IEEE Journal of Translational Engineering in Health and Medicine

Received 21 November 2014; revised 15 June 2015; accepted 12 July 2015. Date of publication 20 August 2015; date of current version 1 September 2015.

Digital Object Identifier 10.1109/JTEHM.2015.2462359

Vigorous Appraisal of Fluoride on Industrial Proponent in Thermal Power Plant over Anthropoid Biosphere Using F^- Ion-Selective Electrode

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ABSTRACT This study was conducted to analyze the impact of fluoride in the anthropogenic condition in an industrial region promoting and affecting the health of the workers. Fluoride is toxic to humans in high concentrations, such as can occur in persons working in fluoride-containing mineral industries like aluminum industries. When workers are exposed to fluoride-containing minerals, they can suffer from a variety of health problems, such as dental disease. This paper presents the relationship of different clinical conditions correlated against the fluoride level. Contributing clinical aspects, such as morbidity, dysentery, overcrowding, and skin disease, are also studied to assess the consequences of fluoride upon consistent exposure. The relationship between pH and hardness of water with fluoride was measured, and then spatial maps were generated. The investigations resulted in a conclusion that hardness of water had a more pronounced impact on the level of fluoride concentration as compared with pH. Water with more hardness contains more fluoride concentration (25 mg/ml) as compared with soft water (4 mg/ml). This paper also revealed the concentration of fluoride content in the bodies of aluminum plant workers, which varied from 0.06 to 0.17 mg/L of blood serum in the case of pot room workers and 0.01 to 0.04 mg/L in the case of non-pot room workers. In fingernails, it varied from 0.09 to 3.77 mg/L and 0.39 to 1.15 mg/L in the case of pot room and non-pot room workers, respectively. In urine, it varied from 0.53 to 9.50 mg/L in pot room workers and 0.29 to 1.80 mg/L in non-pot room workers. This paper concluded that water was safe for drinking purposes if it has a low hardness (60–140 mg/ml) and pH (7.1–7.4).

INDEX TERMS Detrimental effects, fluoride, human health, ion-selective electrode.

I. INTRODUCTION

Fluorine is an element that typically does not occur naturally due to its high reactivity. It accounts for about 0.3 g kg^{-1} of the Earth's crust which subsists in fluoride formations combined with other chemicals in minerals, of which fluorspar, cryolite and fluorapatite are the most frequent in nature. Most of the occurrence of fluoride in water is present either physically or in free fluoride ions [1]. Water hardness in the range of 0 to 500 mgl^{-1} has little impact on ionic dissociation and thus leads to fluoride bioavailability [2]. Absorption of fluoride from drinking water varies from 60% with a calcium-rich breakfast to 100% in a fasting stomach. A comprehensive review of fluoride and the resulting impacts on health has been carried out by IPCS [3]. Appraisals have focused not only on bone breakage, skeletal fluorosis, cancers and birth defects but investigations have also been carried out on many other disorders that are argued to be aggravated by fluoridation [4]–[10]. However, there is a lack of evidence of any unsympathetic medical effects coupled with consumption of water with fluoride in isolated form at a concentration of 0.5-1.0 mgl^{-1} except the increase in dental fluorosis pointed out above. In fact, the concentration of fluoride depends upon climatic conditions of a region but the recommended level suggested by WHO varies within the range of 0.5 mgl^{-1} to 0.1 mgl^{-1} [11]–[14]. Around 355 million people worldwide are receiving artificially fluoridated water and around 50 million people are supplied with naturally fluoridated water at a concentration of around 1 mgl^{-1}. Drinking water in some regions of India, Africa and China contains higher concentrations of spontaneously occurring fluoride which add up 1.5 mgl^{-1} to the WHO's recommended levels. Fluorides are widely seen in the several essential materials such as coal, clay and minerals. Fluoride content of food products ranges from about 0.02 mg/kg at the low level to 8.85 mg/kg at the high level. Fluoride content of water sources ranges from 2.36 to 3.10 mg/L.

Thermal power plant workers may be exposed to high levels of cryolite in the air if their work involves certain machinery; in addition, workers in air transportation, medical and other health services, textile and metal manufacturing, or petroleum and coal production may be exposed to fluoride [15]–[19]. Workers in these types of jobs may breathe in levels as high as 2.5 milligrams of fluoride per cubic meter (mg/m^3) of air. Some hazardous waste sites contain containers of hydrofluoric acid. If material leaks from these containers, clean-up workers can be exposed to hydrofluoric acid. In areas near hazardous waste sites, you are not likely to be exposed to hydrofluoric acid because the acid reacts with soil to form fluoride salts before it reaches you. Some hazardous waste sites may contain fluorine in pressurized containers [20]–[22]. Fluorine reacts even faster than hydrofluoric acid. It is very unlikely that people living near a hazardous waste site would be exposed to fluorine.

II. MATERIALS AND METHODS

A. STUDY AREA

The study was conducted on workers of Hindalco Industries Limited (HINDALCO), a flagship company of the Aditya Birla Group in the largest integrated Al plant in Asia. Beginning its production in May 1962 with an annual capacity of 20,000 tons per annum (TPA) of Al metal, it is presently an integrated Al manufacturing complex with a production capacity of 3,56,000 TPA of primary metal. It is located at Renukoot, U.P. India (See Figure 1). The overall steps taken during the study from selection of regions to methodology and results is demonstrated in Figure 2. The human subjects (here workers or residents) portion of the study was conducted under the aegis of and approved by the environmental cell division of Hindalco during its industrial training program (BHU- MSc course). The human data was anonymous, with informed consent and with no personally identifiable information recorded.

