996).

Fluoride homeostasis in the body is maintained by the combined effects of fluoride assimilation by bone and urinary excretion bearing in mind that soft tissues do not take up fluoride. When the fluoride uptake by bone is low, urinary excretion of fluoride increases.

Other elements also influence the fluoride homeostasis by interaction and complex formation mostly in the alkaline small intestine. Calcium and magnesium form insoluble complexes with fluoride thereby decreasing fluoride uptake by bone and teeth (Cerklewski, 1997b). However, if the fluoride is in the form of monofluorophosphate in contrast to sodium fluoride, there is no effect by the presence of calcium (Villa et al., 1992).

The interaction of aluminium with fluoride has been the subject of several studies (Lubkowska et al., 2002; Ahn et al., 1995). Aluminium is known to suppress the uptake of fluoride by modifying the metabolism of phosphorus, calcium, magnesium and fluorine and enhances the development of osteomalacia and osteodystrophia (Ahn et al., 1995).

Dental Fluorosis

Figure 4.5 illustrates the cross section of a human tooth. The outermost layer of the exposed tooth is a hard thin, translucent layer that envelopes and protects dentin, the main portion of the tooth structure. Enamel, dentin and cementum are all composite materials composed of the mineral hydroxylapatite (HA) (Figure 4.6), protein and water. Enamel is the hardest substance found in the human body and has ~90% mineral, 1% organic matter and 3% water. On account of its hardness, it is also brittle. Enamel has the carbonate- rich apatite arranged in enamel rods or prisms 4-5 μm in diameter (Marshall et al., 2003). These are held together by a cementing substance and surrounded by an enamel sheath. The rods that make up enamel are formed by cells known as ameloblasts.

The mineral apatite $Ca_5(PO_4)_3(OH, F, Cl)$ has varying amounts of fluorine, chlorine or the hydroxyl group, though in some cases one of these may approach the 100% level, and according to the major presence of F^-, Cl^- or OH^-, they are termed fluorapatite, chloroapatite and hydroxyapatite, respectively.

When fluoride is present in the water ingested, some of it is incorporated into the apatite crystal lattice of the tooth enamel during its formative stages, the enamel becomes harder and discolouration results (Figure 4.7).
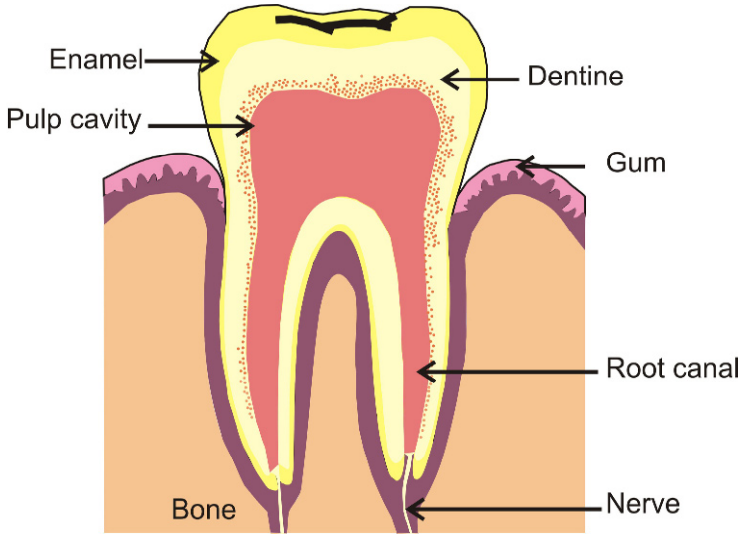
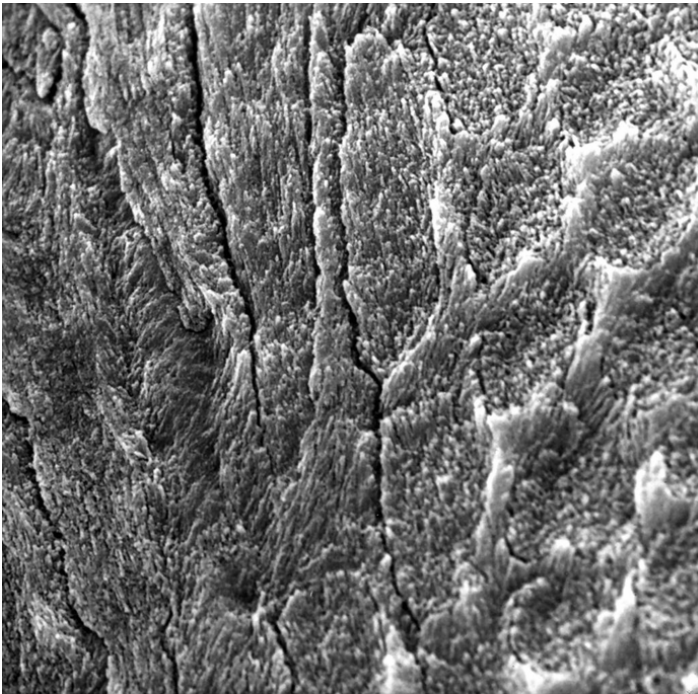**Fig. 4.5.** Schematic cross section of a human tooth

Fig. 4.6. Scanning Electron Microscope image of the dental enamel of a front tooth with well orientated rod structure from apatite (photo courtesy of Prof. Minoru Wakita, Hokkaido University, Japan)

Fig. 4.7. Discolouration of teeth in dental fluorosis

Clinically the appearance of enamel fluorosis is known to vary with the amount of fluoride ingested during early childhood, appearing in its mildest forms as a white flecking of the enamel coalescing to become more visible in its moderate forms and marked by a dark brown staining of the enamel, with actual breakdown of the enamel in the most severe cases (Dean and McKay, 1939, Rozier, 1994). Table 4.5 shows the classification of dental fluorosis. Even though the WHO guidelines have recommended an upper limit of fluoride concentration in drinking water as 1.5 mg/L, in many tropical countries where there is a high sweat loss and a high intake of water due to the hot weather such an upper limit may be unsuitable (Brouwer et al., 1988).

In several other tropical countries (India-Handa, 1975; Tanzania- Aswathanaryana et al., 1985; Kenya- Manji et al., 1986; Sri Lanka- Warnakulasuriya et al., 1992; Ghana- Apambire et al., 1997) it has been found that the WHO recommended levels for fluoride in drinking water are not acceptable and that the incidence of dental fluorosis is common even in areas with lower levels of fluoride in water. Brouwer et al. (1988), who observed that the WHO guidelines were unsuitable for Senegal, showed that in the hot climate of Senegal, both dental and skeletal fluorosis are more prevalent and more severe than would be expected from the WHO recommended maximum limits. They found that 66.5% of children had mild dental fluorosis at the 1.0 mg/L level and beyond the 4.0 mg/L level dental fluorosis had reached 100%.

Table 4.5. Dental fluorosis classification by Dean (1942)

Classification	Criteria-Description of Enamel
Normal	Smooth, glossy, pale creamy-white translucent surface
Questionable	A few white flecks or white spots
Very Mild	Small opaque, paper-white areas covering less than 25% of the tooth surface
Mild	Opaque white areas covering less than 50% of the tooth surface
Moderate	All tooth surfaces affected; marked wear on biting surfaces; brown stain may be present
Severe	All tooth surfaces affected; discrete or confluent pitting; brown stain present

In Sri Lanka, Warnakulasuriya et al. (1992) showed that the optimal level of fluoride in groundwater for caries protection should be 0.6-0.9 mg/L. Even at these moderate levels, only 34% of the children were entirely fluorosis free. They recommended that the WHO limit of 1.5 mg/L fluoride in drinking water is not appropriate for hot and dry climates and that an upper limit of 0.8 mg/L is more suitable.

