

Fluorine in Environment : A Review

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INTRODUCTION

With electronic configuration $1s^2\ 2s^2\ 2p^5$, elemental fluorine is just one electron short of the configuration of inert gases and as such, it is most reactive of all the elements. On account of this high chemical reactivity, it occurs as F in minerals. Rarely, it is also involved in the formation of fluoro-anions such as BF_4^- and SiF_6^- . Though electronegativity of fluorine is highest among all elements, its electron affinity (79.5 K cal/gm atoms) is between chlorine (83.3 K cal/gm atoms) and bromine (77.5 K cal/gm atoms). On account of its high chemical reactivity, fluorine is one of the most dispersed elements in the environment.

FLUORINE IN COSMOS

In stellar space fluorine has been detected only in gaseous nebula, NGC 7027, and one star, r-Pegasi, and in these cosmic bodies its abundance is 5 to 10 times higher than in meteorites (Brown, 1950; Aller, 1961; Suess, 1965). According to Suess (1965), cosmic abundance of fluorine is 1.60×10^{-3} on atoms F/ 10^6 atoms Si basic. Abundance of F in Sun, Earth's crust and meteorites is near about the same. Very little is known about the mineral phase in meteorites in which F is hosted. However, Reed (1964) observed an inverse

correlation between F and Ca in the composition of meteorites. Interestingly, apatites from meteorites are nearly pure chloroapatites, unlike apatites in crust (Van Schmus and Ribbe, 1969).

Fluorine concentration in lunar rock and soil estimated from samples of Apollo-11, has wide range of variations from 30 to 340 ppm and compares closely with F distribution in W-1 standards and stony meteorites. Apatite however, is the only F bearing mineral identified in Lunar samples (Mason and Nelson, 1970).

FLUORINE IN EARTH'S ATMOSPHERE

The normal fluorine content in unpolluted air is less than $0.01\ \mu g/m^3$ according to Bowen (1966) and between $0.3-0.4\ \mu g/m^3$ according to Oelschlager (1965). With industrial pollution atmospheric fluorine content can range between $5-111\ \mu g/m^3$ (Oelschlager and Rheinwald, 1968). Presence of Hieratite (K_2SiF_6) and Malladrite (Na_2SiF_6) is reported in dust particles in air over North Sea, Germany (Radczewski, 1968). Fluorine is very toxic for both plant and animal life. Industrial plants manufacturing hydrofluoric acid, aluminium, superphosphate, enamel, bricks and industries consuming high sulphur non-coking coal like

thermal power plants are the main sources of fluoride pollution (Griffin et al., 1980, Deshmukh et al., 1996).

FLUORINE IN EARTH CRUST

On account of similar ionic radii, OH ions are replaced by F ions, provided the OH is not an electron donor. Thus, in amphiboles and micas, complete solid solution between OH and F end members is observed.

Strunz (1970) has ennumerated 150 fluorine bearing minerals, of which 63 are silicates, 34 are halides and 24 are phosphates. In nature, fluorite is the most widely distributed fluorine bearing mineral while, fluorapatite is a very common member of the immiscible phase generated during early differentiation of mafic and ultramafic magmas, forming apatite-magnetite rocks. With progressive differentiation fluorine is enriched into the residuum and therefore, its Clarke in granitoids and pegmatites is highest (0.08; Perel'man, 1977).

Under supergene environment, on account of its high reactivity coefficient, the element occurs as highly mobile fluoride ion but its mobility is severely restricted across a calcium barrier due to CaF_2 precipitation (Perel'man, 1977). It is for this reason that, under supergene environment, the average fluorine content of calcium rich sedimentary rocks, like calcareous shale, limestones, dolomite, calcareous sandstone etc., is high.

FLUORINE IN MAGMATIC MINERALS AND COMMON IGNEOUS ROCKS

In magmatic rocks, only topaz and fluo-

rite contain fluorine as an essential part of the composition. Other minerals, in which fluorine is an essential component, like villiaumite or cryolite are accessory minerals. Fluorine occupies OH positions in the structure of one of the components of the mixed crystals, with possibility of complete replacement from OH to F end member. Therefore in magmatic rocks, F contents in magma and the co-ordination number of the OH position determine the F content in the mineral. Despite similar ionic size of F (1.33\AA) and OH (1.40\AA) ions, the difference in their electronegativity is quite large. Hence, substitution of OH by F in the structure of the minerals entirely depends upon bond energy and co-ordination number of the OH sites (Rimsaite, 1967).