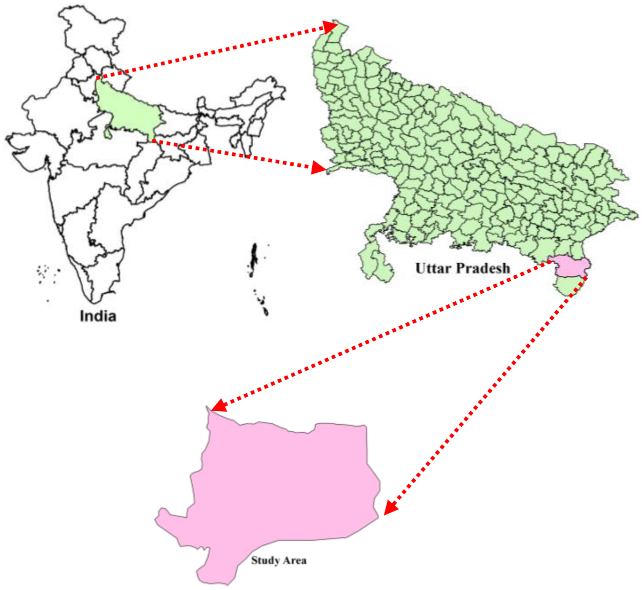

FIGURE 1. Location map of study area.

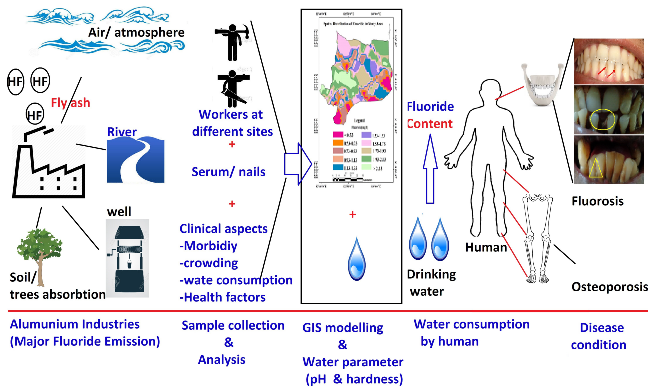

FIGURE 2. Overall pictorial representation of the GIS modeling for fluoride-related health impact used in the study.

B. DIRECT MEASUREMENT OF FLUORIDE

For measuring large number of samples, direct measurement technique is one of the simplest procedures. A single reading is all that is necessary for each sample. Before following the procedure, the ionic strength of samples and standard solutions should be prepared in the same manner by adjustment using TISAB for all fluoride solutions. Before analysis, the temperature of the sample solution, serum and urine, and standard solution should be kept the same. The stepwise procedure that was used for preparation of the standard solution for analysis is discussed here by.

First of all, three standard solutions were prepared from 0.1M, 100 ppm and 1000 ppm stock standard using serial dilution methods. The resultant standard solutions should be either in 10^{-2} M, 10^{-3} M, and 10^{-4} M or 100, 10 and 1 ppm range. Now 50 ml of each of three sample solutions were taken and 50 ml of TISAB 1 or TISAB 3 were added to them. It was also assumed the addition of TISAB to standard solution has no effect on concentration of the standard solutions. Now, the standard solutions were placed on the magnetic stirrer in the following order- the most dilute solution, mid-range solution and finally most concentrated solutions for analysis. First of all, as the most dilute solution was placed on magnetic stirrer and it was operated at constant rate, the electrode tip was lowered in to the solution. The reading was taken from the display unit when it became stabilized. Similarly, mid-range solution and most concentrated solutions were analyzed for the voltage reading when the reading was stabilized. One thing to be kept in mind before performing procedure of voltage reading with all concentrations that electrode tip should be rinsed/washed with distilled water, and then dried with blotting paper. Now the voltage readings of the most dilute, mid-range and most concentrated solutions were plotted against the concentration reading using semi-logarithmic plot. The curve was extrapolated down to about $1.0 * 10^{-5}$ M. A typical calibration curve was achieved which is displayed in the Figure 3.

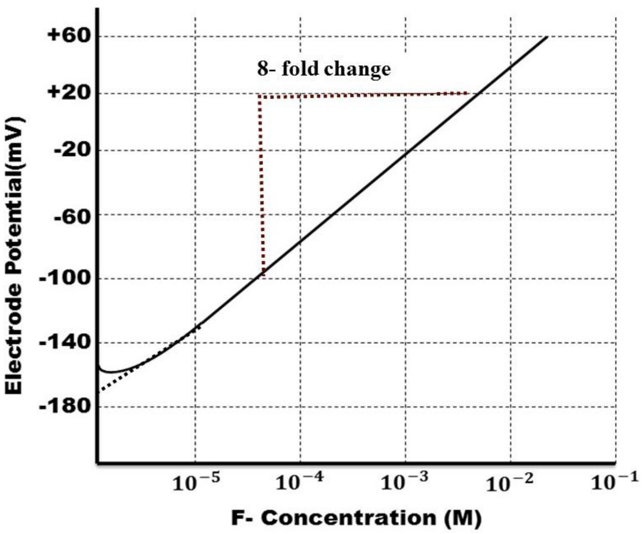

FIGURE 3. Calibration curve of sample Fluoride ion selective electrode.

