FLUORIDE DEPOSITION ON SOILS LOCATED IN THE SURROUNDINGS OF AN ALUMINIUM SMELTER PLANT IN RENUKUT, UTTER PRADESH, INDIA.

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Abstract: The purpose of this investigation was to determine the fluoride content in soils, located in the vicinity of the aluminium plant in Renukoot district Sonbhadra are polluted with fluoride. For this purpose 30 soil samples of cultivated soil were collected from depths (0 to 15 cm). Total and available fluorine were determined by potentiometric method, after necessary preparations of soil samples for analysis. It was found that in almost all soil samples content total fluorine was above 300 mg/kg – maximum permissible value for the content of this element in agricultural soils. Highest values were found on locations Kharpatthar of the aluminium plant. However, the content of available fluorine (soluble in water) in the soil samples in average value is 6.20 mg/kg 6.20 indicating that major part of deposited fluoride had transformed itself into insoluble compounds like CaF_2

Keywords: **Fluoride deposition, Total Fluoride, Hot water fluoride, Aluminum Plant**

I. INTRODUCTION:

The content of total fluorine in normal soils is usually in the range from 150 to 400 mg/kg. Values that exceed 1000 mg/kg have been registered in some heavy clayey soils. Fluorine is usually present in soils in the form of the following minerals: fluorite - CaF_2; fluoroapatite - Ca10 $(PO_4)6F_2$; cryolite - Na_3AlF_6. These minerals are sparingly soluble in water, so that only small amounts of F are taken up by plants. Artificial sources of soil pollution with fluorine are: aluminium smelters, phosphorus fertilizer factories, ceramic and glass industry, combustion of coal. This halogen element is also introduced into soil through the application of phosphorus fertilizers, sewage sludges and some pesticides.

Fluorides are released into the environment naturally through the weathering of minerals, in emissions from volcanoes and in marine aerosols Symonds *et al.* (1988). The main natural source of inorganic fluorides in soil is the parent rock (WHO, 1984). During weathering, some fluoride minerals (e.g., cryolite or Na_3AlF_6) are rapidly broken down, especially under acidic conditions (Fuge and Andrews, 1988). Other minerals, such as fluorapatite [Ca_5 $(PO4)_3F$] and calcium fluoride, are dissolved more slowly (Kabata-Pendias and Pendias, 1984). The mineral fluorophlogopite (mica; KMg_3 $[AlSi_3O_{10})$ $F^2]$ is stable in alkaline and calcareous soils (Elrashidi and Lindsay,1986). However, its solubility is affected by pH and the activities of silicic acid (H_4SiO_4) and aluminium ($Al^{3+),}$ potassium (K^+) and magnesium (Mg^{2+}) ions. The most important natural source of inorganic fluorides in the environment is bedrock, from which inorganic fluoride containing minerals are leached by ground water, and then into surface and sea-water. Another major natural source of inorganic fluorides is volcanoes which release gases and ash into the atmosphere either by explosive eruptions or by continual low energy release (Kawaratani and Fujita 1990). The average fluoride content of most soils world-wide has been documented as 329 ppm (Kabata- Pendias *et al.*, 1992). In general, the lowest F contents are found in sandy soils in humid climate, whereas higher F concentrations occur in heavy clay soils and in soils from weathered mafic rocks (Fuge and Andrews, 1988).

Anthropogenic sources of fluoride into the environment include the following: the industrial production and use of chemicals such as, hydrogen fluoride (HF), calcium fluoride (CaF_2), sodium fluoride (NaF), fluorosilicic acid (H_2SiF_6), sodium hex fluorosilicate (Na_2SiF_6), sulfur hexafluoride (SF_6), and phosphate fertilizers (Weas, 1986). Phosphate fertilizers are the major source of fluoride contamination of agricultural soils. They are manufactured from rock phosphates, which generally contain around 3.5% fluorine (Hart *et al.,* 1934).Soil contamination by atmospheric fluorides was studied in the vicinity of an alumina production plant. Samples were collected at depths of 0-5, 5-15 and 15-30 cm. Natural vegetation fluoride levels were used to determine areas of relatively high and low airborne fluoride impact, and soil sampling locations within these respective areas were segregated accordingly. Soil samples were analyzed for total and water-extractable F. Both measurements, especially the water-extractable fraction, reflected the gradient of F exposure. The F concentration in the soil solution exhibited a similar dependence upon distance from the emission source. Total soil fluoride decreased with depth at high impact sites, but increased with depth at

low fluoride impact sites. The water-extractable F concentration increased systematically and significantly with depth at high impact areas. Total soil fluoride for all depths decreased with distance from the emission source and approximated to background levels at about 20 km. (Haidouti. 1991)