Range and average fluorine content of some rock forming minerals is given in Table 1. In general it is observed that, the more evolved the rock is in a given series, higher is its F content. It is also commonly observed that, in similar rocks, the fluorine content of the mineral increases as the alkali content of the rock increases. From Table 1, it is also clear that, the fluorine content of the hornblende increases as the silica content of the host rock increases.

Similarly, in apatite, the common host of fluorine in magmatic rocks, the fluorine content increases as the parent rocks become richer in their silica content. The fluorine content of biotite from highly evolved granite (0.24% Table 1) is also much higher compared to that of biotites occurring in lesser evolved gabbros (0.097%). It is interesting, however, to note that, the fluorine content of phlogopite from volcanic ejecta is 2.57% while

Fluorine in Environment

TABLE 1
FLUORINE CONTENT IN SELECTED IGNEOUS ROCK-FORMING MINERALS

Name of the Mineral	Name of Rock	Range of F in Wt%	Avg. F in Wt %	References
Aegirine	—	—	0.3	Vlasov et al. (1966)
Apatite	allivalite	—	0.09	Kokubu (1956)
Apatite	gabbro	1.46-1.86	1.83	Taborszky (1962)
Apatite	diorite	2.01-2.17	—	Taborszky (1962)
Apatite	quartz diorite	2.23-2.50	—	Taborszky (1962)
Apatite	quartz monzonite	—	2.68	Taborszky (1962)
Apatite	granodiorite	2.49-3.31	2.81	Taborszky (1962)
Apatite	Pegmatite	2.37-3.36	2.97	Shmakin & Shiryayeva (1968)
Augite	—	0.01-0.1	—	Troger (1935) in Correns (1956)
Biotite	gabbro	—	0.097	Seraphim (1951)
Biotite	gabbro diorite	—	0.10	Seraphim (1951)
Biotite	quartz diorite	—	0.26	Seraphim (1951)
Biotite	Kersantite	—	0.42	Nemec (1968)
Biotite	syenites	0.08-1.04	0.78	Solov'yev et al. (1967)
Biotite	granite	0.08-0.415	0.24	Koritnig (1951)
Biotite	pegmatite	0.22-3.05	1.40	Seraphim (1951)
Biotite	hornblende granite	—	1.67	Nemec (1968)
Biotite	Tonalite	—	2.38	Nockolds & Mitchell (1948)
Hornblende (basaltic)	Quartz latite	—	0.35	Deer et al. (1967)
Hornblende	gabbro	—	0.23	Deer et al. (1967)
hornblende	diorite pegmatite	—	0.53	Deer et al. (1967)
Hornblende	lamprophyric dyke	0.16-1.43	—	Nemec (1968)
Hornblende	granite	—	1.50	Buddington (1953)
Hypersthene	—	—	0.03	Lokka (1950) in Correns (1956)
Lepidolite	—	0.62-9.19	5.41	Correns (1956)
Muscovite	granodiorite	—	0.16	Deer et al. (1967)
Muscovite	granite	0.02-0.77	0.17	Seraphim (1951)
Muscovite	pegmatite	0.04-2.06	0.93	Deer et al. (1967); Nemec (1969)
Olivine	—	—	0.045	Kokubu (1956)
Phlogopite	Kimberlite	—	0.27	Bouvier (1970)
Phlogopite	Volcanic ejecta	—	2.57	Pierruccini (1950) in Correns (1956)
Sphene	Nepheline syenite	—	0.68	Kostetskaya and Mordinova (1968)
Sphene	syenite	0.41-1.36	—	Kostetskaya and Mordinova (1968)
Sphene	Diorites	0.30-0.75	—	Kostetskaya & Mordvinova (1968)
Sphene	Granitie	0.28-1.36	0.67	Kostetskaya & Mordvinova (1968)
Topaz	—	13.01-20.43	—	Deer et al. (1967); Gmelin (1959)
Tourmaline	—	0.07-1.27	—	Deer et al. (1967); Nemec (1969)

its content in phlogopites in kimberlite is only 0.27% (Pierruccini, 1950; Bouvier, 1970).