Now, a clean and dry 150 ml plastic beaker was taken, and 50 ml of sample solution and 50 ml of TISAB1 or TISAB 3 was added to them. The solution was also placed on magnetic stirrer and stirring was operated for voltage reading. The electrode was rinsed with distilled water and dried with blotting paper before immersing it into solutions. The voltage reading was noted after the reading was stabilized. The sample concentration was determined using the calibration curve.

Finally, the concentration was checked for every 1 - 2 hours' time duration. Now the electrode tip was placed in the mid-range standard solution with no change in the ambient temperature. The voltage reading was measured and compared with the original reading of mid-range solution recorded earlier. The difference in reading was noted, if the reading differed by more than 0.5 mV or a there is a change in ambient temperature, this will force to repeat the above procedure (starting from most dilute solution to most concentrated solutions).

C. THE FLUORIDE SELECTIVE ELECTRODE

The study has been carried out using fluoride selective electrode method for sensing fluoride ion activity [23]. The approach is proved to be a key method for quantifying fluoride in a wide variety of environmental and industrial samples due to its outstanding performance, speed, and handiness [24], [25]. The Nernst equation provides the hypothetical basis for the determination of ions by ISE where E, the calculated electrical potential across a pair of electrodes, is associated as follows:

$$\mathrm{E} = \mathrm{E}_0 + \frac{2.303\, RT \log \mathrm{a}}{\mathrm{nF}} \quad \text{(i)}$$

Where,

Eo = Standard electrode potential for the selective ion
R = Gas Constant (8.314 J/K/mol
T = Temperature (in units of K; 25 °C = 298.15K)
a = Activity of the ion
n = Charge on the ion (−1 for fluoride)
F = Faraday's Constant (9.648 × 104 Coulomb/mol)

If all the measurements are made at a constant temperature (*e.g.* 25°C), then the term 2.303 RT/nF for fluoride ion (where n = -1) is assumed as constant and the Nernst equation can be rewritten as:

$$E = \mathrm{E}_0 - 59.16 \log \mathrm{a} \quad \text{(ii)}$$

The movement of the ion is associated to the concentration of the ion as follows:

$$a = kC \quad \text{(iii)}$$

Where,

K = Activity Coefficient
C = Concentration of the ion

The numerical value of k approaches unity (1) at very low concentration and it follows that a = C.

D. URINE FLUORIDE ESTIMATION

Urinary fluoride levels are one of the best indicators of total fluoride consumption. For more reliable results of fluoride measurement, 24-hour samples of urine were taken instead of random or morning samples as excretion of fluoride is uniform throughout the day, Commonly, an individual's urinary fluoride ranges between 0.1 and 2.0 PPM with an average of about 0.4 PPM in the case when fluoride content of drinking water is 0.3 PPM. As a general rule, fluctuation in urinary fluoride is closely related to total intake of fluoride and it fluctuates usually from day to day. In cases of skeletal fluorosis, the level of urinary fluoride ranges from 0.5 to 4.48 PPM minimum and 1.5 to 13.0 PPM maximum.

TABLE 1. Summary of fluoride content in serum and nails.

	No. of workers investigated	Fluoride content in serum (mg/l)	Fluoride in nails (mg/kg. of ash wt.)
Pot – Room Workers	50	0.06 – 0.15	0.09 – 3.77
Non Pot – Room Workers	10	0.02 – 0.04	0.39 – 1.15

TABLE 2. Summary of urinary fluoride content.

	No. of workers investigated	Urine pH	Workers having the urine pH
Pot – Room Workers	50	<5.5	20 (40%)
		5.5 – 6.5	25 (50%)
		>6.5	5 (10%)
Non Pot – Room Workers	10	<5.5	6 (60%)

It could be as high as 26 PPM or more in high endemic areas. A study on the excretion pattern of urinary fluoride indicated that in fertilizer workers urinary fluoride varies from 1.5 to 7.5 PPM with an average of 4.2 PPM Urinary fluoride levels could be low in cases with renal disease. Fluoride patients on low fluoride regimen abolish more fluoride than absorb.

E. SERUM FLUORIDE ESTIMATION

Wide discrepancies were noticed in the results from measuring fluoride levels in serum using chemical methods and those employed by different research workers. In our study, when the investigation was carried out using fluoride ion electrode for fluoride levels measurement in serum, the results were found to be considerably lower *i.e.,* 0.4 to 0.9 PPM in case of fluorotic patients and 0.19 to 0.4 PPM in normal cases. Normal values of serum fluoride levels varied from 0.002 to 0.008 mg/100ml innon-endemic regions, while in endemic regions it varied from 0.02 to 0.15 mg/100ml, whereas in case of skeletal fluorosis patients, it ranged between 0.02 and 0.19 mg/100 ml [11]. Serum fluoride levels measured in 500 healthy adults were found in the range of 0.03 to 0.13 PPM with an average value of 0.08 PPM and 0.04 to 0.28 PPM with an average value of 0.16 PPM in 17 fluorotic patients in our test site. The urinary levels of fluorides of these 17 fluorotic patients was also measured which was varied from 0.68 to 7.80 PPM with a mean value of 3.28 PPM.