The fluoride is a major pollutant originating from aluminum smelting polluting the air, water and soil. An Aluminum smelter has been operating at Hirakud in western Orissa since 1958 producing primary aluminum by horizontal Soderberg Technology. Starting with a capacity of 10,000 T of aluminums per annum in 1959 it has increased its capacity to 1, 00,000 T in 2007. A detailed investigation (Mishra *et al.*, 2009) 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 bio concentration of fluoride in relation to surface water ranged from 79.30 in vegetation to 304.21 in leaf tissues.

II. MATERIAL AND METHODS:

GEOGRAPHICAL LOCATION STUDY AREA

Sonbhadra is the largest district of Uttar Pradesh. It lies to the extreme South Eastern part of the state, It has geographical area 6788.0 sq. km, average height from sea level 285 feet, average, rainfall 1036.6 mm and temperatures in summer 10-45^{0}C in winter 8-25 ^{0}C. Renukut is located at 24°12' of Northern latitude and 83°02' Eastern latitude. It has an average elevation of 283 meters (931 feet). Rain starts around third week of June. Renukut is 1,400 feet above sea level, with nearby hills exceeding 2000 feet. Renukut has the largest integrated Aluminum plant in Asia. Renukut lies in one of the most important Industrial belts of India constituting of cement factories, aluminum industry, chemical Industries, hydel power projects, thermal power projects. To name a few there exists HINDALCO India's largest aluminum company, and then in the same belt around some 40 km away is India largest NTPC plant. Fig. 1 Location map of the study area.

COLLECTION, PROCESSING OF SOIL SAMPLES

Representative soil samples were taken from a network of circle position of which, in relation to aluminum smelter plant, is presented in figure 1. The sampling points in each village were selected on the basis of flat terrain agricultural land and far from major roads. Soil samples from 30 locations were collected at the depth of 0–15 cm of the surface soil. The sampling sites fall within 10 km circle of the Aluminium plant. All the soils were air dried, grounded and passed through 2 mm sieve prior to analysis.

ANALYSIS OF FLUORIDE

The total soil fluoride was determined by using alkali fusion-Ion selective technique (Mc Quaker and Gurney 1977). Approx. 0.5 g of the dried (105^{0}C), grounded and sieved through 100 mesh sieve, was taken in a 130 mL nickel crucible and, the sample was moistened slightly with distilled water. Then 6 mL of 17 N NaOH was added to it. The crucible was tapped slightly to mix the content and placed in oven at 150^{0}C for 1 h. After the sodium hydroxide solidified, it was placed in the muffle furnace at 300^{0}C. The temperature was raised to 600^{0}C and kept for 30 min. Then the crucible was removed from the furnace and cooled, 10 mL of distilled water was added and heated slightly to dissolve NaOH cake. After cooling, about 8 mL of conc. HCl was added slowly by stirring to adjust the pH 8-9. The content was then transferred to 100 mL volumetric flask, diluted to the volume and filtered through Whatman 40 filter paper. To the 5 mL of the above extract, 5 mL of TISAB (58 mL glacial acetic acid + 12 g Sodium Citrate dihydrate in 1 L distilled water adjusted at the pH 5.2 by using 6 N NaOH) was added and mixed, and the fluoride measurement was done by fluoride ion selective electrode using ORION 5 Star ion analyzer.The detection limit of method (LOD) was 0.05 mg/L.

For the determination of soluble fluoride in the soil, an extract was made (1:1) using distilled water (Brewer 1965). To 25 mL of the extract, 25 mL of the TISAB (4 g CDTA + 58 g NaCl and 57 mL glacial CH3COOH in 1 litre of distilled water adjusted to pH 5–5.5 by 6 N NaOH) was added and the fluoride concentration in the extract was measured by fluoride ion selective electrode using ORION 5 Star ion analyzer. The detection limit of method (LOD) was 0.03 mg/L. All the soil fluoride was calculated on dry weight basis. The village-wise mean and standard deviations (SD) were computed. The pH of the soil was determined by taking 20 g of the soil sample into 40 mL of distilled water. Measurement was done by ORION 5 Star Analyser.

