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, India

4

5 Abstract:

6

7 Fluorine is a highly reactive element and readily hydrolyzes to form hydrogen fluoride and 8 oxygen. Hydrogen fluoride reacts with many materials both in the vapor phase and in aerosols. 9 Fluorides are naturally-occurring components of rocks and soil and are also found in air, water, plants, and animals. Fluorine gas pollutes the atmospheric environment originating from 10 aluminium smelting plant operating at Renukoot, district Shonbhadra. Volcanic emissions also 11 12 emit hydrogen fluoride. A detailed investigation undertaken during 2008-2012 to objective fluoride Distribution in Aquatic Environment in Vicinity of Aluminum Industry and its 13 14 Correlation with Rainwater Chemistry and Weather Parameter. For this investigation Collect 57 15 rainwater samples in rainy season in pre-cleaned and sterilized polyethylene bottles of two litre 16 capacities from roof of the local society of Hindustan Aluminum Company Renukoot, district 17 Sonbhadra. The collected samples were analyzed for pH, Electrical Conductivity, Sodium, 18 Potassium, Calcium, Carbonates, Bicarbonates, Chlorine, Sulphate, Fluoride, Residual Sodium 19 Carbonates, and Sodium Adsorption Ratio with standard procedures.

20

21 *Keywords* Fluoride; Aquatic environment; rainwater; Uttar Pradesh

22

23 Introduction

24 Fluorides are naturally-occurring components of rocks and soil and are also found in air, 25 water, plants, and animals. They enter the atmosphere through volcanic emissions and the 26 resuspension of soil by wind. Volcanoes also emit hydrogen fluoride and some fluorine gas from 27 industrization. Fluorine is a highly reactive element and readily hydrolyzes to form hydrogen 28 fluoride and oxygen. Hydrogen fluoride reacts with many materials both in the vapor phase and 29 in aerosols. Marine aerosols also release small amounts of gaseous hydrogen fluoride and fluoride salts into the air (Friend 1989). Anthropogenic fluoride emissions include the 30 31 combustion of fluorine containing materials, which releases hydrogen fluoride, as well as particulate fluorides, into the air. Coal contains small amounts of fluorine, and coal-fired power 32

33 plants constitute the largest source of anthropogenic hydrogen fluoride emissions. According to 34 the Toxic Chemical Release Inventory (TRI), in 2001, the largest contributing industrial sectors 35 were electrical utilities (TRI01 2003). Total air emissions of hydrogen fluoride by electrical 36 utilities in 1998, 1999, 2000, and 2001 were reported as 64.1, 58.3, 58.3, and 55.8 million tons, 37 respectively. Major sources of industrial fluoride emissions are aluminum production plants and 38 phosphate fertilizer plants; both emit hydrogen fluoride and particulate fluorides (EPA, 1998b). 39 Other industries releasing hydrogen fluoride are: chemical production; steel; magnesium; and 40 brick and structural clay products. Hydrogen fluoride would also be released by municipal 41 incinerators as a consequence of the presence of fluoride-containing material in the waste stream. 42 Hydrogen fluoride is one of the 189 chemicals listed as a hazardous air pollutant (HAP) in Title 43 III, Section 112 of the Clean Air Act Amendments of 1990. Maximum achievable control 44 technology (MACT) emission standards are being developed by the EPA for each HAP. Other 45 anthropogenic sources of fluoride in the environment are coal combustion causing air pollution, 46 and waste production by various industries, including steel, aluminum, copper and nickel 47 smelting; and the production of glass, phosphate fertilizers, brick and tile (Pickering, 1985; 48 Skjelkvsle, 1994). Simultaneous air and groundwater pollution by F and As, due to coal 49 combustion, causes serious health diseases over large areas of southern China (Zheng et al., 50 1996; An et al., 1997; Finkelman et al., 2002) and Inner Mongolia (Wang et al., 1999; Smedley 51 et al., 2002), although F does not coexist with As in polluted groundwater in most other areas.

