Fluoride Distribution in Aquatic Environment in Vicinity of Aluminum Industry and its Correlation with Rainwater Chemistry and Weather Parameter. A case study of Renukoot, District Sonbhadra, Uttar Pradesh

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Abstract:

7 Fluorine is a highly reactive element and readily hydrolyzes to form hydrogen fluoride and oxygen. 8 Hydrogen fluoride reacts with many materials both in the vapor phase and in aerosols. Fluorides are 9 naturally-occurring components of rocks and soil and are also found in air, water, plants, and animals. 10 Fluorine gas pollutes the atmospheric environment originating from aluminium smelting plant operating at 11 Renukoot, district Shonbhadra. Volcanic emissions also emit hydrogen fluoride. A detailed investigation 12 undertaken during 2008-2012 to objective fluoride Distribution in Aquatic Environment in Vicinity of 13 Aluminum Industry and its Correlation with Rainwater Chemistry and Weather Parameter. For this 14 investigation Collect 57 rainwater samples in rainy season in pre-cleaned and sterilized polyethylene 15 bottles of two litre capacity from roof of the local society of Hindustan Aluminum Company Renukoot, 16 district Sonbhadra. The collected samples were analyzed for pH, Electrical Conductivity, Sodium, 17 Potassium, Calcium, Carbonates, Bicarbonates, Chlorine, Sulphate, Fluoride, Residual Sodium Carbonates, 18 and Sodium Adsorption Ratio with standard procedures.

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20 Keywords Fluoride Aquatic environment chemical composition of Rainwater chemistry

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Introduction

22 Fluorides are naturally-occurring components of rocks and soil and are also found in air, water, 23 plants, and animals. They enter the atmosphere through volcanic emissions and the resuspension of soil by 24 wind. Volcanoes also emit hydrogen fluoride and some fluorine gas from industrization. Fluorine is a 25 highly reactive element and readily hydrolyzes to form hydrogen fluoride and oxygen. Hydrogen fluoride 26 reacts with many materials both in the vapor phase and in aerosols. Marine aerosols also release small 27 amounts of gaseous hydrogen fluoride and fluoride salts into the air (Friend 1989). Anthropogenic fluoride 28 emissions include the combustion of fluorine containing materials, which releases hydrogen fluoride, as 29 well as particulate fluorides, into the air. Coal contains small amounts of fluorine, and coal-fired power 30 plants constitute the largest source of anthropogenic hydrogen fluoride emissions. According to the Toxic 31 Chemical Release Inventory (TRI), in 2001, the largest contributing industrial sectors were electrical 32 utilities (TRI01 2003). Total air emissions of hydrogen fluoride by electrical utilities in 1998, 1999, 2000, 33 and 2001 were reported as 64.1, 58.3, 58.3, and 55.8 million tons, respectively. Major sources of industrial