F. SAMPLING METHODOLOGY AND OBSERVATION TECHNIQUE

The study was done by observation technique and taking into account factors such as crowding, education level as well as purification techniques used in that area as shown in Table 3. The women were asked about cleanliness and asked to take preventive measures such as washing up of utensils, washing of hands, drinking purified water as these are the basic measures that control the frequency of occurrence of disease.

The standard statistical techniques were applied during analysis. The chi-square test for goodness of fit was used to test whether an observed frequency distribution of a nominal variable matches with expected frequency distribution. If the calculated value of χ^2 is less than table at a certain level of significance, the fit is considered to be good one which means divergence between the observed and expected frequencies is attributable to fluctuations of sampling. But if the calculated value of χ^2 is greater than its table value, the fit is not considered to be a good one.

$$\chi^2 = \sum \frac{(\text{Observed frequency} - \text{Expected frequency})^2}{(\text{Expected frequency})} \tag{iv}$$

G. GROUNDWATER QUALITY DATA ACQUISITION

The ground sampling points were collected through GPS from different places in Renukoot, U.P during field work done in 2008 and coded. Total 44 groundwater sampling points were taken and collected samples were tested (as per laid down process in [26]) in laboratory to measure the concentration of F-parameter shown in Table 8. Spatial data analysis was done on the water quality parameter along with the location of the sampling point from where we took sample data for making spatial variability model and spatial variability map with the help of GIS [27], [28].

H. GEOSPATIAL APPROACH OF SPATIAL VARIABILITY MODELS

Geostatistical methods for interpolation were started with the recognition that the spatial variation of any continuous attribute is often too irregular to be modeled by simple, smooth mathematical function. Kriging is a geostatistical method for interpolation and assumes that the distance between sample points reflects a spatial correlation that can

TABLE 3. Summary sheet of surveyed study area.

Sample	Age	Crowding		Education		Use of water			Water Purification		visit to a doctor			Children's delivery		Suffered from these disease		
		Y	N	NL	L	Tap	Tube	Hand pump	Y	N	W	M	O	GH	PH	DF	SD	DF
1.	23	+	-	+	-	+	-	e -	-	+	+	-	-	+	-	+	+	-
2.	52	+	-	+	-	-	+	l -	-	+	+	-	-	+	-	+	+	-
3.	14	+	-	+	-	-	-	l +	-	+	+	-	-	+	-	+	+	-
4.	45	-	+	-	+	+	-	+	-	+	+	-	-	+	-	+	+	-
5.	59	-	+	-	+	+	-	+	+	-	+	-	-	+	-	+	+	-
6.	73	-	+	-	+	+	+	-	+	-	+	-	-	+	-	-	-	+
7.	64	-	+	-	+	-	-	+	+	-	+	-	-	+	-	-	-	+
8.	32	-	+	-	+	+	-	-	-	+	+	-	-	+	-	-	-	+
9.	34	-	-	-	+	+	-	-	-	+	+	-	-	+	-	+	-	+
10.	67	+	-	+	-	+	-	-	-	+	+	-	-	+	-	+	-	+
11.	87	+	-	+	-	-	+	-	-	+	-	+	-	+	-	+	-	+
12.	13	-	+	-	+	-	+	-	+	-	-	+	-	-	+	+	-	+
13.	43	-	+	-	+	-	+	-	+	-	-	-	+	-	+	-	-	+
14.	42	-	+	-	+	-	+	-	+	-	-	-	+	-	+	-	-	+
15.	18	-	+	-	+	-	+	-	+	-	+	-	-	-	+	-	+	-
16.	28	+	-	+	-	+	-	+	+	-	+	-	-	-	+	-	+	-
17.	56	+	-	+	-	+		+	+	-	+	-	-	-	+	-	+	-
18.	34	+	-	+	-	+	+	-	+	-	+	-	-	+	-	-	+	-
19.	45	+	-	+	-	+	+	-	+	-	+	-	-	-	+	-	+	-
20.	49	+	-	+	-	-	+	-	+	-	+	-	-	+	-	-	+	-
21.	46	+	-	+	-	+	-	-	+	-	+	-	-	+	-	-	+	-
22.	14	+	-	+	-	+	-	-	-	+	-	+	-	-	+	-	+	-
23.	33	-	+	-	+	+	-	+	-	+	-	+	-	+	-	-	+	-
24.	34	-	+	-	+	+	-	+	-	+	-	+	-	+	-	-	+	-
25.	37	-	+	-	+	+	-	+	-	+	-	+	-	+	-	+	-	+
26.	65	-	+	-	+	+	-	+	-	+	-	+	-	+	-	+	-	+
27.	23	+	-	+	-	-	+	-	+	-	-	+	-	+	-	+	-	+
28.	73	+	-	+	-	-	+	-	+	-	-	+	-	+	-	+	-	+
29.	27	+	-	-	+	-	+	-	+	-	-	+	-	+	-	+	-	+
30.	58	+	-	-	+	-	+	-	-	+	+	-	-	+	-	+	-	+
31.	65	-	+	-	+	-	-	+	-	+	+	-	-	+	-	+	-	+
32.	72	-	+	-	+	-	-	+	-	+	+	-	-	-	+	+	-	+
33.	43	-	+	-	+	-	-		-	+	+	-	-	-	+	-	-	+
34.	21	-	+	-	+	+	-	+	+	-	+	-	-	-	+	-	-	+
35.	25	-	+	-	+	+	-	+	+	-	+	-	-	-	+	+	-	+
36.	56	-	+	+	-	+	-	+	+	-	+	-	-	-	+	+	-	+
37.	58	-	+	+	-	+	-	+	+	-	+	-	-	-	+	+	-	+
38.	19	-	+	-	+	+	-	+	-	+	-	+	-	-	+	+	-	-
39.	26	-	+	-	+	+	+	-	-	+	-	+	-	+	-	+	-	-
40.	56	-	+	-	+	+	+	-	-	+	-	+	-	+	-	+	-	+
41.	55	-	+	-	+	-	+	-	-	+	-	+	-	+	-	+	-	+
42.	73	+	-	+	-	+	-	-	-	+	-	-	+	+	-	-	+	+
43.	84	+	-	+	-	+	-	+	+	-	-	-	+	+	-	-	+	+
44.	45	+	-	+	-	+	-	+	+	-	-	-	+	+	-	+	+	+
45.	23	-	+	+	-	+	-	+	+	-	-	-	+	+	-	+	+	+
46.	78	+	-	-	+	-	+	+	+	-	-	+	-	+	-	+	+	+
47.	23	-	+	-	+	-	+	-	-	+	-	+	-	+	-	+	+	-
48.	67	+	-	-	+	-	+	-	-	+	-	+	-	+	-	+	+	-
49.	23	-	+	-	+	-	+	-	-	+	-	+	-	+	-	-	+	-
50.	18	-	+	-	+	-	+	-	-	+	-	+	-	+	-	-	+	-