52 In the atmosphere, gaseous hydrogen fluoride will be absorbed by atmospheric water 53 (rain, clouds, fog, snow) forming an aerosol or fog of aqueous hydrofluoric acid. It will be 54 removed from the atmosphere primarily by wet deposition. Particulate fluorides are similarly 55 removed from the atmosphere and deposited on land or surface water by wet and dry deposition. 56 Atmospheric precipitation weathers crustal rocks and soil, but dissolves out very little fluoride; 57 most of the fluoride mobilized during weathering is bound to solids such as clays. Upon reaching bodies of water, fluorides gravitate to the sediment (Carpenter 1969). Fluorides have 58 59 been shown to accumulate in some marine aquatic organisms (Hemens and Warwick 1972). 60 When deposited on land, fluoride is strongly retained by soil, forming complexes with soil 61 components. Fluorides in soils are transported to surface waters through leaching or runoff of 62 particulate-bound fluorides. Leaching removes only a small amount of fluorides from soils. 63 Fluorides may be taken up from soil and accumulate in plants. The amount of fluorides 64 accumulated depends on the type of plant and soil and the concentration and form of fluoride in the soil. Fluorides may also be deposited on above-ground surfaces of the plant. Tea plants are particularly known to accumulate fluoride, 97% of which is accumulated in the leaves (Fung et al. 1999). Fluoride accumulates primarily in the skeletal tissues of terrestrial animals that consume fluoride-containing foliage. However, milk and edible tissue from animals fed high levels of fluorides do not appear to contain elevated fluoride concentrations (NAS 1971a).

70 In natural water, fluoride forms strong complexes with aluminum in water, and fluorine 71 chemistry in water is largely regulated by aluminum concentration and pH (Skjelkvale 1994). 72 Below pH 5, fluoride is almost entirely complexed with aluminum and consequently, the concentration of free F is low. As the pH increases, Al-OH complexes dominate over Al-F 73 complexes and the free F levels increase. Fluoride forms stable complexes with calcium and 74 magnesium, which are present in sea water. Calcium carbonate precipitation dominates the 75 76 removal of dissolved fluoride from sea water (Carpenter 1969). Fluorine is incorporated into the 77 calcium salt structure and removed from solution when the latter precipitates. Fluoride occurs in 78 soil in a variety of minerals and complexes with aluminum, iron, and calcium. Fluorides occur 79 predominantly as aluminum fluorosilicate complexes in acidic soils and calcium fluoride in 80 alkaline soils. The availability of these soluble complexes increases with decreasing pH (Fung et al. 1999; Shacklette et al. 1974). This explains why acidic soils have both higher water-soluble 81 82 fluoride and higher extractable aluminum levels. The retention of fluoride in alkaline soils 83 depends largely upon the aluminum content of the soil.

84

85 Material and Methods

86

A. Site Description of the Study Area

87 Sonbhadra is the largest district of Uttar Pradesh. It has geographical area 6788.0 sq km, 88 average height from sea level 285 feet, average, rainfall 1036.6 mm and temperatures in summer 10-45°C in winter 8-25 °C. Renukut is located at 24°12' of Northern latitude and 89 83°02' Eastern latitude. It has an average elevation of 283 meters (931 feet). Summers peak in 90 91 May and June. Renukut has the largest integrated Aluminum plant in Asia. Monsoon generally 92 sets in the First week of June and last up to last week of September. 90-95 percent rainfall is 93 received during June to September. The temperature begins to rise from the first week 94 February and reaches it maximum by the middle of May or end of June. The location map of 95 the study area has been shown in fig.1

96

97

98 Sampling of Rainwater

99 Rain water was collected in rainy season around Hindustan Aluminum Company, Uttar Pradesh. 100 The time schedule for collection of rain water was 2th June to 8^{ht} August 2008. The total samples 101 were 33.In Hindustan Aluminum Company Ltd the sample collector was placed about 10 m 102 above the ground level on the roof of the quarter of the employee. Each collector had a 19 cm 103 diameter plastic fennel tightly fitted to 2.5L borosilicate glass bottle. The rain water samples 104 were then filtered and only aqueous phase was analyzed, between two rainfall events collectors 105 were properly rinsed with distilled water.