34 fluoride emissions are aluminum production plants and phosphate fertilizer plants; both emit hydrogen 35 fluoride and particulate fluorides (EPA 1998b). Other industries releasing hydrogen fluoride are: chemical 36 production; steel; magnesium; and brick and structural clay products. Hydrogen fluoride would also be released by municipal incinerators as a consequence of the presence of fluoride-containing material in the 37 38 waste stream. Hydrogen fluoride is one of the 189 chemicals listed as a hazardous air pollutant (HAP) in 39 Title III, Section 112 of the Clean Air Act Amendments of 1990. Maximum achievable control technology 40 (MACT) emission standards are being developed by the EPA for each HAP. Other anthropogenic sources 41 of fluoride in the environment are coal combustion causing air pollution, and waste production by various 42 industries, including steel, aluminum, copper and nickel smelting; and the production of glass, phosphate 43 fertilizers, brick and tile (Pickering, 1985; Skjelkvsle, 1994). Simultaneous air and groundwater pollution 44 by F and As, due to coal combustion, causes serious health diseases over large areas of southern China (Zheng et al., 1996; An et al., 1997; Finkelman et al., 2002) and Inner Mongolia (Wang et al., 1999; 45 46 Smedley et al., 2002), although F does not coexist with As in polluted groundwater in most other areas. In the atmosphere, gaseous hydrogen fluoride will be absorbed by atmospheric water (rain, clouds, 47 48 fog, snow) forming an aerosol or fog of aqueous hydrofluoric acid. It will be removed from the 49 atmosphere primarily by wet deposition. Particulate fluorides are similarly removed from the atmosphere 50 and deposited on land or surface water by wet and dry deposition. Atmospheric precipitation weathers 51 crustal rocks and soil, but dissolves out very little fluoride: most of the fluoride mobilized during 52 weathering is bound to solids such as clays. Upon reaching bodies of water, fluorides gravitate to the sediment (Carpenter 1969). Fluorides have been shown to accumulate in some marine aquatic organisms 53 54 (Hemens and Warwick 1972). When deposited on land, fluoride is strongly retained by soil, forming 55 complexes with soil components. Fluorides in soils are transported to surface waters through leaching or 56 runoff of particulate-bound fluorides. Leaching removes only a small amount of fluorides from soils. 57 Fluorides may be taken up from soil and accumulate in plants. The amount of fluorides accumulated 58 depends on the type of plant and soil and the concentration and form of fluoride in the soil. Fluorides may 59 also be deposited on above-ground surfaces of the plant. Tea plants are particularly known to accumulate 60 fluoride, 97% of which is accumulated in the leaves (Fung et al. 1999). Fluoride accumulates primarily in 61 the skeletal tissues of terrestrial animals that consume fluoride-containing foliage. However, milk and 62 edible tissue from animals fed high levels of fluorides do not appear to contain elevated fluoride 63 concentrations (NAS 1971a). 64 In natural water, fluoride forms strong complexes with aluminum in water, and fluorine chemistry

65 in water is largely regulated by aluminum concentration and pH (Skjelkvale 1994). Below pH 5, fluoride is

66	almost entirely complexed with aluminum and consequently, the concentration of free F is low. As the pH
67	increases, Al-OH complexes dominate over Al-F complexes and the free F levels increase. Fluoride forms
68	stable complexes with calcium and magnesium, which are present in sea water. Calcium carbonate
69	precipitation dominates the removal of dissolved fluoride from sea water (Carpenter 1969). Fluorine is
70	incorporated into the calcium salt structure and removed from solution when the latter precipitates.
71	Fluoride occurs in soil in a variety of minerals and complexes with aluminum, iron, and calcium. Fluorides
72	occur predominantly as aluminum fluorosilicate complexes in acidic soils and calcium fluoride in alkaline
73	soils. The availability of these soluble complexes increases with decreasing pH (Fung et al. 1999;
74	Shacklette et al. 1974). This explains why acidic soils have both higher water-soluble fluoride and higher
75	extractable aluminum levels. The retention of fluoride in alkaline soils depends largely upon the aluminum
76	content of the soil.
77	Material and Methods
78	A. Site Description of the Study Area
79	Sonbhadra is the largest district of Uttar PradeshIt has geographical area 6788.0 sq km, average height
80	from sea level 285 feet, average, rainfall 1036.6 mm and temperatures in summer 10-45 ⁰ C in winter 8-25
81	⁰ C Renukut is located at 24°12 of Northern latitude and 83°02 Eastern latitude. It has an average
82	elevation of 283 meters (931 feet). Summers peak in May and June. Renukut has the largest integrated
83	Aluminum plant in Asia. Monsoon generally sets in the First week of June and last up to last week of
84	September. 90-95 percent rainfall is received during June to September. The temperature begins to rise
85	from the first week February and reaches it maximum by the middle of May or end of June. The location
86	map of the study area has been shown in fig.1
87	Sampling of Rainwater
88	Rain water was collected in rainy season around Hindustan Aluminum Company, Uttar Pradesh. The time
89	schedule for collection of rain water was 2 th June to 8 ^{ht} August 2008. The total samples were 33.In
90	Hindustan Aluminum Company Ltd the sample collector was placed about 10 m above the ground level
91	on the roof of the quarter of the employee. Each collector had a 19 cm diameter plastic fennel tightly fitted
92	to 2.5L borosilicate glass bottle. The rain water samples were then filtered and only aqueous phase was
93	analyzed, between two rainfall events collectors were properly rinsed with distilled water.
94	Methods of Analysis of cations and anions in Aquatic Environment