Figure 4.8 illustrates the Community Fluorosis Index (CFI) where

$$CFI = \sum \frac{\left(\text{number of children} \times \text{Dean's Index Score}\right)}{\left(\text{Total number of children examined}\right)}$$

and the Dean's Index Score classifies individuals into 5 categories depending on enamel alteration. Figure 4.9 shows the relationship between fluoride concentration of drinking water and dental caries/dental fluorosis. It can be observed that the CFI value detrimental to human dental health varies with mean annual temperature (Minoguchi, 1974).

Accordingly if the CFI is below 0.4, the water is considered safe from a health point of view. If the value is above 0.6, the excess quantity of fluoride in drinking water in the area has to be removed. CFI in the range 0.6 to 3.5 often indicate the onset of dental fluorosis and a CFI greater than 3.5 points to the possibility of skeletal fluorosis.
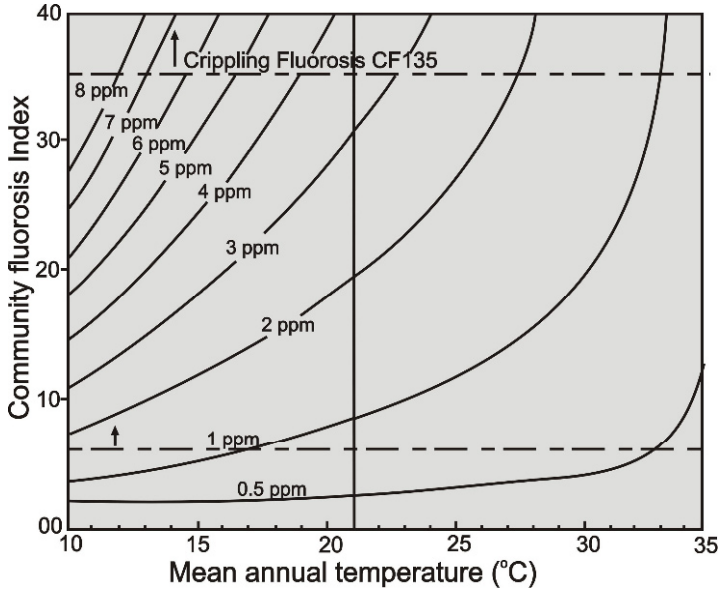
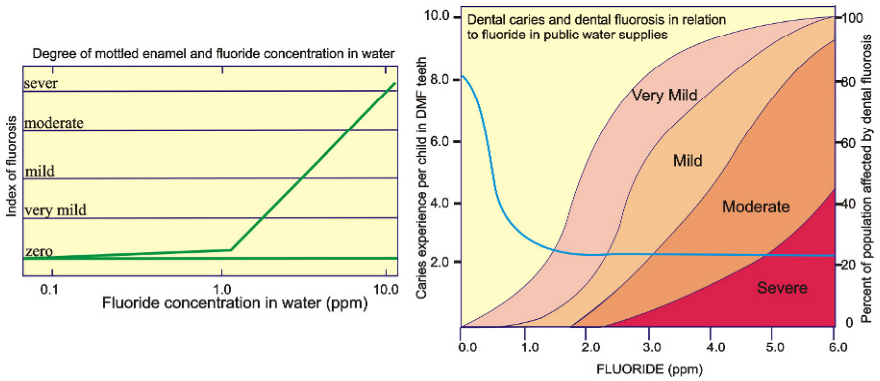**Fig. 4.8.** Relationship between community fluorosis index and the mean annual temperature (Minoguchi, 1974)

Fig. 4.9. Degree of enamel mottling in relation to fluoride concentration in water (Latham et al., 1972)

Skeletal Fluorosis

As discussed above, high ingestion of fluoride-rich water causes dental fluorosis. If the levels of fluoride ingestion are still higher, and if it continues over several years, a serious debilitating disease which affects the bones, termed skeletal fluorosis (Fig. 4.10) results. This may even cause neurological complications. About 96-99% fluoride retained in the body combines with mineralised bones and when the ingestion is >4 mg/day, 50% is retained by the skeleton and the rest is excreted through urine. The skeletal fluoride concentration is known to increase almost proportionately to the amount of fluoride ingested and its resident time (Spencer et al., 1975). There are several varieties of bones in the skeleton and the fluoride content of these vary with pelvis and vertebrae having higher fluoride contents than limb bones. Once incorporated into the hard tissues, the fluoride is retrievable though with difficulty and involves a very slow process of osteoclastic resorption spread over many years. The progress of skeletal fluorosis symptoms are as follows (Reddy et al., 1969):

> (a) Vague discomfort and paraestheria in limbs and trunk.
> (b) Pain and stiffness in back.
> (c) Stiffness increases steadily with restriction of movement.
> (d) Appearance of a "poker- back" spine.
> (e) Spread of stiffness to various joints.
> (f) Fluorosis deformity at hips, knee and other joints.
> (g) Bony exostosis seen in limb bones.

In the endemic regions, crippling skeletal fluorosis occurs between the ages of 30 to 50 years. According to Siddiqui (1955), newcomers to a hyperendemic region may develop symptoms within years of their arrival. The main factors which influence the development of skeletal fluorosis (Reddy, 1985) are (a) high fluoride intake (b) continual exposure to fluoride (c) strenuous manual labour (d) poor nutrition (e) impaired renal function due to the disease.

Contrary to earlier thinking, if the levels of fluoride in the drinking water of a region are extremely high, younger age groups including children are also affected. It should be borne in mind that the incidence of fluorosis is higher in tropical countries on account of the higher quantity of water (fluoride-bearing) consumed. Poor nutrient intake may also be a significant factor.

Fig. 4.10. A case of skeletal fluorosis due to ingestion of excessive fluoride from drinking water (photo: courtesy of Ministry of Water, The United Republic of Tanzania)

In its simplest terms the mechanism of the onset of skeletal fluorosis is that in order to immobilise fluoride from circulating fluids in the body, excess fluoride is fixed in the hydroxyl apatite material of the bone by replacement of OH^- by F^- irreversibly till the exposure continues. During this process, the rate of synthesis of bone material (hydroxyl apatite) is considerably increased and this leads to bone formation or osteosclerosis, as seen in those with skeletal fluorosis (Teotia and Teotia, 1992). With the deposition of calcium fluoro-apatite, the bone density and bone mass increases. In the backbone, the perforations through which nervous and blood vessels pass through, are constricted and this leads to pressure on nerves and blood vessels resulting in paralysis and extreme pain.