Y= Yes, N= No; NL= Non-literate, L= Literate; W= Weekly, M= Monthly, O= Occasionally; GH= Government Hospital, PH= private Hospital, SF= Skeleton Fluorosis, SD= Skin Disease, DF= Dental Fluorosis

be used to explain variation in the surface. However, a study conducted in some parts of the study site has that used empirical Bayesian kriging [31] has shown the presence of the fluoride concentration only over a large distance due to transportation. Here, the method is applied to pH and hardness of water along with the fluoride samples (see Figure 4). The

TABLE 4. Chi-square distribution for purification-morbidity.

	OBSERVED VALUE(O)	EXPECTED VALUE(E)	DEVIATION (O-E)	$(\text{DEVIATION})^2$	$(\text{O-E})^2/\text{E}$
1	8	15	-7.00	49.00	3.27
2	15	10	5.00	25.00	2.50
3	24	14	10.00	100.00	7.14
4	3	11	-8.00	64.00	5.82
TOTAL	*P-Value is < 0.001. The result is significant at p=≤0.05.*				18.728

TABLE 5. Chi-square distribution for overcrowding-dysentery.

	OBSERVED VALUE(O)	EXPECTED VALUE(E)	DEVIATION (O-E)	$(\text{DEVIATION})^2$	$(\text{O-E})^2/\text{E}$
1	14	11	3.00	9.00	0.82
2	11	14	-3.00	9.00	0.64
3	12	13	-1.00	1.00	0.08
4	13	12	1.00	1.00	0.08
TOTAL	*P-Value is 0.655. The result is not significant at p=≤0.05.*				1.621

TABLE 6. Chi-square distribution for education-morbidity.

	OBSERVED VALUE(O)	EXPECTED VALUE(E)	DEVIATION (O-E)	$(\text{DEVIATION})^2$	$(\text{O-E})^2/\text{E}$
1	6	14	-8.00	64.00	4.57
2	16	8	8.00	64.00	8.00
3	24	18	6.00	36.00	2.00
4	4	10	-6.00	36.00	3.60
TOTAL	*P-Value is < 0.001. The result is significant at p=≤0.05.*				18.171

TABLE 7. Chi-square distribution for overcrowding-skin disease.

	OBSERVED VALUE(O)	EXPECTED VALUE(E)	DEVIATION (O-E)	$(\text{DEVIATION})^2$	$(\text{O-E})^2/\text{E}$
1	11	8	3.00	9.00	1.12
2	14	16	-2.00	4.00	0.25
3	4	10	-6.00	36.00	3.60
4	21	16	5.00	25.00	1.56
TOTAL	*P-Value is 0.088. The result is not significant at p=≤0.05.*				6.538

general formula for both interpolators is formed as a weighted sum of the data:

$$Z(S_0) = \sum_{i=0}^{N} \lambda\, i * Z(\text{Si}) \qquad \text{(v)}$$

Where,

Z(Si) = The measured value at the i^{th} location

λi = An unknown weight for the measured value at the i^{th} location

S_0 = The prediction location

N = The number of measured values

The Kriging tool fits a mathematical function to a specified number of points, or all points within a specified radius, to determine the estimated surface for each location.

III. RESULTS

The most impact phytotoxic pollutants emitted in the aluminium reduction process is fluoride and is found as Hydrogen fluoride and particulate Fluoride *i.e.* cryolite (Na_3AlF_6) Calcium Fluoride (CaF_2). These are produced mainly by volatilization of fluoride containing electrolyte. In Table 1 and 2, samples of urine, serum and nails were taken for the analysis. Fluoride content varied in serum from 0.06-0.17 mg/lit in case of pot room workers and 0.01-0.04 mg/lit in case of non-pot room workers. In nails, it varies from 0.09-3.77 mg/lit and 0.39-1.15 mg/lit in case of pot room workers and non-pot room workers, respectively. In urine, it varied from 0.53-9.50 mg/lit in pot room workers and 0.29 to 1.80 mg/lit in non-pot room workers, respectively.