III. RESULTS AND DISCUSSION

An examination of the data revealed that the mean value of hot water and total fluoride in the soils of Sonbhadra district were 6.20 and 3217 mg kg^{-1} with ranges from 1.24-29.9 mg kg^{-1}and 835-8008 mg kg^{-1}, respectively. The highest plant available form of fluoride was noticed in Shaudhi village and total fluoride was noticed in Kharpatthar. The ratio of F (NaOH)/F (H_2O) extractable fluoride in was found 513.8 i.e. to is high due to F containing minerals are present obviously higher quantity in soil investigated area. Data on fluoride content in soil was represented in Table1 and fig.2 and Fig. 3 In soils generally fluoride is associated with mica and other clay minerals (WHO, 1984). The natural F content of soils depends upon its type, depth, texture and pH. Heavy textured soils contain higher concentration of F than coarse textured soils. In the Yamuna alluvial plains of India, F content ranged from 43 to 193 ppm in coarse textured soils, and from 248 to 1500 ppm in heavy textured soils. In India, water soluble fluoride in Madhya Pradesh ranged from 8.50 to 153.5 mg/kg (Ramteke, 2007). In the state of Rajasthan from the fluoride toxic regions, the water soluble fluoride ranges 27 to 129 mg/kg (Madhavan and Subram Subramaniam, 2002) The soluble F^- ranged from 22.6 to 99.1 mg/kg in Unnao district of Uttar Pradesh. Thus, in comparison with the other states and different

districts in the Uttar Pradesh, water soluble fluoride in shonbhadra districts, was noticed low. Moreover, maximum permissible value for the total F content in agricultural soils is 300 mg/kg (Blagojević et al., 2002). All the investigated soil samples in Sonbhadra district have values for total fluorine above maximum permissible limit (300 mg kg^{-1}). These soils have naturally high contents of fluorine. The content of available fluorine (soluble in water) in the most of soil samples is mean values 6.97 ppm, indicating that major part of possible deposited fluorine through aluminium smelters of combustion of coal in Renukut, Sonbhadra district.

IV. CONCLUSION

From the results it's proved that the Most of the investigated soil samples have values for total fluorine above 300 mg/kg $^{-1}$ maximum permissible value for the content of this element in agricultural soils. These soils have naturally high contents of fluoride. Highest values were found on locations within Near of the aluminum plant, indicating the existence of artificial pollution of these soils with fluodine. The content of available fluorine (soluble in water) in the most of soil samples is low (mean values 6.97 ppm) compare to total fluoride , indicating that major part of possible deposited fluorine through aluminium smelters of combustion of coal in Renukut, Sonbhadra district had transformed itself into insoluble compounds like CaF2.

V. REFERENCES

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Table: 1 Fluoride distribution in the Soils of Renukut

S. No	Location		pH	EC	O M	Hot Water fluoride	Total fluoride
					%	mgkg^{-1}	
1	Patritola	N 24^0 07.156 'E 83^0 0.941'	7.1	1.190	11.40	2.42	1144
2	Myorpur	N 24^0 07.729 'E 83^0 0 .031'	7.2	0.752	2.40	4.80	928
3	Rajpahari	N 24^0 09.271 'E 8303.520'	6.9	0.328	1.80	7.08	4528
4	Labhari	N 24^0 12.491' E 8356.966'	7.4	0.452	3.96	5.20	2016
5	Balliary	N $24^0$07.080 'E 83^0 04.241'	5.9	0.521	2.06	1.84	5952
6	Balliary	N 24^0 07.404' E $83^0$03625'	7.1	0.325	1.94	1.48	2264
7	Patritola	N 24^0 07.094 'E $83^0$02.799'	5.4	0.840	2.52	5.94	4960
8	Balliary	N 24^0 07.524' E $83^0$03.423'	5.7	0.230	1.51	2.98	1536
9	Myorpur	N 24^0 06.923' E $83^0$09.555'	6.4	0.880	7.70	3.08	1736
10	Patritola	N 24^0 07.118 'E $83^0$02.741'	5.9	0.156	10.0	1.40	835