106 Methods of Analysis of cations and anions in Aquatic Environment

107 The pH was measured with a digital pH meter using reference (KCl) and glass electrodes standardized with pH 4.0 and pH 9.2 reference buffers before and after pH determination. 108 109 Since pH is influenced by extreme values of rainfall amount, rainfall weighted mean values of 110 pH were used instead of arithmetic means. Electrical conductivity is used for determination of 111 total concentration of soluble salts or ionized constituents in water. It is related to the sum of 112 cations and anions as determined chemically. The E.C. of water was measured with 113 Conductivity Bridge using standard potassium chloride solution for calibration and 114 determination of cell constant. Since it is influenced by temperature, maintenance of 115 temperature is important on account of the fact that specific conductance is increased by 2% 116 per degree centigrade rise of temperature. The temperature in water samples were maintained in water bath at 25°C. Calcium (Ca2+), magnesium (Mg2+), carbonate (CO3 2-), bicarbonate 117 118 (HCO3 -) and chloride (Cl⁻) were analyzed by volumetric titration methods, sodium (Na⁺) and potassium (K^+) were measured using the flame photometer, sulphate (SO₄²⁻),were 119 120 determined by spectrophotometric technique as per the methods described by the American 121 Public Health Association (APHA 1995). The analyses were completed within a week from 122 the date of collection of the water samples at the Department of Soil Science and Agricultural Chemistry, Institute of Agricultural Sciences, Banaras Hindu University, Varanasi. Table 1 123 124 provides physico-chemical data of rainwater samples of the present study.

125 Analysis of Fluoride in Aquatic Environment

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.

B. Preparation of TISAB Solution for F⁻ 58 mL of glacial acetic acid and 12g of sodium
citrate were added to 300 mL distilled water and pH of the solution was adjusted to 5.2 using
6N sodium hydroxide and then cools and diluted to 1000 mL.

134

135 **Results and Discussion**

The present investigation entitled "Fluoride Distribution in Aquatic Environment in Vicinity of Aluminum Industry and its Correlation with Chemistry of Rainwater and Weather Parameter. A case study of Renukoot, District Sonbhadra of Uttar Pradesh" was carried out in the Department of Soil Science & Agricultural Chemistry, Institute of Agricultural Sciences, Banaras Hindu University to investigate the status of fluoride in rainwater, Renukut (Sonbhadra district).

141 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.

149 Anions Chemistry of Aquatic Environment

Samples of rain water were collected on 1^{st} week of June to 4^{th} week of August, 2008 in Renukut, Uttar Pradesh. The values of anionic composition *viz.*, carbonate, bicarbonate, chloride, sulphate and residual sodium carbonate (RSC) are given in Table 1.It was revealed from the data that the chloride and sulphate were found in all the rain water samples in each locations; but carbonate was not found in rain water samples and Bicarbonate was found enriched with 100% water samples.it is also revealed that in comparison with other anions, HCO₃ was found in 156 highest amount followed by chloride and sulphate. In waters, containing high concentration of bicarbonate ions, there is a tendency for Ca^{2+} and Mg^{2+} to precipitate as carbonates. This can be 157 shown as RSC (residual sodium carbonate) = $(CO_3^2 + HCO_3) - (Ca^{2+} + Mg^{2+})$, where CO_3^2 , 158 HCO_{3} , Ca^{2+} and Mg^{2+} represents the concentrations in meg L⁻¹ of respective ions. RSC from 159 160 carbonate is more harmful than bicarbonate. But the values of RSC in most of the samples of rain 161 water in studies area were negative; thus precipitation problems will not occur in future. 162 Moreover, rainfall, soil texture and plant species to be grown has great impact in deciding the 163 limits of RSC for suitability of irrigation water in a particular area. For example studies conducted at CSSRI has revealed that water up to RSC 5.0 meg L^{-1} can be used where rainfall is 164 700 to 900 mm per annum. The limit of RSC (5.0 meg L⁻¹) in rain water had not crossed in 165 166 Renukut but only 10.5% rain water samples in Varanasi had crossed the limit.