Therefore, it follows that, fluorine during initial stages of mafic-ultramafic differentiation is enriched into Fe, Ti, V, Mn rich immiscible phase along with chlorine and is occluded in apatite, of the apatite-magnetite (Nelsonite) assemblage (Narasayya, 1977; Malpe, 1993). It is for this reason that out of all major rock forming minerals, the fluorine content of apatite is significantly high. Nevertheless, the OH sites in hydroxyapatite structure are partly replaced by fluoride under varied physicochemical conditions.

In all acidic melts, evolved either by differentiation or by any other process, all minerals which contain alkali and OH bond are good geochemical hosts for fluorine. On account of this character, the F abundance in coloured micas is higher as compared to that in amphiboles and pyroxenes.

It is commonly observed that, there is a strong and positive correlation between F and SiO₂ content of the rocks, since, the average fluorine content of ultramafic rocks is 100 ppm, followed by intermediate rocks (400 ppm) and granitoids (800 ppm). The average fluorine content of alkaline rocks, however, despite their low SiO₂ content, is one of the highest (mean 1000 ppm) in igneous rocks (Wedepohl, 1974).

Phlogopite is the sole mineral in ultramafic rocks like kimberlites, which carries significant amount of fluorine in its composition (Rimsaite, 1970a). The average fluorine

content of ultramafic rocks like dunite (12 ppm, Huang and Johns, 1967) and peridotites (20 ppm) is low, while the mean fluorine content of garnet peridotites and kimberlites, which are phlogopite bearing, is significantly high (252 ppm). The mean F content of basalts is 450 ppm (Seraphim 1951). The range of fluorine content in syenites varies from 600 ppm to 1480 ppm (Troger, 1935; Saito, 1950; Seraphim, 1951; Turekian and Wedepohl, 1961). Koritnig (1951) and Troger (1935), have reported average fluorine content in nepheline syenite as 1190 ppm and 8000 ppm, respectively.

The fluorine content of alkali granite reported by Troger (1935) is 1400 ppm while a Riebeckite granite from Northern Nigeria contains 12,400 ppm fluorine (Bowden, 1966). The fluorine contents of alkaline intrusive rocks like larvikite (600 ppm; Barth & Bruun, 1945), pulaskite (1950 ppm; Seraphim, 1951) and shonkinite (1410 ppm; Shepherd, 1940) are significantly high.

In volcanic landscapes, during periods of eruption, F from depth is introduced into the air, soil, water and plants. This fluorine remains in the landscapes under arid climatic conditions for a long period of time, whereas under humid climatic conditions it is relatively rapidly removed from the landscape with runoff. In Iceland, severe fluorosis has been observed during volcanic activity, which declines during quiescence.

FLUORINE DURING WEATHERING

During weathering in humid tropical/subtropical climates the geochemical fate of

fluorine, is controlled by a series of intricate processes, involving adsorption - desorption and dissolution - precipitation reactions. During weathering of granite massifs, fluorine is leached out in the initial stage itself (Koritnig, 1951). In the uppermost part of the weathered profile, however, some increase in fluorine content is observed. The fluorine in apatite is very stable while, the fluorine from mica is leached out rapidly. Fluorite (CaF_2), if present, is dissolved slowly by the circulating water. In soil profiles, decreasing fluorine content with increasing distance from the parent rock is observed (Robinson and Edgington, 1946; Michael and Blume, 1952). It is noted that most of the fluorine in clastic sedimentary rocks is hosted in their micaceous constituents (Koritnig, 1951). In a particular case, the average F content of an argillitic limestone is 200 ppm while the average content of its micaceous residue is 800 ppm (Koritnig, 1951). Hubner (1969 a & b) has noted that F to OH exchange in clay minerals depends upon concentration of fluoride ions and pH of the circulating water. Other factors also play an important role in fluorine adsorption on clay structures. The dioctahedral and trioctahedral illites are the principal clay minerals which can host fluorine by OH to F replacement. It is known that, under acidic circulating solution, fluorine is readily adsorbed in clay structure, while in alkaline environment it is desorbed (Hubner, 1969 b). During natural hydration and devitrification of glassy rocks and glasses, about half of the original fluorine present is solubilised, leached and lost, through fluorine adsorption by hydrated and devitrified glass from coexisting ground water (Noble et al., 1967). Fluorine content of the soils entirely depends upon their composition and

fluorine content of the rocks from which they have been derived. The average fluorine content in soil ranges between 90-980 ppm (Fleischer and Robinson, 1963). Decomposition of organic remains are the main source of F in soil in warm and humid climate. From acid soil, F is readily leached, while biogenic accumulation prevents it.