11	Navatola	N 24^0 06.690 'E 83^{0}04.839'	7.3	0.370	2.41	1.90	2112
12	Navatola	N 24^0 06.934 'E 83^{0}04.996'	5.2	0.440	8.00	8.08	1912
13	Navatola	N 24^0 06.729' E 83^{0}04.857'	7.0	0.136	2.13	5.12	928
14	Balliary	N 24^0 07.265 'E 83^{0}03.849'	8.5	0.284	2.08	5.72	1888
15	Rajpahari	N 24^0 08.523' E 83^{0}04.437'	5.2	0.140	2.28	5.24	960
16	Kharpatthar	N 24^{0}14.247' E 83^0 04.249'	7.2	0.786	2.28	10.36	8008
17	Makara	N 24^{0}12.787 'E 83^{0}57.719'	8.3	1.430	5.86	6.40	4608
18	Sidhwa	N 24^0 12.796 'E 83^{0}45.292'	6.5	0.156	4.03	4.20	5376
19	Sidhwa	N 24^0 12.803' E 83^{0}56.390'	5.7	0.147	5.17	1.24	1296
20	Bairpan	N 24^0 12.817 'E 83^{0}53.586'	7.0	0.760	3.48	7.13	1040
21	Hathwnia	N 24^0 16.056 'E 83^{0}05.785'	6.3	0.220	2.55	5.60	5704
22	Hathwnia	N 24^0 06.679 'E 83^{0}05 849'	7.1	0.744	2.26	6.78	1488
23	Shaudhi	N 24^0 16.257' E 83^{0}05.932'	6.1	0.282	6.06	29.9	5448
24	Shaudhi	N 24^0 16.049 'E 83^{0}05.795'	6.8	0.523	3.06	5.92	1648
25	Dhaulinala	N 24^0 14.498' E 83^{0}04.486'	6.4	0.402	3.86	5.20	1960
26	Dhaulinala	N 24^0 18.909' E 83^{0}06.813'	6.3	0.361	4.93	6.00	6144
27	Dhaulinala	N 24^0 13.418 'E 83^{0}04.347'	6.1	0.245	6.89	3.56	2480
28	Dhaulinala	N 24^0 13.022 'E 83^{0}04.588'	7.4	0.390	4.44	3.70	5704
29	Hathnia	N 24^0 15.086 'E 83^{0}04.849'	6.9	0.354	3.97	8.44	6464
30	Hathnia	N 24^0 19.196 'E 83^{0}09.101'	7.3	0.435	3.30	19.36	5448
		Range	5.2-8.5	0.136-0.143	0.151-11.40	1.24-29.9	835-8008
		Mean	6.65	0.480	4.14	6.20	3217
		S.D±.	0.82	0.27	2.52	5.66	2172
		C.V.	099	12.73	19.41	63.98	78.31