167 Cations Chemistry of Aquatic Environment

Results given in Table 1 presented the concentration of cations, *viz.*, sodium, potassium, calcium 168 169 and magnesium in rain water samples during South West monsoon period. It was revealed from the data that K^+ and Mg^{2+} were found in all the rain water samples account more than 75 %. The 170 order of basic cations (mean) found in rain water was as follows: $Mg^{2+} \ge K^+ > Na^+ \ge Ca^{2+}$. The 171 mean total basic cations $(Na^+ + K^+ + Ca^{2+} + Mg^{2+})$ (4.03 meq L⁻¹) Thus, neutralization of acidic 172 anions (viz., Cl, SO_4^{-} etc.) by basic anions (CO_3^{-} and HCO_3^{-}) was noticed higher in water 173 samples. The alkaline properties of the particulate matter in rain water were responsible for 174 175 neutralizing the acidic ions and consequently, for the observed increase in pH. The cations are 176 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 meg L^{-1} of Na⁺, 0.2-2.3 meg L^{-1} of K⁺, 0.00-1.44 meg 177 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 178 observed in samples. The principal cations present in rain water are Ca^{2+} , Mg^{2+} , Na^{+} and K^{+} . 179 The alkali hazard involved in the use of water for irrigation determine the absolute and relative 180 181 concentration of the cations. If the proportion of sodium is high, the alkali hazard is high. If the 182 calcium and magnesium is high, the hazard is low. The Sodium Adsorption Ratio (SAR) of a 183 solution or water is related to the adsorption of sodium by the soil. This is expressed by the 184 equation:

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

186 Where all ionic concentration are expressed in meq L^{-1} . It was revealed from Table 1 that SAR 187 values of rain water varied from 0.0-1.8. It was noticeable that SAR values were < 10 and EC 188 were < 2.0 d Sm⁻¹ in all the samples of the rain water. Thus, this rain water is suitable for safe 189 irrigation, without any sodicity problems.

190 Fluoride Distribution in Aquatic Environment

191 Presence of fluoride in pure rain water is depended on the atmospheric deposition from soil dust 192 and industrial emission. Thus, the soluble fluoride in upper crust of the earth and the fluoride 193 emission as a dust from industry, e.g. aluminum industry are the source of fluoride in rain water. 194 It is not essential to crops, but it can cause toxicity of sensitive crops at higher level. The data on 195 fluoride content in rain waters of Renukut have been presented in Table 1. The fluoride content in rain water ranged from from 0.02-0.45 meg L^{-1} . Maximum fluoride in rain water was noticed 196 197 in the month of July. The fluoride contamination was noticed in all the incidences of rain water samples of studies area. The mean value $(0.17 \text{ meg } \text{L}^{-1})$ of fluoride in rain water was represented 198 199 in Fig.1

.Considerably higher concentrations of fluoride around 0.3 mg L⁻¹ in rain water have been also 200 201 reported from two sites in Uttar Pradesh (Satsangi et al., 1988) and Madhya Pradesh (Singh et al., 2001). Das et al. (1981) reported 0.1 mg L⁻¹ for monsoon rain water at Bhopal in Central 202 203 India. According to these authors, a large fraction of the dissolved material in the rain water in 204 their investigations, including the fluoride, may be derived from local soil dust. Chandrawanshi 205 and Patel (1999) have presented an extensive investigation from eastern Madhya Pradesh 206 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 207 208 plant. Thus, the higher amount of fluoride in Renukut is obviously influenced by Al factory 209 (Hindustan Aluminum Company, LTD).

210 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

213 respectively. Fluoride content in rain waters were negatively correlated with Ca^{2+} and Mg^{2+} . An

inverse relationship was also found between \overline{F} and Ca^{2+} 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.