Dissanayake et al. (1994) have reported a case of skeletal fluorosis with spinal cord compression from Sri Lanka, following consumption of water

with high fluoride content for about 20 years (Figure 4.11). The fact that fluoride is not entirely irreversibly bound to the bone has been demonstrated in persons who had lived in areas of fluoride- rich drinking water and subsequently moved to fluoride-low areas. The urinary fluoride concentration in these individuals decreased gradually over long periods indicating that fluoride was being mobilized continuously from the skeleton and subsequently excreted (Hodge et al., 1970).
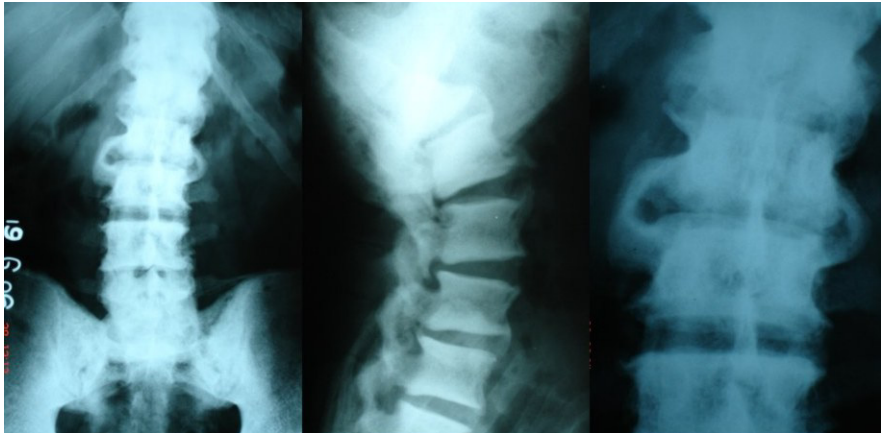

Fig. 4.11. X-ray pictures taken from a 33 year old male skeletal fluorosis patient from Sri Lanka, showing generalized increase of bone density with cortical thickening and coarse tubercular pattern. Ligamentous calcification in the spine and pelvis is observed. Bridging osteophytes in the spine are clearly seen in the picture (photo courtesy Dr. Tilak Abeysekara)

CASE STUDIES

Dental Fluorosis in Sri Lanka

Sri Lanka, a developing country with a population of nearly 20 million and lying in the tropical belt, has well defined wet and dry zones. In the dry zone, dental fluorosis is highly prevalent and a population of about one million people is affected. In some areas in Sri Lanka, dental fluorosis has been recorded as high as 80-98% (Warnakulasuriya et al., 1992; Nunn et al., 1994).

The close relationship between the physical environment and community health is very clearly seen in Sri Lanka. This is mainly due to the large majority of the population of Sri Lanka living in close association with the actual physical environment with only about 25-30% of the population having piped water. Further, nine out of the ten great soil groups are present in Sri Lanka and the effect of the chemistry of the soil and water on the health of the population is seen quite prominently in Sri Lanka (Dissanayake, 1984b; Dissanayake and Weerasooriya, 1987).

Geologically Sri Lanka consists of over 90% metamorphic rocks of presumed Precambrian age and these form 3 major units, the Highland complex, Wanni complex and the Vijayan complex (Figure 4.12). A suite of metasedimentary and metavolcanic rocks formed under granulite facies conditions comprises the Highland complex. Among the metasediments, quartzites, marbles, quartzo-feldspathic gneisses and meta-pelites form the major constituents. In the south-western part, calciphyres, charnockites and cordierite-bearing gneisses are present.

The Wanni complex consists of leucocratic biotite gneisses, migmatites, pink granitic gneisses and granitoids with compositions varying from granitic, syenitic to granodioritic. The granitoids frequently have enclaves of amphibolite and hornblende gneiss. The Vijayan complex is composed of biotite-hornblende gneisses, granitic gneisses and scattered bands of metasediments and charnockitic gneisses. Small plutons of granites and charnockites also occur close to the east coast (Cooray, 1978).

It is apparent from the lithology that there are abundant fluoride-bearing minerals such as micas, hornblende, sphene and apatite. Further, minerals such as fluorite, tourmaline and topaz are also found in many locations and these also contribute to the general geochemical cycle of fluorine in the physical environment.

A further source of fluorine is probably the lower crustal volatiles of which fluorine is known to be an important component. These volatiles are found in deep-seated fractures and lineaments and hence tend to get concentrated in materials associated with such faults and fractures.

Vitanage (1989) studied the Precambrian and later tectonic events in Sri Lanka and observed that the rocks of all three complexes are dissected by about 4330 lineaments with lengths varying from 1.25 km to over 100 km in an area of 30,000 km^2 investigated. It is conceivable that many of these lineaments are deep seated and hence the loci for fluorine outgassing.

These could well be of great significance in the general geochemistry of fluorine in Sri Lanka.
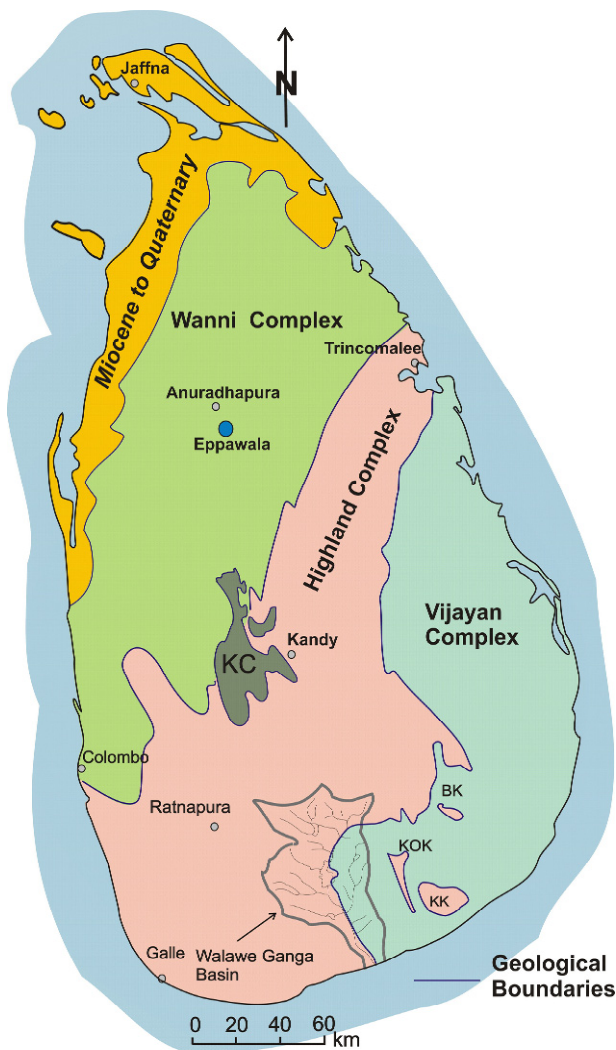

Fig. 4.12. Simplified geological map of Sri Lanka (KC- Kadugannawa Complex; KK- Kataragama Complex; BK- Buttala Klippe; KOK- Kudaoya Klippe)

The plate tectonic model for the geological evolution in Sri Lanka as put forward by Munasinghe and Dissanayake (1982), envisages the central Highland Complex of Sri Lanka to have been a highly metamorphosed assemblage of marine deposited volcanic, volcano-clastic and sedimentary

rocks, which evidently carried significant quantities of chlorine and fluorine concentrated in the marine-based sediments (Wedepohl, 1972). The later metamorphism and repeated deformation of these volatile-rich materials within the central Highland Basin probably incorporated fluorine in the minerals leading to an enrichment of fluorine in the crustal rocks of Sri Lanka.

Distribution of fluoride in the groundwater of Sri Lanka

Figure 4.13 illustrates the distribution of fluoride-rich groundwater in Sri Lanka. In the compilation of the Hydrogeochemical Atlas of Sri Lanka, Dissanayake and Weerasooriya (1986) delineated the fluoride zones of Sri Lanka based on the fluoride content in dug well water samples. The histograms for fluoride concentrations in groundwater in seven fluoride-rich districts of Sri Lanka are shown in Figure 4.14 (Raghava Rao et al., 1987; Christensen and Dharmagunawardhena, 1987). The high fluoride areas coincide with the high dental fluorosis areas of Sri Lanka.