In permafrost regions, decomposing plant remains are the main sources of F in water. Peaty horizon in soil can contain upto 25% water-soluble F and the halogen migrates in the form of organic complexes.

Due to higher Ca distribution in arid climate F migration is inhibited. In semi-arid climates, which are most prevalent in Peninsular India, fluoride migration is controlled by chemistry of surface and subsurface waters. During dessicated summer season, mobility of fluoride ions is inhibited by higher calcium and low TDS of the surface and subsurface waters. During post monsoon, the mobility is enhanced due to relatively low calcium distribution and higher ionic strength of the waters (Handa, 1975 and 1977).

FLUORINE IN SEDIMENTS

Except for evaporites, fluorine is the most abundant halogen in the sedimentary rocks (Wedepohl, 1974). Fluorite (48.7% F), apatite (3.5% F), mica (between 0.14 to 0.22% F), illite (between 0.11 to 0.26% F) and montmorillonite (0.03% F) are the chief fluorine bearing minerals in sedimentary rocks (Koriting, 1951 and 1963). Therefore, the kind and the distribution of fluorine bearing

mineral ultimately determine the fluorine content of the sedimentary rocks. Among sedimentary rocks volcalniclastics and their secondary derivative, bentonite contains the highest amount of average fluorine of 5950 ppm, 1000 ppm, respectively (Robinson and Edgington, 1946; Kokubu, 1956).

Fluorine abundance in sandstones varies widely and ranges from 270 to 450 ppm (Koritnig, 1951; Turekian & Wedepohl, 1961). From Carboniferous (360 ± 10 m.y., to Cretaceous (130 ± 5 m.y., Ershov et al., 1988), there is distinct and progressive decrease in the average fluorine content of the sandstones. The average fluorine content of Carboniferous sandstone

is 450 ppm, that of Triassic sandstones (245 m.y.) is 320 ppm, while the average F content of Cretaceous sandstone is 280 ppm. In shales, the fluorine content varies from 510 to 800 ppm. There appears to be a space and time relationship with respect to fluorine distribution in shales, too. The average fluorine contents in limestones of different age and place is widely different and ranges from 90 to 940 ppm (Seraphim, 1951; Michael and Blume, 1952). The lower limit of fluorine distribution in dolomites (180 ppm) is higher than that in lime stones (Koritnig 1951). Different types of oceanic clays are considerably enriched in fluorine (430 ppm, Shepherd 1940; 730 ppm, Fleischer and Robinson, 1963).

TABLE 2
THE AVERAGE FLUORINE CONTENT IN DIFFERENT SEDIMENTARY ROCKS
(Fleischer and Robinson, 1963).

Rocks	Range in ppm	Avg. in ppm
Limestone	upto 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

It is interesting to note that fluorine in sedimentary rocks is due to presence of fluorine bearing minerals like fluorite and apatite or due to presence of clays which adsorb fluorine by F to OH replacement or by admixture of skeletal debris in which hydroxyl bonds are replaced by fluorine in the hydroxyapatite structure (Carpenter, 1969).

It should be noted that out of the total fluorine content of the clays associated with clastic rocks, 80-90% is hosted in the minerals of the mica group while the remainder is occluded in ion exchange in clay minerals like, 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. Fluorine enrichment over chlorine by a factor of 10^5 during CaCO_3 precipitation, as suggested by Carpenter (1969), is most probably due to co-precipitation of very small amounts of CaF_2 with CaCO_3 . It is for this reason that out of the total solubilised fluoride added by rivers, only 10 to 20% fluorine co-precipitates as CaF_2 alongwith CaCO_3 and $\text{Ca}(\text{PO}_4)_2$, in oceans (Carpenter, 1969).

