

Full Length Research Paper

# Fluoride distribution in different environmental segments at Hirakud Orissa (India)

P. C. Mishra<sup>1\*</sup>, Kumarmani Meher<sup>2</sup>, Dullav Bhosagar<sup>2</sup> and K. Pradhan<sup>3</sup>

<sup>1</sup>P.G. Department of Environmental Sciences, Sambalpur University, Jyoti Vihar-768019, Orissa, India.

<sup>2</sup>Rajib Gandhi National Fellow, India.

<sup>3</sup>Environment Engineer, NTPC, Kaniha, Talcher, Orissa, India

Accepted 10 August, 2018

Fluoride is a major pollutant originating from aluminium smelting polluting the air, water and soil. An Aluminium smelter has been operating at Hirakud in western Orissa since 1958 producing primary aluminium by Horizontal stud Soderberg Technology. Starting with a capacity of 10,000 T of aluminium per annum in 1959 it has increased its capacity to 1,00,000 T in 2007. A detailed investigation undertaken during 2005 - 2006 on fluoride status of Hirakud environment reveals that the fluoride content varied from a minimum of 0.5 to a maximum of 0.65 (ppm) in pond water, 0.4 - 0.60 mg/L in ground water, 88.30 - 191.20 in soil, 23.75 - 65.96 in paddy straw, 15.60 - 70.36 in grass and 10.00 - 44.60 in leaf tissue. The level of bioconcentration of fluoride in relation to surface water ranged from 79.30 in vegetation to 304.21 in leaf tissues.

**Key words:** Fluoride, water, soil, vegetation, bioconcentration.

## INTRODUCTION

Whatever may be the source of fluoride in the environment, it passes to and from air, water and soil and living organisms through some biochemical pathways and ultimately reaches the higher trophic levels (Figure 1). The excess accumulation of fluorides in vegetation leads to visible leaf injury, damage to fruits, changes in the yield (Moeri, 1980; Anil and Bhaskara, 2008). Hirakud Smelter, a unit of Hindalco is operating at Hirakud town of western Orissa since 1958 producing primary aluminium by Horizontal stud Soderberg Technology. Starting with a capacity of 10,000 T of aluminium per annum in 1959. It has increased its capacity to 30,000 T in 1996 - 1997, 65,000 T in 2003 and 100000 T in 2007. Fluoride is a major pollutant in Aluminium smelter polluting the air, water and soil. A study conducted in 1996 by the senior author revealed a fluoride levels of 0.12 - 0.34 ppm in ground water, 0.13 - 0.87 ppm in surface water, 76.99 - 359.0 ppm in soil, 25 ppm in leaf tissue with a concentration factor from 260 - 941 in surface soil, 160 - 605 in deeper soil (>10 cm), 5 - 150 in herbaceous vegetation and 5 - 260 in leaf samples of perennial trees from surface water fluoride content (Mishra et al., 1998).

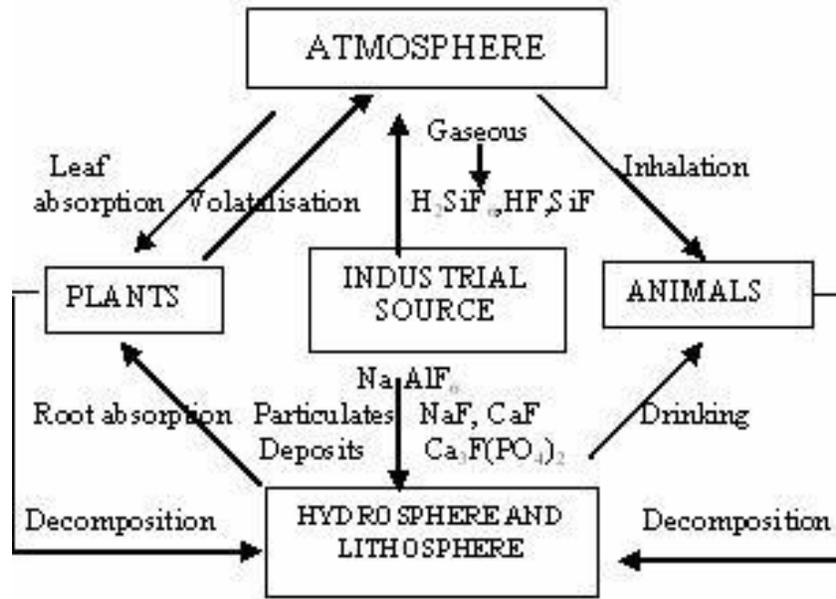
Mishra and Pradhan (2008) have reported the prevalence of fluorosis among the cattle population of Hirakud. Presently the capacity of the Smelter has increased by 300% with more emission of Fluoride to the environment. The present study is a part of the comprehensive research project to assess the environmental status of Hirakud urban ecosystems with reference to Aluminium Smelter and Thermal Power Plant. Here an attempt has been made to evaluate the extent of fluoride content in Hirakud environment in order to develop appropriate management strategy to contain it.