95	The pH was measured with a digital pH meter using reference (KCl) and glass electrodes standardized
96	with pH 4.0 and pH 9.2 reference buffers before and after pH determination. Since pH is influenced by
97	extreme values of rainfall amount, rainfall weighted mean values of pH were used instead of arithmetic
98	means. Electrical conductivity is used for determination of total concentration of soluble salts or ionized
99	constituents in water. It is related to the sum of cations and anions as determined chemically. The E.C.
100	of water was measured with Conductivity Bridge using standard potassium chloride solution for
101	calibration and determination of cell constant. Since it is influenced by temperature, maintenance of
102	temperature is important on account of the fact that specific conductance is increased by 2% per degree
103	centigrade rise of temperature. The temperature in water samples were maintained in water bath at 25°C.
104	Calcium (Ca2+), magnesium (Mg2+), carbonate (CO3 2-), bicarbonate (HCO3 -) and chloride (Cl ⁻)
105	were analyzed by volumetric titration methods, sodium (Na ^{$+$}) and potassium (K ^{$+$}) were measured using
106	the flame photometer, sulphate $(SO_4^{2^-})$, were determined by spectrophotometric technique as per the
107	methods described by the American Public Health Association (APHA 1995). The analyses were
108	completed within a week from the date of collection of the water samples at the Department of Soil
109	Science and Agricultural Chemistry, Institute of Agricultural Sciences, Banaras Hindu University,
110	Varanasi. Table 1 provides physico-chemical data of rainwater samples of the present study.
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112 113 114 115	Fluoride content in water was determined electrochemically, using the direct ion selective electrode method. In this method, 25 mL of water sample and 25 mL of the TISAB solution (total ionic strength adjustment buffer) were taken in a 100 mL plastic beaker. The ratio of aliquot and TISAB Solution should be 1:1. After proper calibration, the fluoride electrode was dipped in the sample and concentration
 112 113 114 115 116 	Fluoride content in water was determined electrochemically, using the direct ion selective electrode method. In this method, 25 mL of water sample and 25 mL of the TISAB solution (total ionic strength adjustment buffer) were taken in a 100 mL plastic beaker. The ratio of aliquot and TISAB Solution should be 1:1. After proper calibration, the fluoride electrode was dipped in the sample and concentration in mg/L was displayed on the screen.
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Electrochemical Characterization of Rain Water

The pH value of tested water samples refers to the intensity of the acidic or alkaline condition of a solution
(Murhekar, 2011). The data on important electrochemical properties of rain water, *viz.*, pH and EC of rain
water of Renukut, collected in different days have been presented in the Table 1. The pH values of rain water
samples collected from Renukoot ranging from 4.9-8.1 with mean 6.5. More than 35% incidence of
rainwater was observed acidic due to the influence of industries (aluminum and thermal power plant).
Neutral pH was observed in latter incidences of rain of Renukoot. The Electrical conductivity of rain water
of Renukut ranged from 0.017-0.471 dSm⁻¹.

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Anions Chemistry of Aquatic Environment

Samples of rain water were collected on 1st week of June to 4th week of August, 2008 in Renukut, Uttar 136 Pradesh. The values of anionic composition *viz.*, carbonate, bicarbonate, chloride, sulphate and residual 137 138 sodium carbonate (RSC) are given in Table 1.It was revealed from the data that the chloride and sulphate 139 were found in all the rain water samples in each locations; but carbonate was not found in rain water 140 samples and Bicarbonate was found enriched with 100% water samples it is also revealed that in comparison with other anions. HCO_3 was found in highest amount followed by chloride and sulphate. In 141 waters, containing high concentration of bicarbonate ions, there is a tendency for Ca^{2+} and Mg^{2+} to 142 precipitate as carbonates. This can be shown as RSC (residual sodium carbonate) = $(CO_3^{=} + HCO_3) - (Ca^{2+})$ 143 + Mg²⁺), where $CO_{3}^{=}$, HCO₃, Ca²⁺ and Mg²⁺ represents the concentrations in meg L⁻¹ of respective ions. 144 145 RSC from carbonate is more harmful than bicarbonate. But the values of RSC in most of the samples of 146 rain water in studies area were negative; thus precipitation problems will not occur in future. Moreover, 147 rainfall, soil texture and plant species to be grown has great impact in deciding the limits of RSC for suitability of irrigation water in a particular area. For example studies conducted at CSSRI has revealed 148 that water up to RSC 5.0 meg L^{-1} can be used where rainfall is 700 to 900 mm per annum. The limit of 149 RSC (5.0 meq L^{-1}) in rain water had not crossed in Renukut but only 10.5% rain water samples in Varanasi 150 151 had crossed the limit.