Data obtained from a large number of deep wells indicate that a large part of the landmass of Sri Lanka is fluoride-rich. Several regions, in the North Central Province, notably the Anuradhapura and Polonnaruwa districts have fluoride concentrations in groundwater often reaching 10 mg/L and these areas, as expected, have a very high incidence of dental fluorosis.

It is of interest to correlate the fluoride-high and fluoride-low areas delineated with natural factors such as climate and geology. Low-fluoride areas are situated mainly in the wet zone where the average annual rainfall exceeds 5000 mm in certain instances. In these regions, leaching of soluble ions is high and fluoride is rapidly leached. In the dry zone, however, evaporation is high and this brings the soluble ions upwards due to the capillary action in soils. This, although not the sole explanation for the observed distribution of fluoride in the groundwater of Sri Lanka, could nevertheless be a major factor (Dissanayake, 1991a).

In the study of geochemical distribution of fluoride in the groundwater of Sri Lanka, the geology of the terrains needs special consideration. The composition of the rocks in the area, particularly the easily leached constituents coupled with the climate is the key factor in the geochemical distribution of elements in a tropical region. The abundance of fluoride in the rocks and the ease with which it is leached under the effect of groundwater has an important bearing on the abundance of fluoride in the groundwater of the areas concerned and hence the prevalence of dental diseases.

Raghava Rao et al. (1987) studied the fluoride concentration in the groundwater as influenced by the lithology of the terrain (Fig. 4.14). His observations are as follows.
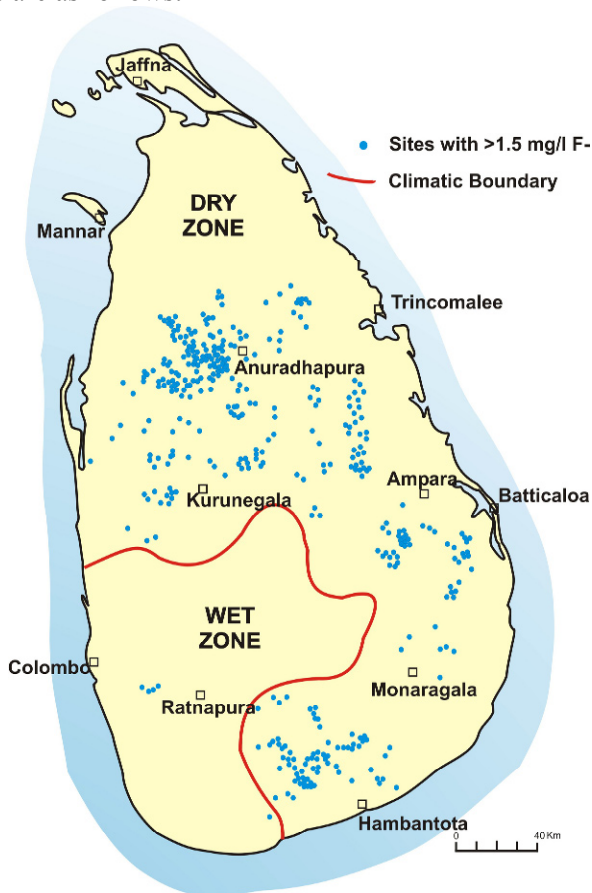

Fig. 4.13. Distribution of deep water wells with fluoride-rich ground water in Sri Lanka (modified after Dissanayake, 1991a)

Anuradhapura district - High fluoride levels throughout the district. Associated rocks: charnockites, charnockitic gneisses, granitic gneisses and hornblende gneisses (granitised through pegmatite intrusions).

Kurunegala district - High fluoride areas (3-5 mg/L), associated with charnockites, intrusive granites, hornblende biotite gneisses and granitic gneisses. Moderately rich fluoride areas (2-3 mg/L) were recognized in garnet-biotite-sillimanite gneisses associated with intrusive granites and granitic gneisses.

Ratnapura district - Fluoride-rich areas were recognised in the undifferentiated metasediments (granitic in composition) and charnockitic gneisses associated with pegmatites and intrusive granites. Marbles and calcgneisses also constituted a rock assemblage associated with high fluoride zones.

Ampara district - High fluoride areas associated with hornblende-biotite gneisses and granite gneisses/augen gneisses.

Monaragala district - A cluster of high fluoride wells were associated with charnockites and hornblende gneisses.

Matale and Polonnaruwa districts - Christensen and Dharmagunawardana (1987) observed that in the Matale and Polonnaruwa districts high fluoride concentrations are associated with charnockites, biotite gneisses, granulites and gneisses.
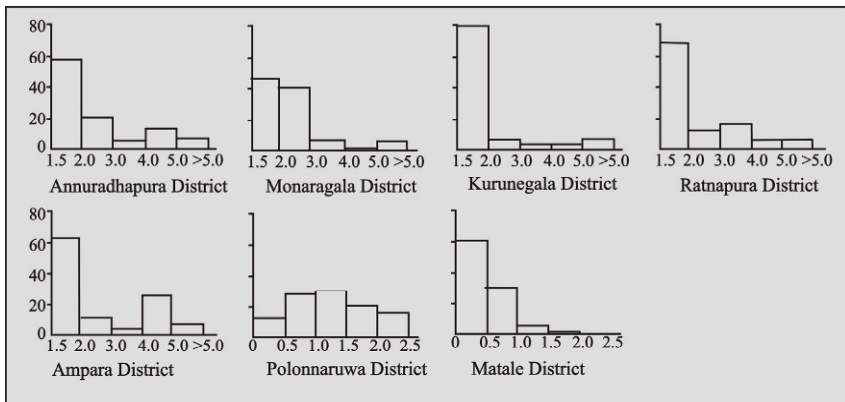

Fig. 4.14. Fluoride (mg/L) in water wells in some selected districts of Sri Lanka (Raghava Rao et al., 1987)

A further point of interest in the geology of Sri Lanka which has a bearing on fluoride geochemistry is the presence of a mineralized belt at the boundary of the Highland-Vijayan complexes (Munasinghe and Dissanayake, 1982). Fluorine, being a volatile element is known to be abundant in such tectonic zones and is enriched in rocks at such locations. Granites are generally rich in fluorine and such granites are found in abundance in the Vijayan Complex. Mineralogically, 30-90% of the fluorine in calc-alkaline granites is generally located in biotite with lesser amounts in hornblende, muscovite, quartz, and accessories. However, accessory minerals-apatite, sphene, fluorite, microlite, pyrochlore, topaz, tourmaline, spodumene,

cryolite among others, occasionally contribute more than 50% of the F notably in F-rich magmatic and metasomatic roof-zone granites (Bailey, 1977). Dissanayake and Weerasooriya (1986) observed high fluoride concentrations along the mineralised boundary.

Nanayakkara et al. (1999) studied the prevalence and severity of dental fluorosis in a high fluoride area at Eppawala located near a fluoride-bearing (1.5-2.4%) large exploitable apatite deposit in the North Central province of Sri Lanka. The fluoride levels in the drinking water ranged from 0.21 to 9.8 mg/L, and 97% of the children in the area were affected by dental fluorosis. About 20% had severe fluorosis (scores of 3 and 7). The prevalence of caries increased as the degree of fluorosis increased. The fluoride content in water of deep wells was much greater than in that of surface well samples and this was a major cause of the dental fluorosis in the area.