FLUORINE IN CARBONATE ROCKS AND EVAPORITES

In carbonate rocks, fluorine is contributed by fluorite, apatite and clay minerals in different proportions. The solubility of fluorites in natural waters depends upon CaF_2 solubility product which, in turn, is affected by formation of ionic complexes and the strength of these complexes in water (Srivastava et al., 1996). As such, in limestones

of chemical origin, co-precipitation of CaF_2 and CaCO_3 is the major process, which controls the fluorine distribution in the rocks. The fluorine content of marine anhydrite is solely due to precipitation of CaF_2 (Schneider, 1953 & 1954; Kruger, 1962 a, b, c). Small amount of isokite (CaMgFPO_4) and wagnerite (Mg_2FPO_4) were found in carbonate rocks, by Braitsch (1960 & 1962).

Therefore, it appears that the average fluorine content of non-marine sediments should be lower than sediments of marine origin. Studies by Bloxam and Thomas (1969/ 1970) have shown that the fluorine content of near-shore sediments is significantly lower than the fluorine content in off-shore marine sediments. Since the fluorine content in the sediments is also influenced by several other factors, it cannot be used as an indicator of marine origin or otherwise.

FLUORINE IN NATURAL WATERS

During weathering and circulation of water in rocks and soils, fluorine can be leached out and dissolved in ground water. The fluorine content of ground water varies greatly (0 to 35 ppm) depending on the type of rocks from which they originate (Bond, 1945; White et al., 1963; Kopf et al., 1968). In general, abundance of fluorine in fresh water varies between 0.25 to 1 ppm (Hawkes and Webb, 1962).

The fluorine content of the hot springs varies from 0.15 to 55.4 ppm (Gmelin, 1959; Matuura and Kokubu, 1955; Sugawara, 1967) and is seen to increase with increasing temperature, but the mol ratio of F/Cl remains

approximately constant. In India, hot springs (35° to 100° C) are mostly distributed along the major lineaments and rifts (Ravi Shanker, 1986). Their fluorine content varies from 10 to 17 ppm (Banerjee, 1967; Chowdhury et al., 1964; Chowdhury and Handa, 1973).

The fluoride content of surface water also varies greatly from 0 to 6.4 ppm, depending on the fluoride content of ground water feeding a given stream (Fleischer and Robinson, 1963). Fluorine content of rivers in humid regions varies from 0.058 to 0.25 ppm.

Fluorine content in lakes varies from 0 to 0.34 ppm. In permafrost regions, F content of lakes is proportional to dissolved organic matter and it varies from 0.16 to 0.34 ppm. In arid regions, it varies with the chemical class of lake, Na-lakes, being generally rich.

According to Bewers (1971), the mean concentration of fluorine in ocean water is 0.03 to 1.32 ppm, and is seen to increase with depth (Riley, 1965).

In rain water, fluorine may originate from the sea and mostly varies from 0 to 0.089 ppm, but near cities and industrial areas, values upto more than 1 ppm are reported (Bewers, 1971; Gmelin, 1959; Handa, 1977).

Solubility of fluorapatite ($\text{Ca}_5\text{F}(\text{PO}_4)_3$) and fluorite (CaF_2) in natural waters is very low (Appelo and Postma, 1993). Solubility and solubility product of fluorite, fluorapatite, chlorapatite and hydroxyapatite are calculated by many workers (Handa, 1977; Valyashko

et al., 1968; Strubel, 1965). The solubility product of fluorapatite at room temperature is lower than solubility product of hydroxy or chlorapatite. But, theoretically calculated values do not match with the experimental data (Valyashko et al., 1968). Similarly, the value of CaF_2 solubility product is also not very certain but, the value of 'K' as $10^{-10.57}$, given by Handa (1977) is commonly accepted. In natural waters, however, on account of the ionic strength of complex forming ions, the solubility of CaF_2 is drastically modified. Calcium and Sulphate ions significantly lower CaF_2 solubility in natural waters, often causing CaF_2 precipitation (Handa, 1977; Perel'man, 1977; Deshmukh et al., 1993). Under supergene environment, fluorides in natural waters get precipitated as CaF_2 , across calcium barrier (Perel'man, 1977). In ground water, the distribution of Ca and F is therefore, antipathetic (Handa, 1977; Viswanadham and Murty, 1977; Deshmukh et al., 1993; Srivastava et al., 1996). On the other hand, higher alkalinity in natural waters tends to increase fluoride solubility. It is for this reason that, despite higher average fluorine concentration in calcareous shales and limestones, the ground water hosted in such aquifers is relatively poor in its fluoride content (Kodate et al., 1996). In arid and semi-arid regions, the fluoride content of ground water is higher, compared to ground water from humid areas. This is probably due to higher TDS in ground water, resulting in increased ionic strength and consequently higher CaF_2 solubility in the ground water. In such cases, viscosity of the ground water would tend to increase and consequently, the yield of the wells would decrease (Deshmukh and Chakravarti, 1996).