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Cations Chemistry of Aquatic Environment

153 Results given in Table 1 presented the concentration of cations, *viz.*, sodium, potassium, calcium and 154 magnesium in rain water samples during South West monsoon period. It was revealed from the data that K⁺ 155 and Mg²⁺ were found in all the rain water samples account more than 75 %. The order of basic cations 156 (mean) found in rain water was as follows: $Mg^{2+} \ge K^+ > Na^+ \ge Ca^{2+}$. The mean total basic cations (Na⁺ + 157 K⁺ + Ca²⁺ + Mg²⁺) (4.03 meq L⁻¹) Thus, neutralization of acidic anions (*viz.*, Cl⁻, SO₄⁼ etc.) by basic anions

 $(CO_{3}^{=} and HCO_{3})$ was noticed higher in water samples. The alkaline properties of the particulate matter in 158 159 rain water were responsible for neutralizing the acidic ions and consequently, for the observed increase in 160 pH. The cations are mainly of soil origin and predominantly present in giant size range. The range of cations in rain water samples were as follows: $0.00-1.44 \text{ meg } \text{L}^{-1} \text{ of } \text{Na}^+$, $0.2-2.3 \text{ meg } \text{L}^{-1} \text{ of } \text{K}^+$, $0.00-1.44 \text{ meg } \text{L}^{-1} \text{ of } \text{Na}^+$, $0.2-2.3 \text{ meg } \text{L}^{-1} \text{ of } \text{K}^+$, $0.00-1.44 \text{ meg } \text{L}^{-1} \text{ of } \text{Na}^+$, $0.2-2.3 \text{ meg } \text{L}^{-1} \text{ of } \text{K}^+$, $0.00-1.44 \text{ meg } \text{L}^{-1} \text{ of } \text{Na}^+$, $0.2-2.3 \text{ meg } \text{L}^{-1} \text{ of } \text{K}^+$, $0.00-1.44 \text{ meg } \text{L}^{-1} \text{ of } \text{Na}^+$, $0.2-2.3 \text{ meg } \text{L}^{-1} \text{ of } \text{K}^+$, $0.00-1.44 \text{ meg } \text{L}^{-1} \text{ of } \text{Na}^+$, $0.2-2.3 \text{ meg } \text{L}^{-1} \text{ of } \text{K}^+$, $0.00-1.44 \text{ meg } \text{L}^{-1} \text{ of } \text{Na}^+$, $0.2-2.3 \text{ meg } \text{L}^{-1} \text{ of } \text{K}^+$, $0.00-1.44 \text{ meg } \text{L}^{-1} \text{ of } \text{Na}^+$, $0.00-1.44 \text{ meg } \text{L}^{-1} \text{ of } \text{Na}^+$, $0.00-1.44 \text{ meg } \text{L}^{-1} \text{ of } \text{Na}^+$, $0.00-1.44 \text{ meg } \text{L}^{-1} \text{ of } \text{Na}^+$, $0.00-1.44 \text{ meg } \text{L}^{-1} \text{ of } \text{Na}^+$, $0.00-1.44 \text{ meg } \text{L}^{-1} \text{ of } \text{Na}^+$, $0.00-1.44 \text{ meg } \text{L}^{-1} \text{ of } \text{Na}^+$, $0.00-1.44 \text{ meg } \text{L}^{-1} \text{ of } \text{Na}^+$, $0.00-1.44 \text{ meg } \text{L}^{-1} \text{ of } \text{Na}^+$, $0.00-1.44 \text{ meg } \text{L}^{-1} \text{ of } \text{Na}^+$, $0.00-1.44 \text{ meg } \text{L}^{-1} \text{ of } \text{Na}^+$, $0.00-1.44 \text{ meg } \text{L}^{-1} \text{ of } \text{Na}^+$, $0.00-1.44 \text{ meg } \text{L}^{-1} \text{ of } \text{Na}^+$, $0.00-1.44 \text{ meg } \text{L}^{-1} \text{ of } \text{Na}^+$, $0.00-1.44 \text{ meg } \text{L}^{-1} \text{ of } \text{Na}^+$, $0.00-1.44 \text{ meg } \text{L}^{-1} \text{ of } \text{Na}^+$, $0.00-1.44 \text{ meg } \text{Na}^+$, 0.00-1.4161 meq L^{-1} of Ca^{2+} and 0.02-2.3 meq L^{-1} of Mg^{2+} . Thus, higher range of Na^{+} and K^{+} in rain water were 162 observed in samples. The principal cations present in rain water are Ca^{2+} , Mg^{2+} , Na^{+} and K^{+} . The alkali 163 hazard involved in the use of water for irrigation determine the absolute and relative concentration of the 164 165 cations. If the proportion of sodium is high, the alkali hazard is high. If the calcium and magnesium is high, 166 the hazard is low. The Sodium Adsorption Ratio (SAR) of a solution or water is related to the adsorption of 167 sodium by the soil. This is expressed by the equation:

168
$$SAR = \frac{Na^{+}}{\sqrt{\frac{Ca^{2+} + Mg^{2+}}{2}}}$$

169 Where all ionic concentration are expressed in meq L^{-1} . It was revealed from Table 1 that SAR values of 170 rain water varied from 0.0-1.8. It was noticeable that SAR values were < 10 and EC were < 2.0 d Sm⁻¹ in 171 all the samples of the rain water. Thus, this rain water is suitable for safe irrigation, without any sodicity 172 problems.

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Fluoride Distribution in Aquatic Environment

174 Presence of fluoride in pure rain water is depended on the atmospheric deposition from soil dust and 175 industrial emission. Thus, the soluble fluoride in upper crust of the earth and the fluoride emission as a dust 176 from industry, e.g. aluminum industry are the source of fluoride in rain water. It is not essential to crops, but it can cause toxicity of sensitive crops at higher level. The data on fluoride content in rain waters of 177 178 Renukut have been presented in Table 1. The fluoride content in rain water ranged from from 0.02-0.45 meq L⁻¹. Maximum fluoride in rain water was noticed in the month of July. The fluoride contamination was 179 noticed in all the incidences of rain water samples of studies area. The mean value (0.17 meq L^{-1}) of 180 181 fluoride in rain water was represented in Fig.1

182 .Considerably higher concentrations of fluoride around 0.3 mg L⁻¹ in rain water have been also reported
183 from two sites in Uttar Pradesh (Satsangi *et al.*, 1988) and Madhya Pradesh (Singh *et al.*, 2001). Das *et al.*184 (1981) reported 0.1 mg L⁻¹ for monsoon rain water at Bhopal in Central India. According to these authors,
185 a large fraction of the dissolved material in the rain water in their investigations, including the fluoride,
186 may be derived from local soil dust. Chandrawanshi and Patel (1999) have presented an extensive

investigation from eastern Madhya Pradesh comprising 13 sites with a mean volume-weighted
 concentration of fluoride in the precipitation ranging from 0.05 to 0.22 mg L⁻¹, the latter being from a site
 close to an industrial Aluminum plant. Thus, the higher amount of fluoride in Renukut is obviously
 influenced by Al factory (Hindustan Aluminum Company, LTD).