A study on the dental fluorosis in the Walawe Ganga basin in the south of Sri Lanka by Van der Hoek et al. (2003) showed that prevalence of dental fluorosis among 14 yr old students of the area was 43.2%. In this area, too, drinking water obtained from surface water sources had lower fluoride levels (median 0.22 mg/L) than water from deep tube wells (median 0.80 mg/L). The study by Warnakulasuriya et al. (1992) on 380 children of about 14 years, living in 4 geographic areas of Sri Lanka with fluoride levels of 0.09 mg/L to 8.0 mg/L showed that even in low-fluoride areas dental fluorosis is still prevalent. Their studies were comparable to the findings from other tropical countries such as Senegal and Kenya.

Dental Fluorosis in India

It has been estimated that about 62 million people in 17 out of the 32 states in India are affected by dental and/or skeletal fluorosis, the extent of fluoride contamination of water varying from 1.0 to 48.0 mg/L (Susheela, 1998). Table 4.6 and Figure 4.15 show the districts and states in India affected by dental fluorosis. Rajastan is one of the worst affected regions in India where all 32 districts are affected. With a population of over one billion, provision of safe drinking water in India is a task of gigantic proportions, bearing in mind that around 300 million people still live in absolute poverty in both rural and urban areas. About 6 million children in India are estimated to be affected by high fluoride ingestion (Sharma, 2003).

Table 4.6. Grading of states based on the extent of endemicity (after Susheela, 2003)

Name of the State	Total Districts	No. of Effected Districts
Andhra Pradesh	23	16
Gujarat	19	18
Rajasthan	32	32
Karnataka	27	18
Orissa	32	18
Punjab	17	14
Maharashtra	32	10
Madhya Pradesh (MP)*	45	16
Haryana	19	12
Bihar*	41	6
Tamil Nadu	29	8
Uttar Pradesh (UP)*		18
West Bengal	18	4
Kerala	14	3
Assam	23	2
NCT of Delhi	13	4
Jammu and Kashmir	14	1

* Undivided states of MP, UP and Bihar.
"NCT" stands for National Capital Territory (Note there are no districts rather it is divided into 13 Blocks.)

Choubisa (2001) who investigated endemic fluorosis in 21 villages in Southern Rajasthan where the fluoride concentrations ranged from 1.5 to 4.0 mg/L, observed a maximum prevalence of dental fluorosis (77.1%) in the 17-22 age group. In the other parts of Rajasthan, there are reports of fluoride concentrations in the drinking water as high as 18.0 mg/L (Somapura, 1998). In some areas of Rajasthan where the fluoride levels in the water are very high, intrusions of granite and rhyolites in metasediments have been observed. Mineralization, notably fluorite are also present (Maithani et al., 1998). High fluoride zones correlated with granites, acidic volcanic rocks and dykes. The water-rock interaction was prolonged due to longer residence times and this resulted in higher fluoride concentrations.
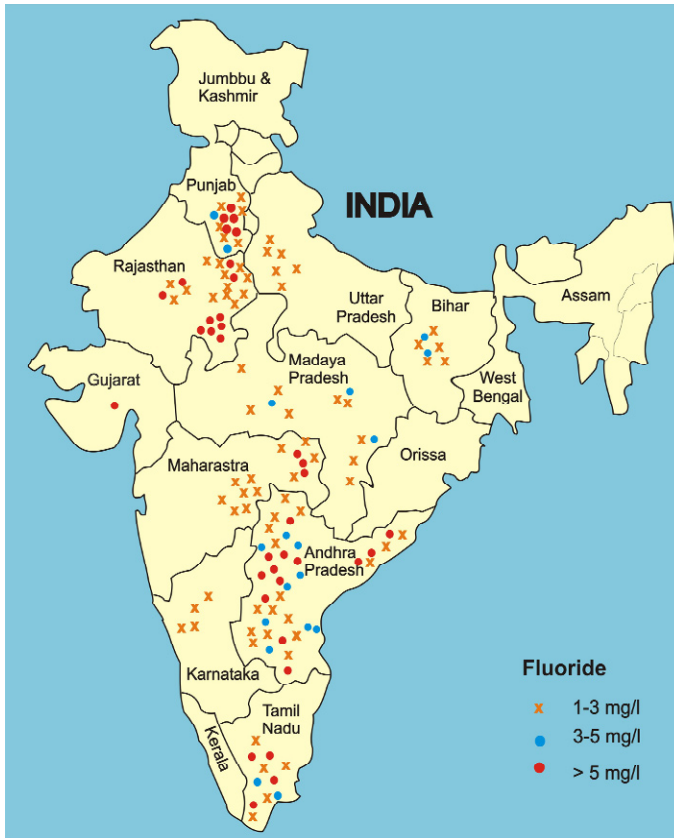
Fig. 4.15. States in India affected by dental fluorosis (Vannappa et al., 1999)

In an interesting case study Saha and Sharma (2002) noted that in the state of Bihar, fluorosis was increasing with time. Earlier work (Ghosh et al., 1986) had shown that in the alluvial plain of Bihar, fluorosis was very low (Table 4.6). Later workers after several years reported high fluoride concentrations from different parts of the state of Bihar (Sharma, 2001), underlain by granite gneisses complexes. Areas underlain by alluvium had also excessive fluoride in groundwater.

The work of Saha and Sharma (2002) showed that over a period of 10 years, the average fluoride content had increased from 0.56 mg/L to 1.3 mg/L with a greater increase recorded in the marginal alluvium than in areas underlain by hard rocks. The correlation between Ca and F which was -0.084 in 1992 had increased to -0.375 in 2002. The fluoride-bearing minerals of the mica schists and granitic gneisses were considered to be the

sources of the fluoride. Further, a comparison of the water level distribution with fluoride distribution in 2002 showed that fluoride accumulates more where there is a shallow water table and where seasonal fluctuations are minimal. These areas were underlain by 30 to 140 m thick unconsolidated sediments. There was also $CaCO_3$ precipitation which caused the fluoride content to increase on account of the prevalent pH range of 7.3 to 7.8.

In the state of Karnataka, fluorosis has been reported in several areas, notably in the hard rock terrains. In all the districts, groundwater is the main source of drinking water. The fluoride concentrations in the drinking water ranged from 1.5 to 18 mg/L with about 90% of school children affected by fluorosis. The geology plays a major role as shown by the higher fluoride concentrations in areas underlain by gneisses, schists and quartzites. Some formations had fluoride-rich mafic minerals that yielded higher fluoride concentrations in the associated groundwater (Vannappa et al., 1999). In the Hasan district, the amphibolites, apatite-rich granitic intrusions and dolerite dykes were considered to be the source materials for the fluoride.

Fluorosis in the East African Rift Valley

The Great Rift Valley (Figure 4.16) is a major geological feature in Africa caused by the separation of the African and Arabian plates about 35 million years ago. It extends for over 5000 km from northern Syria to Mozambique and has a width varying from 30-100 km and a depth ranging from a few hundred to several thousand metres. In the eastern part of Africa, the valley is split into 2 parts, the Eastern Rift and the Western Rift. The Western Rift has some of the highest mountains in Africa and deep lakes such as the 1470 metre deep Tanganyika Lake and Lake Victoria.

In the East African Rift Valley, some of the terrains such as those in the north of Nairobi in Kenya are lying at low levels. The lakes in these regions are characterized by high mineral contents and marked salt formation by strong evaporation. This is exemplified by Lake Magadia Soda Lake, and Lakes Elmenteita, Baringo, Bogoria and Nakuru all of which are strongly alkaline.