## MATERIALS AND METHODS

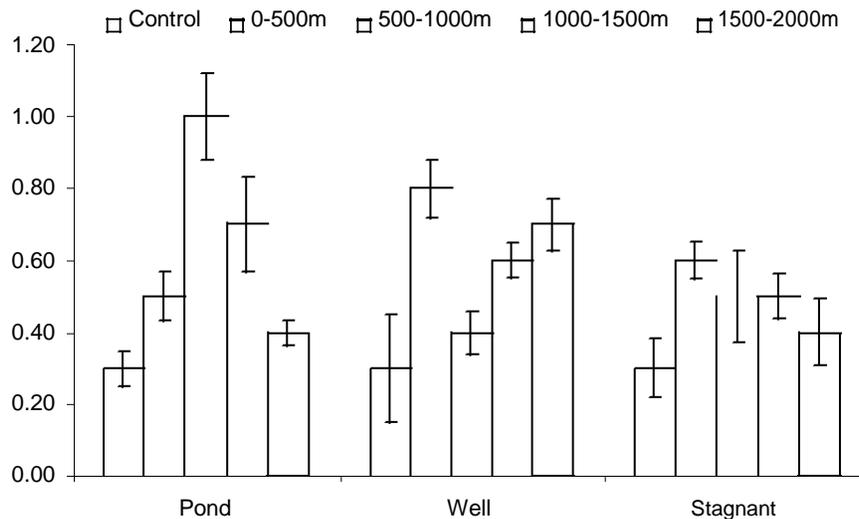
### Study site and sampling

Study site, a small industrial town at the base of famous Hirakud reservoir, is located at 15 km distance from Sambalpur University campus (Latitude 20. 21° N, Longitude 80.55° E and Altitud e 178.8 m). Sixteen sampling sites were selected around the smelter and power plants that is four at each direction (East, West, North and South) at a radius of 500, 1000, 1500 and 2000 m. Samples were collected in three seasons in a year. Sample collections were made during morning hours from 6.0 - 10.0 am and brought to the laboratory of P.G. Department of Environmental Sciences at Sambalpur University, located at 15 km road distance from the ex-

\*Corresponding author. E-mail: [pcm\\_envsu@rediffmail.com](mailto:pcm_envsu@rediffmail.com).



**Figure 1.** Fluoride cycle in the environment (Dash and Mishra 2001).



**Figure 2.** Variation in fluoride (mg/l) content in water in control and experimental sites (Mean  $\pm$  SD).

perimental study site, for analysis. The control site is located near the Laboratory. A control site at an air distance of 5 Km was selected for sampling. Fluoride in water was analyzed by Ion-analyzer (Model Orion, USA). For vegetation, animal and bone samples, analyses were performed after appropriate digestion. Two ways analysis of Variance was performed as per Snedecor and Cochran (1967) to find out the significant difference in fluoride level between the sources as well as the sampling locations (distance from pollution source). As there was no significant variation between seasons, the average values of all three seasons (summer, winter and rainy) have been presented in the result.

## RESULTS AND DISCUSSION

### Fluoride in water

The variations in fluoride content in control as well as the experimental in different types of water are presented in Figure 2. In experimental sites the average fluoride content varied from 0.50 in stagnant water to a maximum of 0.65 in pond water. However, the test of analysis of

variance indicated no significant difference in fluoride content between the water types as well as between the distances from the pollution source. Fluoride levels in surface water varies according to geographical location and proximity to emission sources. Surface water concentrations generally range from 0.01 - 0.3 ppm. Seawater contains more fluoride than fresh water, with concentrations ranging from 1.2 - 1.5 mg/l. Higher levels of fluoride have been reported in areas where the natural rock is rich in fluoride and near industrial outfalls (Harbo et al., 1974). Anthropogenic sources can also lead to increased local levels of fluoride. Harbo et al. (1974) found increased concentrations of fluoride in the surface waters of Kitimat Harbour, Canada in the vicinity of a large smelter. Zingde and Mandalia (1988) found a fluoride levels below 0.3 ppm in unpolluted surface waters. However, levels were higher close to a plant manufacturing fluoride chemical in India. In water, the transport and transformation of inorganic fluorides are influenced by pH, water hardness and the presence of ion exchange materials such as clays (Environment Canada, 1994).