Fluoride concentration in some of the cases recorded beyond the prescribed limits, however there was no visible sign of fluorosis recorded in any of the pot room workers or non-pot room workers. Persons' background information was also recorded in the attached annexure and it was also discussed with them whether they used any fluoride containing material before they joined Hindalco. It came out in many cases that they were using high fluorinated eatables before their joining. We have observed high fluorinated water in nearby villages and also observed some cases of fluorosis

TABLE 8. Water quality parameter in the study area.

Location No.	LAT	LONG	pH	Fluoride (mg/l))	Hardness (mg/l))
1	24.2050	83.0649	7.0	0.64	110
2	24.2163	82.8218	7.5	1.1	246
3	24.2306	82.8218	7.0	0.45	112
4	24.2065	82.8270	7.6	1.2	179
5	24.2069	82.8260	7.5	1.02	186
6	24.9689	82.8264	7.5	1.66	164
7	24.2090	82.8249	7.5	1.03	176
8	24.2165	82.8209	7.1	0.47	100
9	24.1843	82.7710	7.4	0.29	70
10	24.1870	82.7760	7.5	1.77	210
11	24.2166	82.8112	7.0	0.65	112
12	24.2173	82.8101	7.0	1.26	121
13	24.2252	82.8112	7.1	2.33	123
14	24.2157	82.8433	7.5	2.89	160
15	24.2164	82.8222	7.2	0.45	190
16	24.2135	82.7512	7.5	4.01	265
17	24.1263	82.7856	7.4	7.57	220
18	24.1269	82.7926	7.1	11.13	110
19	24.1265	82.7695	7.0	0.65	79
20	24.1235	82.7653	7.0	0.666	103
21	24.2156	82.8112	7.2	6.81	173
22	24.2153	82.8093	7.4	1.02	148
23	24.2069	82.8133	7.5	18.25	225
24	24.2159	82.8123	7.0	1.03	105
25	24.1328	82.8126	7.1	0.47	145
26	24.1325	82.8113	7.0	0.475	146
27	24.1399	82.7622	7.5	10.17	237
28	24.1490	82.7599	7.4	7.3	253
29	24.1460	82.7650	7.2	6.7	176
30	24.1904	82.7648	7.3	11.85	146
31	24.1902	82.7790	7.0	12.41	108
32	24.1763	82.7668	7.6	12.97	215
33	24.1765	82.8156	7.2	13.53	230
34	24.1768	82.8142	7.7	26	226
35	24.1985	82.8335	7.5	14.65	222
36	24.2073	82.8335	7.1	15.21	241
37	24.2263	83.0501	7.0	1.3	76
38	24.2320	83.0501	7.3	16.33	235
39	24.2331	83.0523	7.7	16.89	248
40	24.2064	82.8230	7.5	4.6	206
41	24.2134	82.7512	7.1	11.1	115
42	24.1260	82.7856	7.0	14	87
43	24.1163	82.7856	7.3	0.7	147
44	24.1290	82.7923	7.5	2.4	138

due to consumption of that water and impact of this fluoride resulted in dental fluorosis also (Figure 5). Hindalco has taken some measures to provide clean and safe water to affected villagers. Tables 1 and 2 describe that fluoride concentration in urine is more in comparison to serum.