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Correlation Study of Fluoride with Chemical Composition and Weather Parameters

The data on correlation study of fluoride content in rainwater with chemical composition of rainwater and weather parameters of Renukut have been presented in Table 2 and Table 3 respectively. Fluoride content in rain waters were negatively correlated with Ca²⁺ and Mg²⁺. An inverse relationship was also found between F⁻ and Ca²⁺ in some investigations (Handa, 1975). It was revealed from the data that the fluoride content in rain water was negatively correlated with the atmospheric temperature and evaporation in study the regions of Renukut. Thus, due to increase in atmospheric temperature, rate of evaporation increases which leads to reduction of fluoride concentration in rain water.

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Conclusion

200 The Research data indicated that the heavy air pollution was found around Hindustan Aluminum Company, 201 LTD, which causes pollutant as well other contaminants in Aquatic Environment. So, the findings cleared 202 that the Aluminum plant in Renukoot is the main sources of air pollution in atmosphere as well as in 203 rainwater. The standard method to be used of analysis of Rainwater for monitoring of rainwater chemistry 204 and fluoride. The fluoride in rain water was analyzed by ion selective electrode meter. Presence of fluoride 205 in rain water is depended on the atmospheric deposition from soil dust and industrial emission. The 206 fluoride contamination was noticed in all the rainwater samples of study area. Maximum fluoride 207 contamination in rain water was observed in the month of July. The fluoride content in rain water of Renukut ranged from 0.02 0.45 meg L⁻¹. High fluoride contamination due to industrial emission from 208 aluminum industry, chemical Industries, hydel power projects, thermal power projects. To name a few 209 210 there exists HINDALCO India's largest aluminum company, and then in the same belt around some 40 km 211 away is India largest NTPC plant. Higher fluoride concentration (3.23 mg/L) in rain water was observed in 212 Renukut. Rainwater can be treated by applying appropriate technology to remove the impurities.

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Table 1: Rainwater Chemistry of Renukut