219 Conclusion

220 The Research data indicated that the heavy air pollution was found around Hindustan Aluminum 221 Company, LTD. which causes pollutant as well other contaminants in Aquatic Environment. So, 222 the findings cleared that the Aluminum plant in Renukoot is the main sources of air pollution in 223 atmosphere as well as in rainwater. The standard method to be used of analysis of Rainwater for 224 monitoring of rainwater chemistry and fluoride. The fluoride in rain water was analyzed by ion 225 selective electrode meter. Presence of fluoride in rain water is depended on the atmospheric 226 deposition from soil dust and industrial emission. The fluoride contamination was noticed in all 227 the rainwater samples of study area. Maximum fluoride contamination in rain water was observed in the month of July. The fluoride content in rain water of Renukut ranged from 0.02 228 0.45 meq L^{-1} . High fluoride contamination due to industrial emission from aluminum industry, 229 chemical Industries, hydel power projects, thermal power projects. To name a few there exists 230 231 HINDALCO India's largest aluminum company, and then in the same belt around some 40 km 232 away is India largest NTPC plant. Higher fluoride concentration (3.23 mg/L) in rain water was 233 observed in Renukut. Rainwater can be treated by applying appropriate technology to remove the 234 impurities.

236 237 238 Table 1: Rainwater Chemistry of Renukut

S. No.	Date of	pН	EC dSm ⁻¹	Na ⁺	K ⁺	Ca ⁺⁺	CO ₃	HCO ₃	CL ⁻¹	SO_4^-	Fluoride	RSC	SAR
1	Sampling 02/06/2008	64	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	73	0.093	0.00	0.79	0.00	0.0	0.1	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	12	0.03	0.15	-0.02	0.0
4	13/06/2008	71	0.158	0.00	2.00	0.00	0.0	0.8	13	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 D	29/08/2008	0.8	0.038	0.32	0.56	0.32	0.0	0.3	1.3	0.03	0.09	-0.33	0.8
Kange		4.9 -8.1 6 5	0.017-0.47	0.0-1.44	0.0-00	0.0- 1.44 0.65	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
		0.5	0.000	0.05	0.07	0.05	0-0	1.50	0.55	0.01	0.170	0.050	0.95
±SD. CV		0.03 12.1	0.050	80.67	15.15	0.52 80 30	0.0	54 76	0.23 41 81	100.01	60.0	96.00	65.06
U V.		14.1	0.70	00.04	00	00.50	0.0	54.70	-1.01	100.0	00.0	20.00	05.00

<u>SO4</u>²⁻ <u>C</u>a²⁺ Mg^{2+} CO_3^{2-} HCO₃ RSC Cľ Na^+ \mathbf{K}^+ pН EC **Parameters** SAR Fluoride 1.000 pН EC 0.637 1.000 CO3²⁻ 0.315 0.382 1.000 HCO₃ 1.000* 0.444 -0.121 1.000 RSC 0.455 0.087 0.236 0.215 1.000 Cľ 0.368* 0.215 0.204 0.340 0.163 1.000 SO₄²⁻ 0.267 0.499* -0.085 0.224 0.216 0.109 1.000 Ca²⁺ -0.244 -0.224 -0.065 -0.999* -0.209 -0.218 -0.462 1.000 Mg²⁺ 0.592* -0.999* 0.524** 0.162 0.266 0.270 0.205 -0.206 1.000 Na^+ -0.218 -0.244 -0.462 -0.224 -0.065 0.170 -0.209 1.000 -0.206 1.000 \mathbf{K}^+ 0.592* 0.524** 0.270 0.205 -0.206 1.000 -0.206 0.162 0.266 0.170 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 241

242 243 244

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

245 246 247

248

Table 3: Correlation Study of Fluoride with Weather Parameters

Parameters	Rainfall	Temperature		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