Due to the weakening of the crust caused by the geological processes of rift formation there are several volcanic mountains. Among these are Mount Kilimanjaro, Mount Kenya, Mount Karisimbi and the crater Highlands in Tanzania.
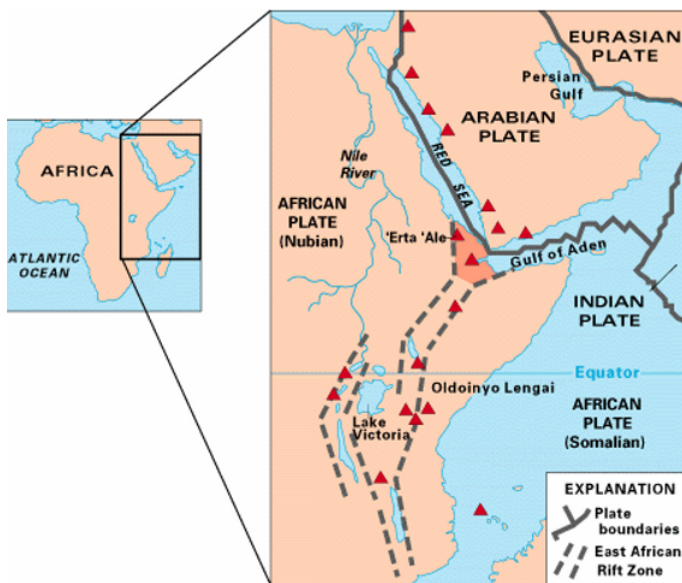
Fig. 4.16. East African rift valley (source: USGS)

These volcanic activities bring about large amounts of volatile releases of CO_2, SO_2, H_2S, HCl and fluorine in the form of HF. In several countries in the East African Rift Valley, fluorosis among people is very high and these volcanic emanations are a primary source of fluoride.

In a recent study on the Ruapehu volcano, New Zealand, Cronin et al. (2003), highlighted the environmental and health hazards of fluoride in volcanic ash. The vent-hosted hydrothermal system of Ruapehu volcano is normally covered by about 10 million m^3 acidic Crater Lake water accumulating volcanic gases. These authors observed that the total F in the ash is often enriched by a factor of 6 relative to original magmatic contents. The carriers of F were considered to be the low soluble minerals such as CaF_2, AlF_3 and $Ca_5(PO_4)_3(OH,F)$. The fluoride therefore was released over long periods of time. In the case of Ruapehu volcanic emissions, several thousand sheep died due to acute fluorosis.

In Kenya the water resources are very limited, particularly in the drier northern regions where groundwater is the main source of drinking water. Table 4.7 shows the percentage distribution of high fluoride groundwaters in Kenya. It is observed that certain provinces such as Nairobi, Rift Valley; Eastern and Central Kenya have highly fluoride-rich groundwater. Clarke

et al. (1990) defined the unmodified waters in the Rift Valley as waters whose chemical composition is derived from normal water-rock interactions at moderate temperatures. Very high fluoride concentrations up to 180 mg/L had been observed in these waters, indicative of highly significant leaching of fluoride-rich Rift Valley volcanic rocks. Gaciri and Davies (1993) observed that the groundwaters associated with these volcanic rocks have high alkalinity and were high in Na, K, HCO_3^-, Cl^-. Ca and Mg were found in low concentrations due to their precipitation as carbonates. It had been observed that the highest levels of fluoride in groundwaters in the Rift Valley were 39.0 mg/L from wells and 43.5 mg/L in bore holes (Wilkister et al., 2002).

Table 4.7. Percentage distribution of high fluoride groundwaters in Kenya (Nair et al., 1984)

Province	Range of Fluoride Content (mg/L)						Number of Samples
	0.1-0.4	0.5-1.0	1.1-3.0	3.1-5.0	5.1-8.0	>8.0	
Nairobi	9.8	9.8	19.7	13.2	15.8	31.7	183
Rift Valley	14	15.7	38.7	13.7	8	9.9	313
Eastern	11.7	23.1	37	6.1	9.4	12.7	181
Northeastern	9.3	28.9	44.7	9.2	3.9	3.9	76
Central	25.8	21.2	30.3	9.1	5.3	8.3	396
Nyanza	25.8	29.1	25.8	9.7	6.4	3.2	31
Coast	40.9	22.6	26.8	5.4	1.1	3.2	93
Western	77	15	-	-	8	-	13
							1286
Total for Kenya	19.3	19.2	31.9	10.1	7.7	11.8	100%

Apambire et al. (1997) studied the geochemistry, genesis and health implications of fluoriferous groundwaters in the upper regions of Ghana and observed that groundwater fluoride levels reached 0.11 to 4.60 mg/L with a mean value of 0.97 mg/L. The highest concentrations were associated with hornblende granite and syenite rock suites (Figure 4.17). The areas of anomalous groundwater fluoride coincide largely with terrains underlain by rocks of the Bongo Granitic Suite which comprised of coarse-grained hornblende-granite grading towards its outer contacts into biotite and hornblende syenitic phases. The highest groundwater fluoride concentrations were found in the interior phases of the intrusions.
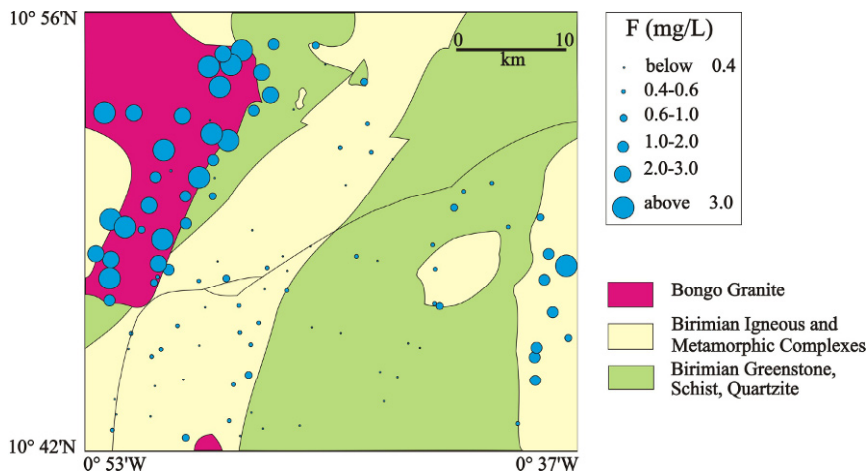
Fig. 4.17. Distribution of fluoride in groundwater in the Bolgatanga area of Northern Ghana. The highest concentrations are associated with granite outcrops and coincide with the incidence of dental fluorosis (Smedley et al., 1995; reproduced with kind permission from the British Geological Survey)

The anomalous fluoride contents in the groundwater associated with the Bongo granitoids were thought to have arisen from fluoride present and to a lesser extent from both dissolution and anion exchange from micaceous minerals and their altered clay products.

Apart from the geology, the climate, as in the case of Sri Lanka, also plays a major role in the enrichment of fluoride in the groundwater of Ghana. The arid zones of the country are notably high in fluoride-rich water formations. Dental fluorosis is also common in such areas. The groundwaters in granitic rocks of the south-west plateau had lower fluoride concentrations due to high rainfall and dilution (Smedley et al., 1995). The fluoride concentrations in parts of northern Tanzania are probably the highest in the world. Aswathanarayana et al. (1985) have recorded abnormally high fluoride contents in the Maji Ya Chan River (21-14 mg/L), Engare Nanyuki river (21-26 mg/L), pond waters of Kitefu (61-65 mg/L), thermal springs of Jekukumia (63 mg/L) and in the soda lakes of Momella (up to 690 mg/L).