### **Fluoride in soil**

Minerals are the major source of fluoride. Soil receives fluoride-contaminated minerals from the environment. Fluorides can cause many damaging effects not only to human beings but also to animals, aquatic organisms and vegetation. The variations in fluoride content in soil collected from both control and experimental sites are presented in Figure 3. The soil fluoride content in control site ranged from a minimum of 112.35 in crop field to a maximum of 138.70 ppm in fallow land soil. In Hiraakud Township, the fallow land soil showed a lower average fluoride content of 127.85 to a maximum of 139.35 ppm in crop field soils. The analysis of variance did not reveal any significant difference in fluoride content in both the type of soil and as well the distances.

Factors that influence the mobility of inorganic fluorides in soil are pH and the formation of stable aluminium and calcium complexes (Pickering, 1985). In more acidic soils, concentrations of inorganic fluoride were considerably higher in the deeper horizons. The low affinity of fluorides for organic material results in leaching from the more acidic surface horizon and increased retention by clay minerals and silts in the more alkaline deeper horizons (Davison, 1983; Kabata-Pendias and Pendias, 1984). This distribution profile is not observed in either alkaline or saline soils (Gilpin and Johnson, 1980; Davison, 1983). The fate of inorganic fluorides released to soil also depends on the chemical form, rate of deposition, soil chemistry and climate (Davison, 1983).

Pickering et al. (1988) determined changes in free fluoride ions and total fluoride levels in materials that had different cation-exchange capacities, such as synthetic

resins, clay minerals, manganese oxide and a humic acid. Increased amounts of fluoride were released from fluoride salts and fluoride-rich wastes when solids capable of exchanging cations were present. The effect was greatest when there were more exchange sites available and when the fluoride compound cation had greater affinity for the exchange material.

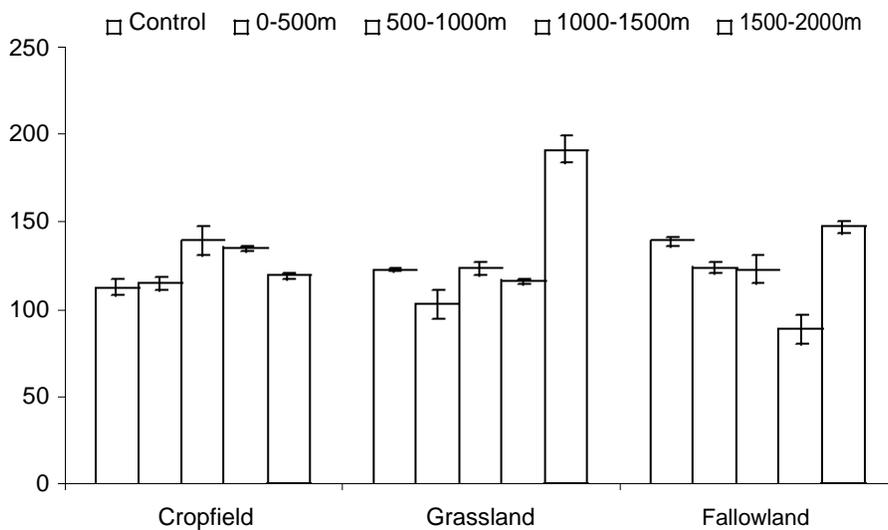
In sandy acidic soils, fluoride tends to be present in water-soluble forms. Street and Elwali (1983) determined the activity of the fluoride ion in acid sandy soils that had been limed. Fluorite was shown to be the solid phase controlling fluoride ion activity in soils between pH 5.5 and 7.0. At pH values below 5.0, the fluoride ion activity indicated super-saturation with respect to fluorite. These data indicate that liming of acid soils may precipitate fluorite, with a subsequent reduction in the concentration of fluoride ion in solution. Murray (1984) reported that low amounts of fluoride were leached from a highly disturbed sandy podzol soil of no distinct structure. Even at high fluoride application rates (3.2 - 80 g per soil column of diameter 0.1 m with a depth of 2 m), only 2.6 - 4.6% of the fluoride applied was leached in the water-soluble form. The pH of the elute increased with increasing fluoride application, and this was probably due to adsorption of fluoride, releasing hydroxide ions from the soil metal hydroxides. Over time, the concentration of water-soluble fluoride decreased due to increased adsorption on soil particles. Mean soil concentrations in Pennsylvania, USA, were 377, 0.38 and 21.7 ppm for total fluoride, water-soluble fluoride and resin exchangeable fluoride, respectively. Fluoride is relatively immobile in soil, since most of the fluoride was not readily soluble or exchangeable (Gilpin and Johnson, 1980).