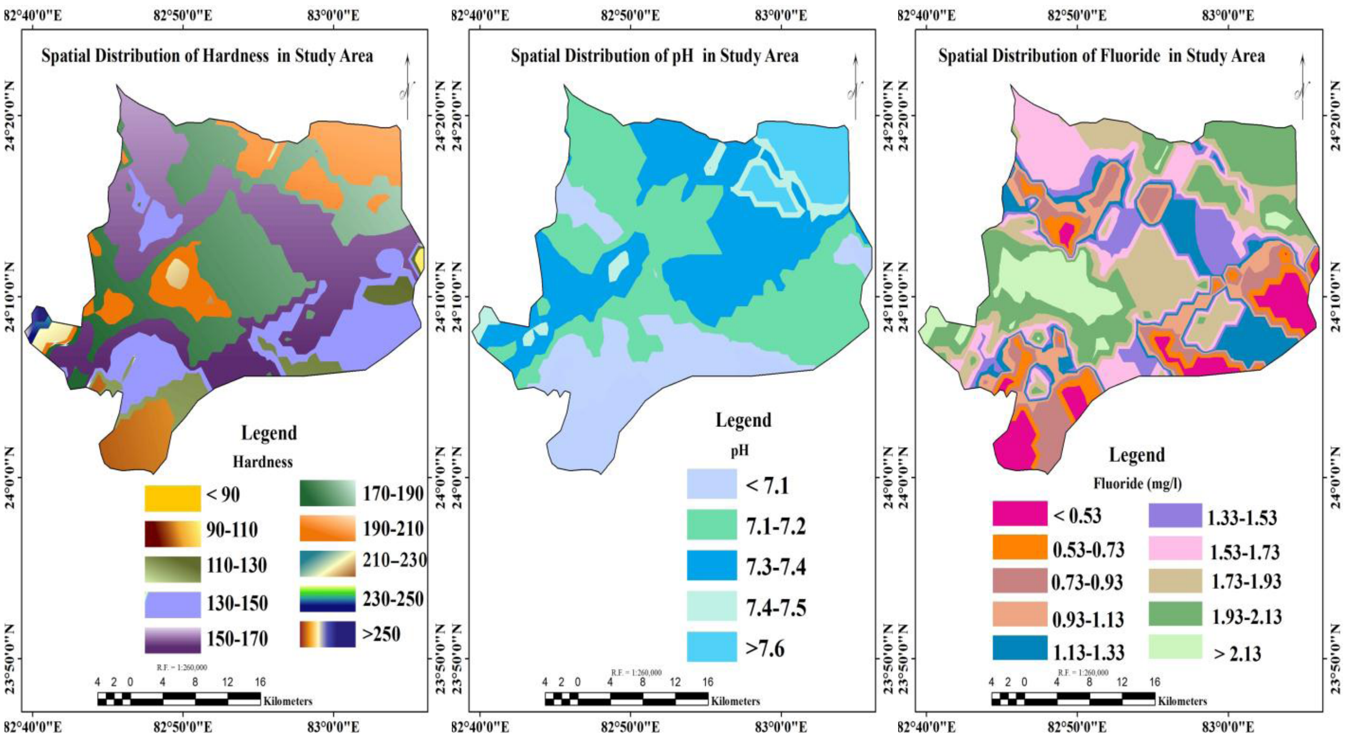

FIGURE 4. Spatial Distribution of Hardness, pH and Fluoride.

A. PURIFICATION-MORBIDITY

Morbidity is defined as extent of illness, injury, or disability in defined population. Information was collected on the type of morbidity occurrence in the family (dental fluorosis, skeletal, skin disease etc.). The association between purification and morbidity is considered negative when expected value (E) is greater than observed value (O) and considered positive when E is smaller than O as shown in Table 4. Applying chi square test provided significant result in case of purification morbidity as the value of $P<0.001$ is less than the ideal value of significance which we assumed ($p<0.005$). The calculated value of χ^2 was 18.728. Hence P stretch out between the range of significance. Occurrence of morbidity was due to improper purification of water, improper storage of drinking water causes a greater numbers of diseases like dental fluorosis, skeletal, skin disease etc.

B. OVERCROWDING-DYSENTERY

The association between overcrowding and dysentery is considered negative when expected value (E) is greater than observed value (O) and considered positive when E is smaller than O as shown in Table 5. Chi square test gives us negative result as the value of $P = 0.665$ is greater than the ideal level of significance which we set ($p<0.05$). The value of χ^2 is 1.621. This shows that occurrence of dysentery is not much influenced by overcrowding but if frequency will increase then it will increase dysentery. Dysentery is very much influenced by purification of water.

C. EDUCATION-MORBIDITY

The association between education and morbidity is considered negative when expected value (E) is greater than observed value (O) and considered positive when E is smaller than O as shown in Table 6. The result is significant as the value of $P<0.001$ lies in the range of significance ($P<0.05$). The value of χ^2 is 18.171. The education and morbidity have direct relation as less the education, greater the occurrence of disease, since they do not have proper knowledge about purification and sanitation. In Sonbhadra area, women are uneducated resulting in a high chance of disease occurrence.

D. OVERCROWDING-SKIN DISEASE

The association between overcrowding and skin disease is considered negative when expected value (E) is greater than observed value (O) and considered positive when E is smaller than O as shown in Table 7. The result is not significant as the value of $P = 0.088$ is greater than the value of significance which we set. The value of χ^2 is 6.538. Overcrowding and skin disease have direct relation if the overcrowding frequency increases then skin disease will increase as problems related to overcrowding affect the livelihood conditions. Skin - disease is very much influenced by poor housing condition.

E. SPATIAL DISTRIBUTION OF HARDNESS, pH AND FLUORIDE

Variability of F^- from its average chemical composition in the region is shown in Figure 4. Major part of the study area

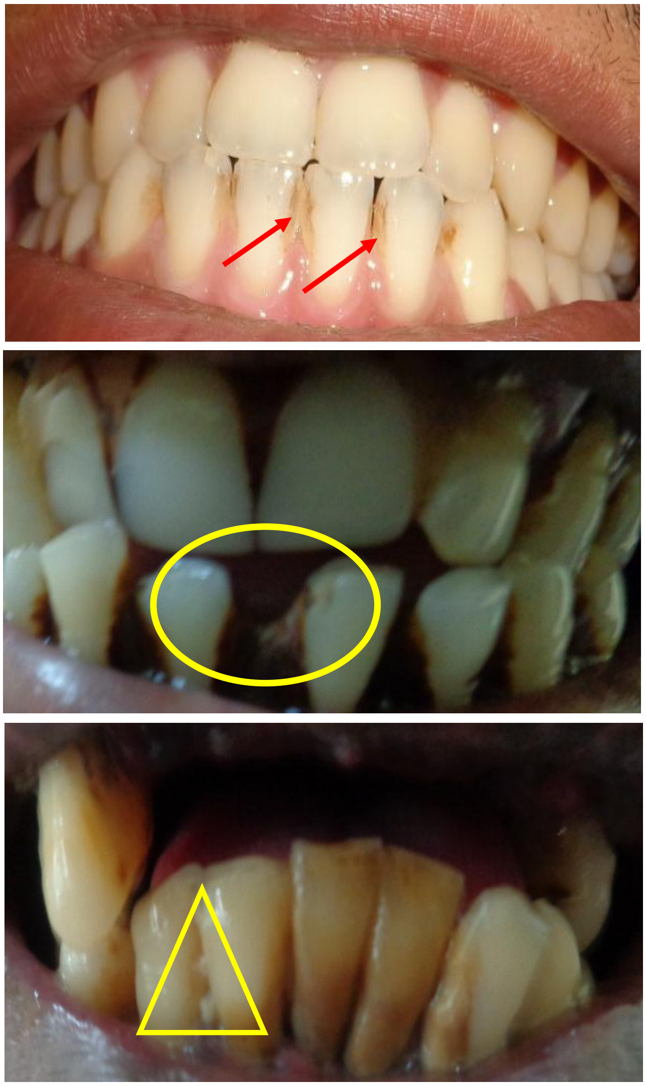

FIGURE 5. **Dental flurosis can occur in people exposed to high levels of fluoride in their drinking water.**