S. No.	Date of Sampling	рН	EC dSm ⁻¹	Na ⁺	\mathbf{K}^+	Ca ⁺⁺	CO ₃	HCO ₃	CL ⁻¹	SO4	Fluoride	RSC	SAR
1	02/06/2008	6.4	0.107	0.00	2.00	0.00	0.0	0.4	1.0	0.01	0.18	-0.06	0.0
2	08/06/2008	7.3	0.093	0.00	0.79	0.00	0.0	0.5	0.4	0.00	0.13	-0.01	0.0
3	10/06/2008	5.7	0.112	0.00	1.10	0.00	0.0	0.6	1.2	0.03	0.20	-0.02	0.0
4	13/06/2008	7.1	0.158	0.00	2.00	0.00	0.0	0.8	1.3	0.17	0.23	-0.04	0.0
5	14/06/2008	8.1	0.227	0.00	2.20	0.00	0.0	1.9	1.5	0.12	0.20	-0.01	0.0
6	16/06/2008	7.1	0.099	0.00	0.90	0.00	0.0	0.4	1.1	0.19	0.22	-0.02	0.0
7	19/06/2008	7.9	0.175	1.12	1.40	1.12	0.0	1.1	2.1	0.11	0.07	-1.13	1.5
8	22/06/2008	7.7	0.166	0.00	1.60	0.00	0.0	1.2	2.5	0.09	0.06	-0.01	0.0
9	23/06/2008	7.9	0.194	0.00	1.50	0.00	0.0	0.3	2.1	0.02	0.21	-0.04	0.0
10	24/06/2008	5.8	0.078	0.80	0.75	0.80	0.0	0.2	1.9	0.02	0.34	-0.82	1.2
11	26/06/2008	5.3	0.074	0.32	0.15	0.32	0.0	0.4	1.6	0.06	0.28	-0.32	0.8
12	27/06/2008	5.0	0.055	1.28	0.18	1.28	0.0	0.3	0.7	0.02	0.29	-1.28	1.6
13	29/06/2008	4.9	0.085	0.48	0.41	0.48	0.0	0.4	1.6	0.07	0.26	-0.48	1.0
14	30/06/2008	5.8	0.056	1.44	0.02	1.44	0.0	0.4	1.3	0.06	0.26	-1.43	1.7
15	05/07/2008	6.5	0.044	1.28	0.49	1.28	0.0	0.3	0.4	0.01	0.26	-1.29	1.6
16	07/07/2008	5.8	0.047	0.48	0.11	0.48	0.0	0.4	0.4	0.08	0.26	-0.47	1.0
17	09/07/2008	5.3	0.023	0.96	0.81	0.96	0.0	0.3	0.0	0.01	0.26	-0.98	1.4
18	11/07/2008	5.8	0.017	0.64	0.41	0.64	0.0	0.4	0.0	0.01	0.26	-0.64	1.1
19	12/07/2008	5.8	0.054	0.96	0.59	0.96	0.0	0.3	1.9	0.10	0.13	-0.97	1.4
20	15/07/2008	5.5	0.024	0.32	0.14	0.32	0.0	0.3	1.8	0.01	0.08	-0.31	0.8
21	16/07/2008	6.8	0.129	0.8	0.36	0.80	0.0	1.2	1.3	0.02	0.07	-0.77	1.3
22	18/07/2008	7.3	0.074	0.96	1.10	0.96	0.0	0.3	2.2	0.01	0.10	-0.99	1.4
23	20/07/2008	6.8	0.040	0.80	0.12	0.80	0.0	1.9	1.8	0.01	0.09	-0.73	1.3
24	23/07/2008	6.4	0.037	0.32	0.42	0.32	0.0	0.2	2.0	0.01	0.11	-0.32	0.8
25	25/07/2008	6.6	0.054	1.12	0.97	1.12	0.0	0.4	1.9	0.08	0.45	-1.14	1.5
26	27/07/2008	6.2	0.023	0.48	0.57	0.48	0.0	0.5	2.0	0.03	0.04	-0.48	1.0
27	28/07/2008	6.2	0.040	1.44	0.78	1.44	0.0	0.6	0.2	0.08	0.09	-1.45	1.7
28	30/07/2008	6.3	0.025	0.64	0.12	0.64	0.0	1.1	0.2	0.03	0.07	-0.60	1.1
29	06/08/2008	6.5	0.017	0.32	1.90	0.32	0.0	0.4	1.8	0.00	0.08	-0.38	0.7
30	17/08/2008	6.4	0.019	1.44	1.50	1.44	0.0	0.2	0.8	0.00	0.06	-1.48	1.7
31	23/08/2008	6.8	0.069	1.28	2.30	1.28	0.0	1.2	1.8	0.03	0.02	-1.32	1.6
32	24/08/2008	6.7	0.034	1.60	1.20	1.60	0.0	0.8	0.9	0.03	0.12	-1.61	1.8
33	29/08/2008	6.8	0.038	0.32	0.56	0.32	0.0	0.3	1.3	0.03	0.09	-0.33	0.8
Range		4.9 -8.1	0.017-0.47	0.0-1.44	0.0-00	0.0- 1.44	0-0	0.2-1.9	0.20- 2.5	0.01-0.17	0.02-0.45	-0.011.61	0.0-1.8
	Aean	6.5	0.080	0.65	0.67	0.65	0-0	1.30	0.55	0.01	0.170	0.050	0.95
±SD.		0.83	0.056	0.53	75.73	0.52	0.0	0.71	0.23	0.01	0.102	0.048	0.62
CV.		12.1	0.70	80.62	00	80.30	0.0	54.76	41.81	100.0	60.0	96.00	65.06