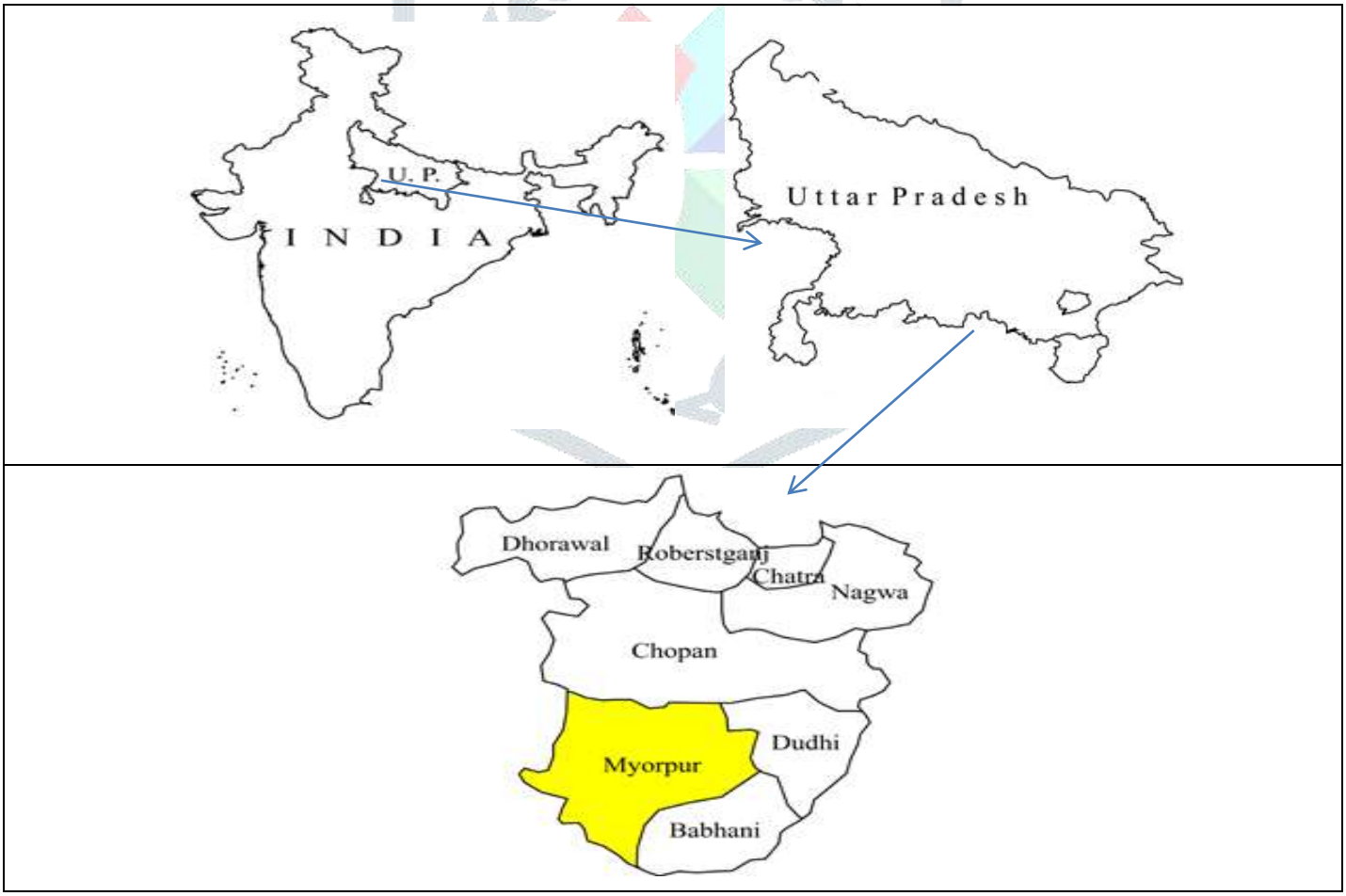

Figure 1 Location Map of Study Area

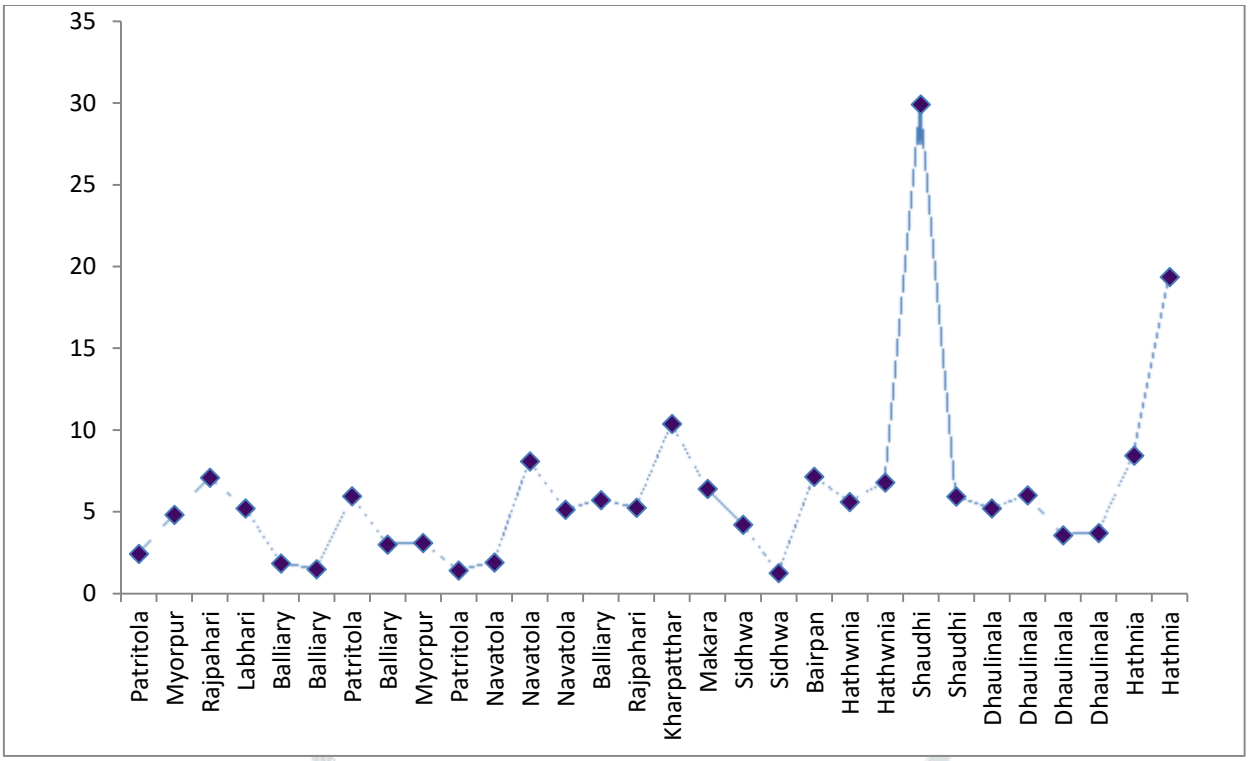

Figure: 2 Hot Water Extractable Fluoride in Soil