The geochemical model proposed by Aswathanarayana et al. (1985) (Figure 4.18) accounts for the enhanced fluoride level as being due to episodic influx of fluoride from volcanic ash exhalations and sublimates related to Miocene to Recent Volcanism. The alkaline volcano of Oldoinyo Lengai had erupted in 1960. Since such geological sources enrich the groundwater

in fluoride, there are severe cases of dental and skeletal fluorosis in many parts of Tanzania.
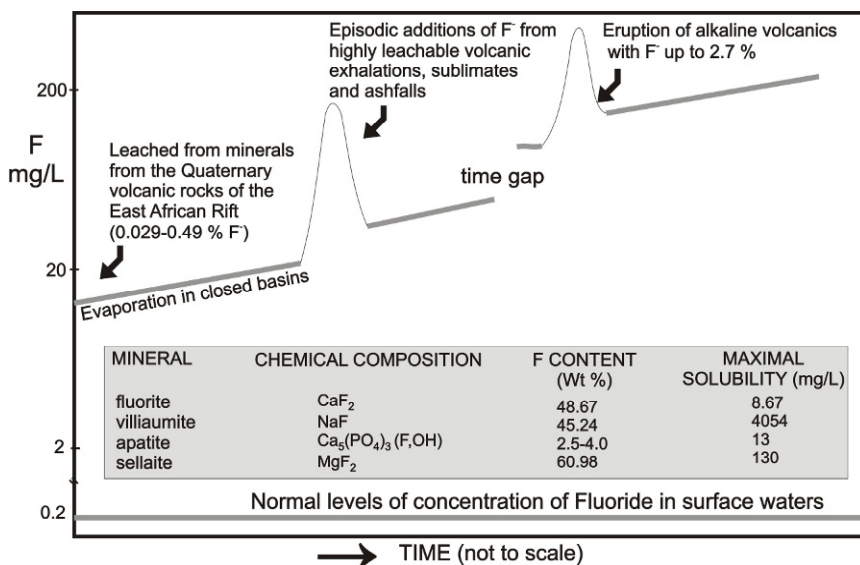

Fig. 4.18. Conceptual model to account for the high fluoride contents in Northern Tanzania (modified after Aswathanarayana et. al., 1985)

In the Rift Valley of Ethiopia, some lakes such as Abiyata and Shalla, located on the rift floor have fluoride concentrations reaching levels as high as 300 mg/L (Chernet and Travi, 1993). These water characteristics have rendered the water rather unsuitable for agriculture. Chernet et al. (2001) subjected chemical analyses of 320 samples taken throughout the region for geostatistical, chemical equilibria and simulation of evaporation-concentration processes using the computer software AQUA.

Their results showed that the water associated with the volcanic rocks have positive alkalinity residual of calcite. Due to the strong evaporation in the arid to semi-arid conditions, calcite precipitation causes a decrease in the chemical activity of calcium, resulting in an increase of fluoride concentrations controlled by equilibrium with CaF_2. When the pH reaches values as high as 9 to 10, fluoride accumulates in the lower zones of the basins. Chernet et al. (2001) showed that the increase in fluoride content and the alkaline-sodic characteristics depend mainly on the unbalanced initial stage between the carbonate alkalinity and calcium. $[(HCO^-_3)>2(Ca+Mg)]$, resulting from the weathering and solution effects of volcanic rocks.

In a more recent study Reimann et al. (2003), collected drinking water samples throughout the Ethiopian part of the Rift Valley and analysed them for 70 chemical parameters. It was observed that fluoride was the most problematic element with 33% of the samples having values over 1.5 mg/L and up to 11.6 mg/L. The incidence of dental and skeletal fluorosis, as expected, was very high.

Endemic Fluorosis in China

In terms of both incidence and severity, China is one of the countries most seriously affected by endemic fluorosis. It occurs in more than 30 provinces, municipalities and autonomous regions affecting a population of 45 million (Ministry of Health PRC, 1997). Figure 4.19 illustrates a map showing the distribution of fluorosis districts in China. Endemic fluorosis areas in China are divided into 6 types according to the fluoride source (Wang et al., 2002);

>   (a) shallow groundwater of high fluoride contents (>1.0 mg/L)
>   (b) deep groundwater with high fluoride
>   (c) hot springs with high fluoride
>   (d) abundant fluoride - bearing rock formations
>   (e) high fluoride coal
>   (f) high fluoride tea

In the large semi-arid and arid regions of China, the enrichment of fluoride in groundwater is due to the leaching of fluoride from the fluoride-bearing rock formations and enrichments in water due to rapid evaporation, aided by poor drainage. In these areas the fluoride concentration is around 5 mg/L.

Zheng and Hong (1988) recorded maximum fluoride contents in surface and phreatic waters as 129 mg/L and 40 mg/L, respectively. In the Mt Da Xinganling and Mt Yanshan areas there are fluoride-bearing volcanic and intrusive rocks (500-800 mg/kg) and these are probable sources of the fluoride. Further, loess present in these regions also acts as carriers of fluoride, the F^- in loess ranging from 490 to 550 mg/kg. Soda salinisation of soils in the affected regions is also considered to be an important factor in the fluoride enrichment.

There are 2493 recorded hot springs in China (Zheng and Hong, 1988). These are distributed in Yunnan, Guangdong, Fujian and Taiwan provinces

and their fluoride concentrations are high, some having fluoride as much as 15 mg/L.
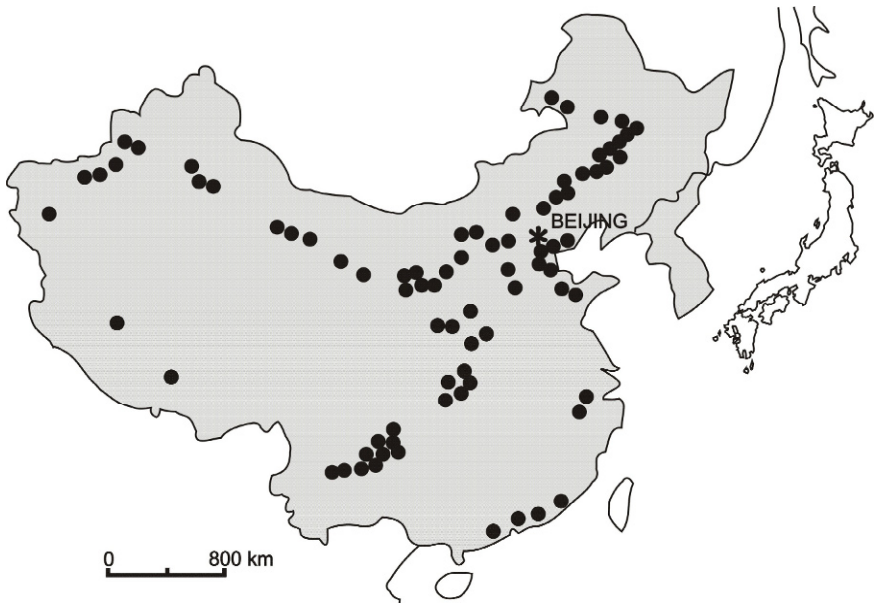

Fig. 4.19. Distribution of high groundwater fluoride contents in China (Zheng and Hong, 1988)