### **Fluoride in vegetation**

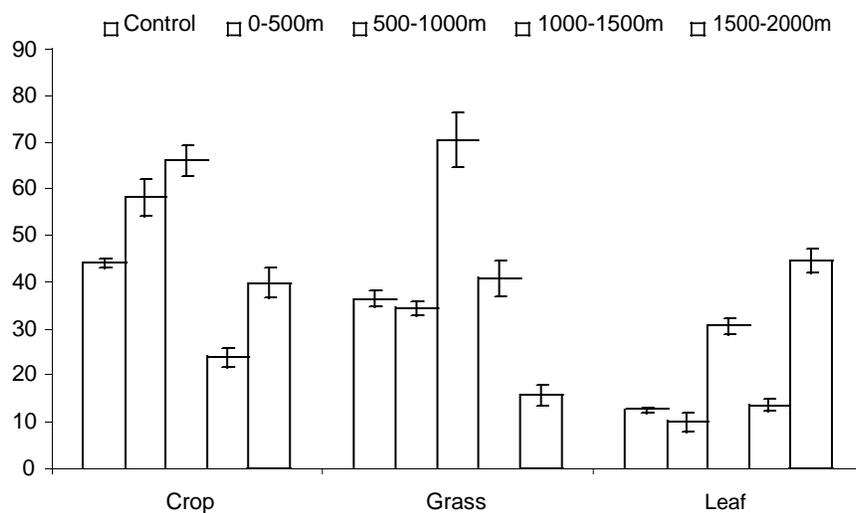
The fluoride content in vegetation (leaf, grass and crop) varied from a minimum of 12.60 mg/kg in plant leaf to a maximum of 43.90 mg/kg in the rice crop vegetations in control site. In experimental sites, the variation was from a minimum of 29.48 in tree leaf to a maximum of 60.90 in crop vegetation (Figure 4). Test of ANOVA shows no significant difference in fluoride content between different vegetation as well as the different distances.

### **Conclusion**

The significance of fluoride in water has always been subject of debate. Where as an intake of fluoride in less quantity (less than 1 ppm) is known to be beneficial for human health in preventing dental caries, high fluoride concentration in water causes dental and skeletal fluorosis. The prescribed norm for fluoride limit in water is 0.8 - 1.5 mg/L. Although the Aluminium smelter in Hiraakud is in operation since last 45 years, the level of fluoride in



**Figure 3.** Variation in fluoride (mg/kg) content in Crop field, Grassland and Fallow land in control and experimental



**Figure 4.** Variation in fluoride (mg/kg) content in Crop, Grass and Leaf samples in control and experimental site (Mean  $\pm$  SD).

water has not crossed the limit giving an indication of their management to control fluoride emission. However, if the values in soil and leaf samples are taken into consideration, the level of bioconcentration of fluoride in relation to surface water ranged from 79.30 in crop and grass to 304.21 in leaf tissues. Fluoride has a tendency to cycle in the environment, which also includes the animals and human beings, thereby causing toxicity in them (Das et al., 1994; Teotia et al., 1998; Susheela et al., 2005). A survey on the prevalence of fluorosis among school children and cattle in Hirakud reveals that there is teeth mottling in few cases of children and tooth abrasions and soiling among cattle of Hirakud to a limited extent

(Mishra and Pradhan, 2008). Unfortunately there is no Indian standard available prescribing a limit to the fluoride in soil and biological tissue. Although around 95% of the fluoride deposited in soil surface is not available for plant uptake because of its conversion to unavailable form, but the plant leaves getting fluoride directly from atmospheric fall is of more concern because of the grazing of animals and ultimately use of animal milk by human beings.