Parameters	pН	EC	CO ₃ ²⁻	HCO ₃	RSC	СГ	SO ₄ ²⁻	Ca ²⁺	Mg ²⁺	Na ⁺	\mathbf{K}^{+}	SAR	Fluoride
рН	1.000												
EC	0.637**	1.000											
CO_{3}^{2}	0.315	0.382*	1.000										
HCO ₃	1.000**	0.444^{*}	-0.121	1.000									
RSC	0.236	0.455	0.215	0.087	1.000								
Cl	0.340	0.368*	0.215	0.163	0.204	1.000							
SO ₄ ²⁻	0.267	0.499**	-0.085	0.224	0.216	0.109	1.000						
Ca ²⁺	-0.244	-0.462*	-0.224	-0.065	-0.999**	-0.209	-0.218	1.000					
Mg ²⁺	0.592**	0.524**	0.162	0.266	-0.999**	0.270	0.205	-0.206	1.000				
Na ⁺	-0.244	-0.462	-0.224	-0.065	0.170	-0.209	-0.218	1.000	-0.206	1.000			
\mathbf{K}^+	0.592**	0.524**	0.162	0.266	0.170	0.270	0.205	-0.206	1.000	-0.206	1.000		
SAR	-0.361*	-0.581**	-0.276	-0.103	-0.950**	-0.166	-0.289	0.958*	-0.366	0.958**	-0.366*	1.000	
Fluoride	-0.358	0.051	0.072	-0.352	-0.007	-0.204	0.208	0.782*	-0.821*	0.002	-0.202	-0.016	1.000

Table 2: Correlation Study of Fluoride with Chemical Composition of Rainwaters

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* Correlation is significant at the 0.05 level (2 tailed) ** Correlation is significant at the 0.01 level (2 tailed)

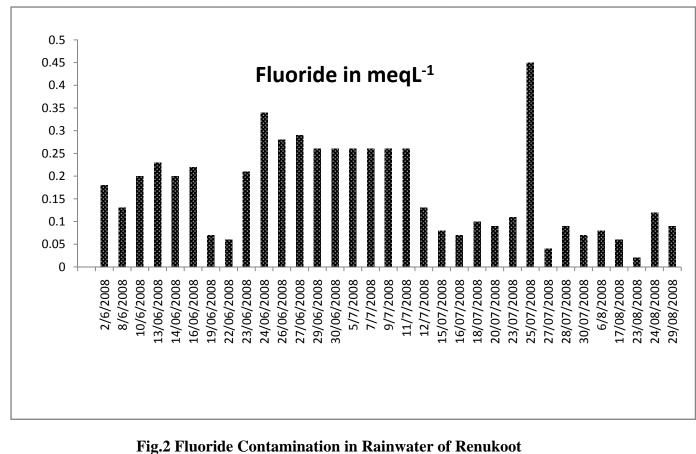
Table 3: Correlation Study of Fluoride with Weather Parameters

Parameters	Rainfall	Tempe	erature	R.	H.	Sunshine	Evaporation	Fluoride
		Max.	Mini.	Max.	Mini.			
Rainfall	1.000							
Temp. Max.	0.246	1.000						
Temp. Mini.	0.684*	0.782**	1.000					
R H Max.	0.203	-0.654	-0.298	1.000				
R H Mini.	0.641*	-0.211	0.306	-0.751*	1.000			
Sunshine	-0.469	0.616	0.062	-0.751*	-0.778**	1.000		
Evaporation	0.096	0.183	0.626	-0.919	-0.532	0.671*	1.000	
Fluoride	-0.456	0.893*	-0.343	-0.032	-0.324	0.596*	-0.646*	1.000

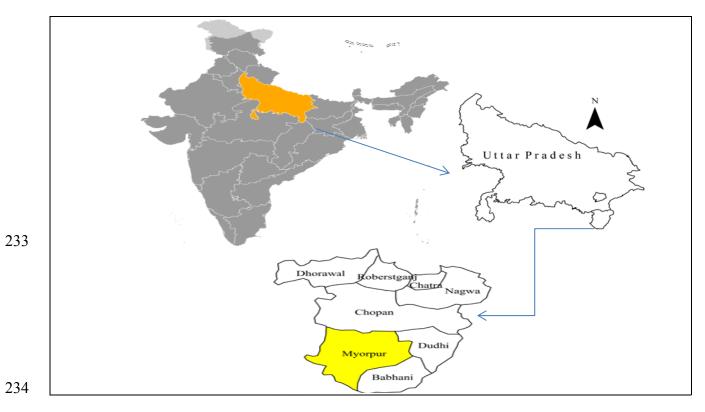
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235 236 237 238	Fig.1 location map of Study area
239 240	Fig.1 Location Map of the Study Area
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