around Hindustan Aluminum Plant at Renukut

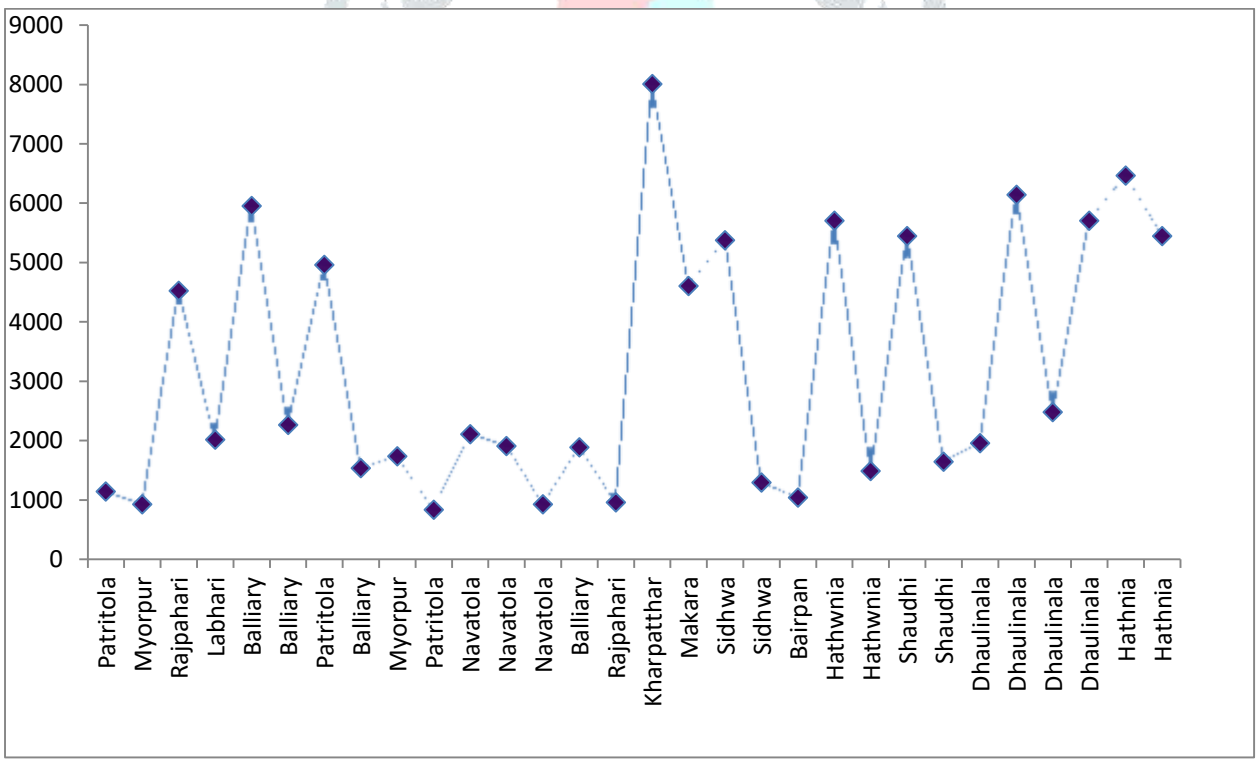

Figure: 3 Total Fluoride Distributions in Soil around Hindustan Aluminum Plant at Renukut