BIOGEOCHEMISTRY OF FLUORINE

In very minute amounts, fluorine is essential for growth and maintenance of plants and vertebrates, including man. Fluorine content of plants, mostly cultivated plants, is generally low, except for tea, which contains upto 400 ppm fluorine (Marais, 1943). Fluorine content in fruits, seeds, stems, wood and bark is generally lower than the content in roots and leaves (Underwood, 1962). Similarly, sea-food contains significantly higher amounts of fluorine compared to fresh water food (Perelman, 1977). In different vegetables, fluorine content in leaves varies from 3-20 ppm, on dry matter basis. In vertebrates, on the ash basis, the fluorine content of the bones is much higher than the fluorine content of the soft tissues. The fluorine content in beef bones ash (cattle) varies from 150-1800 ppm (Oelschlager et al., 1967 a, b). Fluorine intake in plants is through atmosphere (by leaves) and through soil (by roots). In animals, including man, the fluorine ingestion is primarily from drinking water, but considerable amount of fluorides are also ingested through food and polluted atmosphere (Srikantia, 1977; Wakode et al., 1993; Batra et al., 1996). Elemental intake in plants, including fluorine, depends upon biochemical characteristics of plant species, the growth stage of the plant and distribution of the particular element in soil and atmosphere (Deshmukh and Pande, 1983; Pande et al., 1993). As such, the fluorine intake in plants, including food bearing plants, is widely different. Average fluorine content of different plants/plant parts growing in polluted and unpolluted environment is given in Table 3 (Oelschlager and Rheinwald, 1968).

It is observed that, fluorine content of food items grown in fluorosis endemic areas is anomalously high and therefore fluoride ingestion of the affected population, through food, is also significantly large (Wakode et al., 1993; Jyothi Kumari et al., 1996). It is observed that, fluorine intake in jowar (*Sorghum vulgare*), wheat (*Triticum aestivum*), rice (*Oryza sativa*), red gram dal (*Cajanus cajan*) and red chillies (*Capsicum annuum*) is in proportion to the fluorine distribution in their rooting media (Batra et al., 1996; Jyothi Kumari et al., 1996). The average Fluorine Partition Factor (F food/F soil) is highest in dry red chillies (15.76) and is followed by Fluorine Partition Factor in red gram dal (5.319), jowar (3.616), wheat (2.437) and rice (2.40). In human beings, the safe limit of fluorine ingestion is very narrow. Fluorine ingestion from all sources below 2.75 mg/day in adults leads to dental caries while, above 7.75 mg F/day results in various types of fluorosis. It is known that, excessive fluorine ingestion also affects energy cycle (Rao, 1977). Similarly, excessive fluorine in low doses destroys teeth enamel, leading to dental caries while, in very large doses, results in osteosclerosis. It is suggested that, in jowar eating population of fluorosis endemic areas, fluorine ingestion is higher compared to either wheat-or rice-eating subjects, with higher degree of fluoride retention in the former (Srikantia, 1977). It is suggested that due to higher molybdenum content in jowar, compared to wheat or rice, the fluorine retention is enhanced (Deosthale and Gopalan, 1974; Deosthale et al., 1977). Average fluoride contents of some common cereals/millets and pulses cultivated in fluorosis endemic villages of Chandrapur district of Maharashtra are given in Table 4.