249

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

251 252

239



Fig.2 Fluoride Contamination in Rainwater of Renukoot



Fig.1 location map of Study area 261 262 Fig.1 Location Map of the Study Area 263 264 References 265 APHA 1995. Standard Methods for the Examination of Water and Wastewater. , American Public 266 Health Association, Washington, DC. 267 Carpenter R. 1969. Factors controlling the marine geochemistry of fluorine. Geochim Cosmochim 268 Acta 33:1153-1167. 269 Chandrawanshi, C.K., Patel, K.S. (1999). Fluoride deposition in Central India. Environ. Monitor. 270 Assess., 55: 251–265. 271 Das, D.K., Burman, G.K. and Kidwai, A.L. (1981). Chemical composition of monsoon rainwater 272 over Bhopal, Madhya Pradesh during 1977 and 1978. Mausam, **32**: 221–228. 273 1998b. AP-42 Section EPA. Background Report: 12.1. Primary aluminum. 274 http://www.epa.gov/ttnchie1/ap42/ch12/bgdocs/b12s01.pdf. November 12, 1998. 275 Finkelman, R.B., Orem, William, Castranova, Vincent, Tatu, Calin A., Belkin, Harvey E., Zheng, 276 Baoshan, Lerch, Harry E., Maharaj, Susan V., Bates, Anne L., 2002. Health impacts of coal 277 and coal use: possible solutions. International Journal of Coal Geology 50, 425e443. 278 Friend JP. 1989. Natural chlorine and fluorine in the atmosphere, water and precipitation. United 279 Environmental Programme/World Meteorological Association. Nations Scientific 280 Assessment of Stratospheric Ozone: 1989. Alternative Fluorocarbon Environmental 281 Acceptability Study Report. 282 Fung KF, Zhang ZQ, Wong JWC, et al. 1999. Fluoride contents in tea and soil from tea plantations 283 and the release of fluoride into tea liquor during infusion. Environ Pollut 104:197-205. 284 Handa, B. K. (1975). Geochemistry and genesis of fluoride containing ground waters in India. 285 Groundwater, 13: 275-281.

286 Hemens J, Warwick RJ. 1972. Effects of fluoride on estuarine organisms. Water Res 6:1301-1308.

- Murhekar GH (2011). Determination of Physico-Chemical parameters of Surface Water Samples
 in and around Akot City. International Journal of Research in Chemistry and Environment,
 1(2): 183-187.
- 290 Pickering, W.F., 1985. The mobility of soluble fluoride in soils. Environmental Pollution (Series
 291 B) 9, 281e308.
- Satsangi, G.R., Lakhani, A., Khare, P., Singh, S.P., Kumari, S.S., Srivastava, S.S., (1998).
 Composition of rain water at a semi-arid rural site in India. *Atmos. Environ.*, **32**: 3783-3793.
- Shacklette HT, Boerngen JG, Keith JR. 1974. Selenium, fluorine, and arsenic in surficial materials
 of the conterminous United States. Washington, DC: U.S. Department of the Interior.
 Geological Survey Circular 692.
- Singh, S.P., Khare, P., Satsangi, G.S., Lakhani, A., Kumari, S.S., Srivastava, S.S., 2001. Rainwater
 composition at a regional representative site of a semi-arid region of India. Water Air Soil
 Poll. 127, 93–108.
- 301 Skjelkvsle, B.L., 1994. Factors influencing fluoride in Norwegian lakes. Water Air and Soil
 302 Pollution 77, 151e167.
- Smedley, P.L., Nicolli, H.B., Macdonald, D.M.J., Barros, A.J., Tullio, J.O., 2002.
 Hydrogeochemistry of arsenic and other inorganic constituents in groundwaters from La
 Pampa, Argentina. Applied Geochemistry 17, 259e284.
- TRI01. 2003. TRI explorer. Providing access to EPA's toxics release inventory data. Washington,
 DC. Office of Information Analysis and Access. Offices of Environmental Information.
 U.S. Environmental.
- Wang, X.C., Kawahara, K., Guo, X.J., 1999. Fluoride contamination of groundwater and its
 impacts on human health in Inner Mongolia area. Journal of Water Services Research and
 Technology e Aqua 48, 146e153.
- Zheng, B., Yu, X., Zhand, J., Zhou, D., 1996. Environmental geochemistry of coal and arsenic in
 Southwest Guizhou, P.R. China. 30th International Geological Congress Abstracts 3, 410.

314

13