Fluoriferous coal is another major cause of endemic fluorosis in China. In the Guizhon Province in the south west of China, for example, more than 10 million people suffer from various forms of fluorosis (Dai et al., 2004). The rate of incidence of osteofluorosis is about 80% in some villages, and almost every family has at least one member with serious fluorosis that had resulted in disability and paralysis. The main cause of this fluorosis is the burning of clay mixed with coal. The coal in some cases has fluorine contents greater than 500 mg/kg, very much higher than the world average for coal, namely 80 mg/kg (Luo et al., 2003). Further, the villagers use clay as coal-burning additive in the furnace and as a binder in briquette-making. The ratio of the mixture of coal and clay ranges from 2.1 to 4.1. Interestingly, the clay contains fluoride concentrations ranging from 100 to 2455 mg/kg, with an average of 1027 mg/kg. Dai et al. (2004) are therefore of the view that clay is more important than coal in the incidence of fluorosis in the Guizhan Province. Figure 4.20 shows the distribution of endemic skeletal fluorosis prevalence in China.
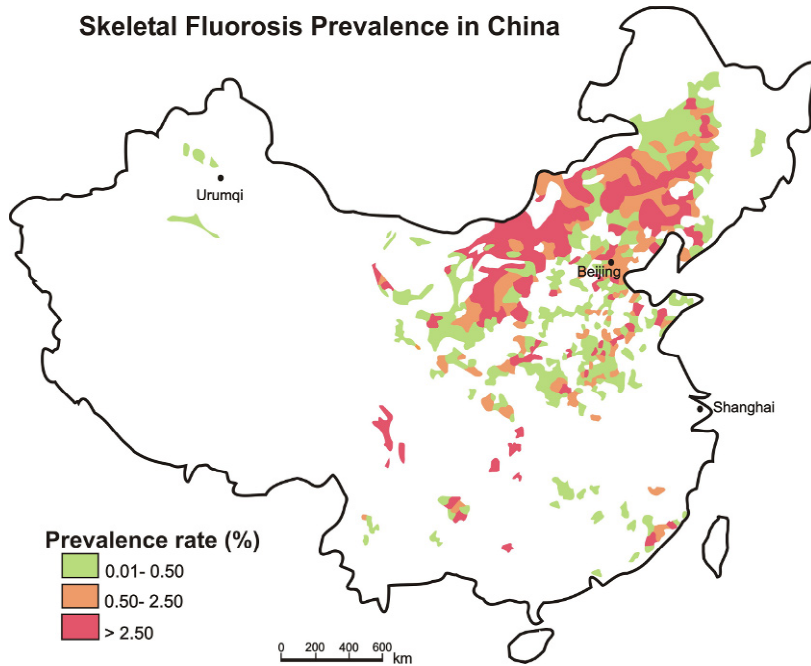
Skeletal Fluorosis Prevalence in China

Fig. 4.20. Distribution of endemic skeletal fluorosis prevalence in China (modified from Tan et al., 1989)

Brick Tea Fluorosis in China

In addition to the water-related and the coal-related fluorosis, a third source of fluorosis is the popular drink brick tea. The brick-tea fluorosis, as it is known in China, was discovered in the 1980s. Tea has the ability to accumulate higher concentrations of fluoride and the tea drink therefore, as in some parts of China, can be a source of fluorosis.

An epidemiological survey was conducted by Cao et al. (2003) in Naqu County, Tibet, to investigate the manifestations of fluorosis in adults drinking brick tea. The fluoride concentration of the water sources was only 0.10 mg/L and there was no evidence of fluoride air pollution. The foods processed from brick tea, zamba and buttered tea however, had fluoride contents of 4.52 and 3.21 mg/L respectively. The adult daily fluoride intake was 12 mg of which 99% originated from foods containing brick tea. Of the cases studied, 74% had osteosclerosis type skeletal fluorosis. Cao et al. (2003) were of the view that brick tea-type fluorosis had even greater health impacts than the water- type and the coal-combustion type.

DEFLUORIDATION OF HIGH FLUORIDE GROUNDWATER

The presence or absence of fluoride in their water supplies is generally not known by the public, particularly in developing countries where in most areas the drinking water is obtained direct from the ground. Unlike in the case of excessive dissolved iron in the dug and deep wells, where a colour and objectionable taste is imparted, fluoride imparts neither colour nor taste. It should be noted that both Fe^{2+} and Fe^{3+} are only soluble at very low pH. Only chemical analyses can detect its presence and the concentration. This is a major reason why such a high percentage of the population living in fluoride-rich areas and who suffer from fluorosis are not even aware of the problem until the later stages.

Since the vast majority of the people affected by fluorosis in tropical countries live in rural areas without central water treatment plants, they obtain their domestic water supplies in the untreated form from lakes, rivers, surface wells and deep wells, which may contain biological and chemical contaminants detrimental to health. The need for simple water treatment techniques at the rural level therefore is a prime need for fluorosis-affected tropical developing countries.

Phantumvanit et al. (1998) who developed a defluoridator for individual households in Northern Thailand noted that the shortcomings of most defluoridation methods are:

> high cost of plants,
> high operational and maintenance costs,
> low capacity for removing fluoride,
> lack of selectivity for fluoride,
> undesirable effects on water quality,
> generation of waste that is difficult to handle and
> complicated procedures.

Based on the nature of process, defluoroidation techniques are classified under:

(a)   adsorption and ion exchange

(b)   precipitation

(c)   electrochemical methods

(d)   membrane techniques

Table 4.8 shows the various materials used in the different defluoridation techniques.

A highly efficient, simple house hold defluoridator using burnt bricks was employed in many areas with high fluorosis in Sri Lanka (Padmasiri and Dissanayake, 1995). This defluoridator is suitable for developing countries and is especially suited on account of its easy installation, maintenance, ready availability of the defluoridating raw material used, i.e., burnt bricks, and low cost, thus achieving Village Level Operation and Maintenance status (VLOM)(Figure 4.21).

Heidweiller (1990) reviewed some of the more common techniques of defluoridation of fluoride-rich water. In the Nalgonda technique, used in the fluorosis-affected Andhra Pradesh, India, a combination of alum and lime mixed with bleaching powder is added to fluoride-rich water, stirred and allowed to settle (Nawlakhe and Bulusu, 1989). The fluoride is removed by the process of flocculation, sedimentation and subsequent filtration. Among the other common defluoridation techniques are: use of activated carbon, activated alumina, ion-exchange resins, clay minerals, clay pots and bone char and gypsum (Edmunds and Smedley, 2004; Weerasooriya et al., 1989; Jinadasa et al., 1988; Weerasooriya et al., 1994; Jinadasa et al., 1991, Schuiling, 1998).

Fig. 4.21. Household defluoridator using burnt bricks distributed in villages in Sri Lanka

Table 4.8. Materials and methods for defluoridation (Mariappan and Vasudevan, 2002)

Adsorption	Ion exchange	Precipitation	Others
Carbon materials	NCL poly anion	Lime	Electrochemical
Wood	Resin	Alum	(Aluminium elec-
LigniteCoal,	Tulsion A27	Lime and Alum	trode) Electrodialysis
Bone	Lewatit-MIH-59	(Nalgonda Tech-	Reverse Osmosis
Petroleum residues	Amberlite IRA-	nique)	
Nut shells,	400	i).Fill and Draw	
Paddy husk	Deacedodite FF-	ii).Continuous	
Avaram bark	IP	flow	
Coffee husk,	Waso resin-14	iii).Package	
Tea waste	Polystyrene	Treatment plant	
Jute waste		for HP	
Coconut shell		Alum floc blan-	
Coir pith,		ket-method	
Fly ash		Poly-aluminium	
Carbion,		chloride- (PAC)	
Defluoron-1		Poly-aluminium	
Defluoron-2		Hydroxy-	
Activated alumina		sulphate (PAHS)	
KRASS, Bauxite			
Serpentine			
Clay minerals			
Fish bone,			
calcite			
Bio-mass			