**TABLE 3
AVERAGE FLUORINE CONTENT OF PLANTS & ANIMALS FROM
AREAS WITH EMISSION OF FLUORINE
(Oelschlager et al., 1968)**

Fluorine emitting source	Sample	Average ppm F (dry wt.) polluted	Average ppm F (dry wt.) unpolluted
Industrial area, Weisweiler/Germany	beet leaves	19.00	8.30
	grass	15.00	6.80
	red clover	20.00	6.70
City area, Mannheim/Germany	digitalis lanata	31.00	8.00
Brickyard, Baden/Germany	pine needles 1 & 2 years old	53.90	3.30
Brickyard, Rheinland/Germany	pine needles 1 year old	37.30	3.30
Glass Factory, Baden/Germany	beet leaves	40.00	8.30
	red clover	46.00	6.70
	pine needles	85.00	3.30
Glass Factory, Wurttemberg/Germany	hornbeam leaves	2585.00	10.00
Enamel Factory, Wurttemberg/Germany	red clover unwashed	1503.00	6.70
	red clover washed	101.00	6.70
Enamel Factory, Wurttemberg/Germany	linden leaves	317.00	14.20
	horse chestnut leaves	408.00	19.20
	maple leaves	211.00	7.00
	copper beech leaves	316.00	10.60
	hornbeam leaves	58.00	10.00

(Table 3 contd.....)

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(Table 3 contd

Fluorine emitting source	Sample	Average ppm F (dry wt.)	
		polluted	unpolluted
Aluminium Smelting Furnace, Baden/Germany	meadowgrass & hay	38.50	6.80
	pelvis bone (cattle)	2730.00	150-1800 (Ash)
	bones (cattle)	5724.00	150-1800 (Ash)
Aluminium Smelting Furnace, France	vine leaves	1733.00	11.90
	rib (cattle)	11300.00	150-1800 (Ash)
	pelvis bone (cattle)	10700.00	150-1800 (Ash)
Aluminium Smelting Furnace, Westfalen/Germany (cattle)	tail vertebra	7085.00	150-1800 (Ash)
	back vertebra	7848.00	150-1800 (Ash)
Hydrofluoric acid Factory, Wurttemberg /Germany	hay	179.00	6.80
	clover	252.00	6.70
	grass	148.00	6.80
	summer barley	157.00	—
	apple leaves	1582.00	19.70
	pear leaves	1189.00	19.80
	pear fruits	10.70	0.70
	strawberry leaves	232.00	2.30
	strawberry fruits	22.00	2.40
	red currant leaves	120.00	13.90
Hydrofluoric Acid Factory, Lower Saxony/Germany	red currant fruits	15.00	2.30
	sweet cherry leaves	934.00	4.90
	sweet cherry fruits	20.00	3.60

TABLE 4
AVERAGE FLUORIDE CONTENTS OF SOME COMMON FOODSTUFFS
FROM FLUOROSIS ENDEMIC VILLAGES OF CHANDRAPUR DISTRICT

Foodstuffs	Avg. F mg/100 gm live wt.	n	References
Wheat	6.789	10	Batra et al., (1996) Ashlesha et al., (1996) Jyothi Kumari et al., (1996)
Rice	5.078	10	—do—
Jowar	8.835	10	—do—
Red Gram Dal	14.42	6	Ashlesha et al., (1996) Jyothi Kumari et al., (1996)
Red Chillies	34.50	6	—do—

Excessive fluorine ingestion in human population results in development of dental fluorosis when exposure is at a low level and skeletal fluorosis when fluorine exposure is critically high. The incidence of fluorosis is higher in tropical and subtropical countries, probably on account of higher drinking water consumption (Srikantia, 1977). It is observed that, in adults, exposed to high fluoride ingestion, the hydroxyl bonds of the hydroxy apatite material in bone are partly replaced by fluorides. The authors surmise that biochemically the body's defensive mechanism, in order to immobilize fluorine from the circulating mobile phase in the body, (blood and cellular fluids), fixes excess fluorides into hydroxy apatite material of the bone by replacement of OH by F (Teotia and Teotia, 1992) irreversibly

till the exposure continues. In the process, the rate of synthesis of bone material (hydroxyapatite) is considerably increased leading to excessive bone formation or Osteosclerosis, a basic symptom of subjects suffering from skeletal fluorosis. It is also observed that in children (2 to 12 years) and adolescents (12-21 years) the impact of excessive fluoride ingestion is significantly milder. The rapid skeletal growth in this age group, probably helps in immobilizing a major part of the excessive fluorine by fixing the halogen in-growing bones by fluoride (F) replacement of OH sites in hydroxy-apatite bone material. It also explains why children and adolescents are affected by dental fluorosis and not by skeletal fluorosis, despite large excessive fluorine ingestion (Kodate et al., 1996; Ashlesha et al., 1996).

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