### Recommendations

Present study shows elevated level of fluoride in vegeta-

tion and soil samples of Hirakud Environment. Therefore it is high time for the Statutory Bodies to prescribe a standard/limit of fluoride in soil and biological tissues in industrial environment. In addition to this the various authorities operating in the industrial environment should adopt some management strategies to reduce the additional fluoride intake by the people. Some of the activities may include:

- 1.) Avoid/minimize fluoride containing tooth paste.
- 2.) Avoid/minimize tea-leaf as it contains high fluoride content.
- 3.) Avoid/minimize outside grazing of cattle.
- 4.) Appointment of specialized doctors in hospitals for diagnosis and treatment of fluoride related diseases in human beings and animals.
- 5.) Provision of fluoride free drinking water to the community.
- 6.) Education and Awareness among all sections of people on the positive and negative impacts of fluoride.

Such simple planning and strategies may go a long way to minimize the impact of fluoride generated from the anthropogenic source on animal and human beings.

## ACKNOWLEDGEMENTS

The authors are thankful to the Head, P.G. Department of Environmental Sciences, Sambalpur University for providing laboratory facilities. The instrument facilities provided by the Govt. of India, Department of Science and Technology in form of FIST grant and the financial assistance provided by Hindalco Industries Limited, Hirakud to the senior author in the form of a research project is gratefully acknowledged.

## REFERENCES

- Anil KK, Bhaskara RAV (2008). Physiological responses to Fluoride in two cultivars of Mulberry. *World J. Agric. Sci.* 4(4): 463-466.
- Dash MC, Mishra PC (2001). *Man and Environ.* Macmillan India Limited. Chennai: 293 pp.
- Das TK, Susheela AK, Gupta IP, Dasarathy S, Tandon PK (1994). Gastrointestinal manifestations in patients with skeletal Fluorosis. *J. Gastroenterol.* 31:333-337.
- Davison A (1983). Uptake, transport and accumulation of soil and airborne fluorides by vegetation. In: Shupe J, Peterson H, and Leone N ed. *Fluorides: Effects on vegetation, animals and humans.* Salt Lake City, Utah, Paragon Press, pp. 61-82.
- Gilpin L, Johnson A (1980). Fluorine in Agric. soils of southeastern Pennsylvania. *Soil Sci. Soc. Am J.* 44: 255-258.
- Harbo RM, Comas FT, Thompson JAJ (1974). Fluoride concentration in two Pacific coast inlets — an indication of industrial contamination. *J. Fish Res. Board Can.* 31: 1151-1154.
- Kabata-Pendias A, Pendias H (1984). Fluorine. In: *Trace elements in soil and plants.* Boca Raton, Florida, CRC Press, pp. 209-215.
- Mishra PC, Pradhan K (2008). Prevalence of fluorosis among school children and cattle population in Hirakud town of Orissa. *Bioscan* 2(10): 31-36.
- Mishra PC, Rath SP, Sarangi PK (1998). Bioaccumulation and Bioconcentration of Fluoride in Environ. segments of Hirakud. *Indian J. Environ. Prot.* 18(3): 15-19.
- Moeri PB (1980). Effect of fluoride emission in enzyme activity in metabolism of Agric plants. *Fluoride* 13 : 122-128.
- Murray F (1984). Fluoride retention in highly leached disturbed soils. *Environ. Pollut. B7:* 83-95.
- Pickering WF (1985). The mobility of soluble fluoride in soils. *Environ. Pollut. B9:* 281-308.
- Pickering WF, Slavek J, Waller P (1988). The effect of ion exchange on the solubility of fluoride compounds. *Water Air Soil Pollut.* 39: 323-336.
- Snedecor GW, Cochran W G (1967). *Statistical Methods.* Oxford and IBH, Calcutta
- Susheela AK, Bhatnagar M, Vig A, Mondal NK (2005). Excess fluoride ingestion and Thyroid hormone derangements in children living in Delhi, India. *Fluoride.* 38(2) 151-161
- Street JJ, Elwali AMO (1983). Fluorite solubility in limed acid sandy soils. *Soil Sci Soc Am J.* 47(3): 483-485.
- Teotia M, Teotia SPS, Singh KP (1998). Endemic chronic fluoride toxicity and dietary calcium deficiency interaction syndromes of bone disease and deformities in India. *Indian J. Pediatric.* 65