falls in the region where the average value of F- is 1.6 mg/l. The value of $F^{-} > 1.5$ mg/l (Table 7) in water makes it unsuitable for drinking purposes [29], [30]. High values of F were noticed at Pipari, Harauli, Murdhava, Kharpathar, Jokahi, Tharpathar, with a maximum of 1.94 mg/l, along with high pH and hardness with max 7.5 and 210, respectively indicating that water in these area is not fit for drinking.

Elevated levels of fluoride, pH and hardness in ground water can be due to leaching from soils or weathering rock, runoff and infiltration of chemical fertilizers from agricultural areas. Septic and sewage treatment system discharging its waste product in communities along with fluoridated water supplies, liquid waste from industrial sources, on Renukoot District is largely a result of base-exchange softening. From the above results, it seems to be a possibility that these processes are responsible for elevated fluoride levels in groundwater around study area (Renukoot District, U.P.). From the above results it is clear that the ground water from Pipari, Jokahi and Tharpathar parts of study area has quality problems like, high fluoride content 1.6, 1.76 and 1.8 mg/l (Table 8). People must be advised to avoid the use of drinking water from these sources which may result in dental fluorosis. Consumption of water with low fluoride concentrations can reduce the risk of dental cavities but higher amounts of fluoride pose a risk as it is known to cause dental fluorosis (Figure 5). Continous intake of high fluoride water for a longer time may result in changes in bones, an illness known as skeletal fluorosis which is cause of joint pains in addition to being hazardous for one's health.

F. SPATIAL DISTRIBUTION OF HARDNESS, pH AND FLUORIDE

The color variance shows the level of fluoride, hardness and pH. It shows when the fluoride concentration is high in dissolved water then hardness of water is also high wheras pH has low value. When the fluoride level is varying between 22-29mg/l at that time hardness of water is also having increasing rates, varying from 270-280 mg/l whereas at that time pH of water is maintained between the range of 6.9-6.95(less alkaline). When the fluoride concentration decrease then equivalently hardness of water also decreases and pH increases. At pH 7.8 the water hardness is varying between 100-120mg/l so the fluoride level is lower. The positive correlation lies between the alkalinity and the pH. When fluoride level decreases pH value increases hence alkalinity increases at the same time hardness of water also decreases with decrease in fluoride level.

IV. DISCUSSION AND CONCLUSION

The study has established the applicability of GIS technology in association with laboratory analysis in evaluation of groundwater quality with special reference to fluoride as well as spatial variability mapping in Renukoot (U.P., India) for the year 2007. It was found that about 70% of the study area lies under a moderately to severely fluoride polluted (1.6 to 2.1 mg/l) level of contamination. Geo-statistical analysis is proved to be an efficient tool for delineation and mapping of not only of fluoride but also for any particular water quality parameter (like pH, hardness etc.). It is found that fluoride concentration is highest (25 mg/ml) in the region with highest hardness of water (280 mg/ml), and is higher as compared to the pH level. Fluoride concentration varies rapidly with change in water hardness as compared to the pH of the water samples. The lower pH contributes to low fluoride concentration (4 mg/ml) and high pH contributes slighly higher up to 14 mg/ml. Thus, water with hardness values above 180 mg/ml and pH ranges lower than 7.1 and higher than 7.4 is not suitable for drinking purposes, as it may contain high fluoride concentration which results in fluorosis and dental disease. The most dangerous level where fluoride concentration is highest (26 mg/ml) is at 280 mg/ ml hardness and 7.8 pH. The study concluded that water is safe for drinking purposes with low hardness (60 to 140 mg/ml) and pH range between 7.1 to 7.4.

As per present study, it was found that fluoride had negligible effect on fauna around Hindalco. The industry has set-up state of the art technology *i.e.* advanced Dry Scrubbing System (DSS) to minimize the emission of fluoride to the environment, which indicates that the industry is an eco-friendly aluminium plant to the environment. The above results were considered while taking precaution or preventive measures of health conditions by the management. The clinical significance lies in maintaining hygienic conditions while preventing any possible effect of fluoride on the workers of the industries, as this will affect the production as well as the human value in terms of physical capabilities and social aspects in providing medical facilities. Thus the above study concludes the named industries as eco-friendly environment while maintaining the healthier working environments. Therefore, monitoring of the industry from time to time and conducting tests of the workers could help in keeping them healthy.

ACKNOWLEDGMENT

Authors are grateful to Dr. A. K. Susheela for providing the valuable suggestion and guidance during lab analysis. They are also thankful to Hindalco industries, Renukoot, UP, India for providing all necessary support throughout for carrying out the research.

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