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Fluoride Concentrations in Ground Waters of Visakhapatnam, India

D. R. R. Sarma, S. L. N. Rao

Public Health & Environmental Engineering Laboratories, Department of Civil Engineering, Andhra University, Visakhapatnam, 530003, India

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The origin of fluoride in groundwater, the incidence and intensity of fluorosis was first recognised during 1940 (Dean, 1942; Eagers, 1969, Hem 1959; Galgon and Lamson, 1953). The chief sources of fluorides in ground waters are the fluoride bearing minerals like fluorspar, cryolite, fluorapatite and hydroxy apatite in the rocks and sediments, the solubility of which were found to be less compared to other fluorides. The fluoride content of the surface and underground water is a function of many factors such as availability and solubility of the patent fluoride minerals, without which these waters come in contact with rock porosity, velocity of the flowing waters, temperature, pH and concentration of calcium ions present in the water (Largent, 1961). The high fluoride content in ground waters generally associated with low concentration of Calcium, magnesium and high concentrations of bicarbonate and in certain cases nitrate ions. The solubility of calcium fluoride would seemingly be the limiting factor for the concentration of fluorides in water with high calcium content.

The fluoride concentration in ground waters of India varies considerably. In some parts of India, the fluoride levels were below 0.5 mg/L, while in certain other places values as high as 20.0 mg/L were noticed (Handa, 1975). The occurrence of fluoride in groundwater and its relationship with other ions for a small region in Visakhapatnam, India was conducted (Sharma, 1983).

In the present study, the fluoride levels in ground waters of Visakhapatnam were studied in an exhaustive way, covering almost all the important areas. Geologically the study area is covered by rocks of Eastern Ghats, Tectonic Complex, of the Archaen era. The major rocks are khondalite, leptynite and charnokite. The rocks constitute essentially sillimanite, quartz, feldspar, garnets and magnetite. The water table in the region is shallow and varies in depth from 10 feet to 40 feet in the plain areas fluctuating weathered and fissured zones. A case study has been taken up on the ground waters of Jaggayyapalem and Sheelanagar, where abnormally high levels of fluoride existed and people were suffering with the dreadful disease of fluorosis. To score the incidence and degree of manifestation of dental fluorosis, classification of Dean (1942) was followed. The information of age, sex, period of stay, incidence and degree of manifestation of fluorosis concerned with every individual was collected using a simplified questionnaire.

Correspondence to: S. L. N. Rao

MATERIALS AND METHODS

Well and borewell water samples collected from 25 major areas covering almost every corner of Visakhapatnam city. The sampling was done at random on yearly basis during the period 1990-92 and analysed for p^H fluoride, E.C. and other relevant chemical parameters. Simultaneously the analysis was performed for chemical parameters in Jaggayyapalem and Sheelanagar areas in order to interpret the prevalence of fluorosis in the area. Soluble Sodium Percentage (SSP) and Residual Sodium Carbonate (Eaten, 1950) were also calculated. Similarly a few soil samples were also collected at different depths so as to ascertain the geological origin and natural occurrence of high fluoride levels in the soils of Jaggayyapalem and Sheelanagar areas. The fluoride concentrations were correlated with the depth of the soil sample.

Fluoride concentrations in water and soil were measured using Orion expandable microprocessor Ion analyser model EA™ 940 with a fluoride ion selective solid state electrode. A.R. grade sodium fluoride was used for preparation of standard solutions. Deionised distilled water was used to make up all solutions. The electrode was calibrated using standards in the ranges of 0.01 -0.1 mg/L; 0.1 - 1.0 mg/L; 1.0- 10.0 mg/L and 10.0 mg/L - 100 mg/L. Standards were buffered with an equal volume of CDTA buffer and all measurements were made at room temperature, 28° C with constant stirring (APHA, 1985). Water samples to be measured were prepared similarly, using two or three standard solutions in the same range, the reproducibility of the instrument was checked. The response time lies between 2-5 seconds. The lower limit of detection is 10^{-6} moles /L. The relative error was found to be less than + 0.2%. Instrument was recalibrated frequently when the concentration of fluoride exceeds the range. As the ion selective electrode analyser is a logarithmic device, the electrode gives a constant precision throughout its dynamic range.

Two types of leaching techniques, distilled water and dilute hydrochloric acid were applied to extract fluoride from soils. Distilled water leachates were obtained by adding 20 ml of distilled water to 2.0 g of air dried soil sample in a 100 ml Torson plastic beaker and stirring until the sample was homogeneously wetted. The mixture was allowed to stand for 30 minutes and then decanted to a filter. A further 20 ml of distilled water was added and swirled, allowed to stand for 10 minutes and then decanted to filter and repeated to give a total of 3 x 20 ml filtered leachate water. After complete draining, the filtrate p^H was determined. After adding equal volume of TISAB (Total Ionic Strength Adjusting Buffer) to the remaining leachate, the fluoride content was determined. Dilute hydrochloric acid leachates were obtained by using 0.1 N HCl in a parallel procedure on the same sample already leached with distilled water. The filtered initial leachates was neutralised with 1 N sodium hydroxide (0.5 to 1.0 ml) and then determined the fluoride content after adding equal volume of TISAB to the leachate.

Total fluoride in all soil samples were determined by the sodium hydroxide fusion method (Hockings et al., 1980). Variation of these leach procedures are given in Table 5.

RESULTS AND DISCUSSION

The mean chemical composition of ground waters having different fluoride concentrations in wells and borewells of Visakhapatnam area during the period 1990-

1992 have been given in table-la& lb. From this table it was observed that in general the concentration of fluoride in ground waters of Visakhapatnam were well within the limits (0.5 -1.5 mg/L) in most of the areas. 42% of the samples analysed possessed fluoride concentration in the range 0.5 - 1.0 mg/L while 52% of them have shown fluoride levels in the range 1.0 -1.5 mg/L. However 4.5% of the borewell and wells showed fluoride levels as high as 4.0 mg/L. It is evident that Jaggayyapalem and Sheelanagar areas (No.22) have shown higher concentrations of fluoride (as high as 8.0 mg/L) in the groundwater thereby indicating the existing endemic fluorosis among the population in the area. Na+ was the dominant cation and its value ranged from 3.0 -13.7 meq/L with a mean value of 4.7 meq/L. It constituted 56% of the total cations. Ca^{+2} (26%) and Mg^{+2} (17%) were next in abundance to Na^{+} the concentration of K^{+} was least of all the cations. The HCO_3^- was the most dominant anion and its concentration ranged from 3.9 - 8.3 meq/1. It constituted around 65% of the total anions. The Cl^- varied from 3.6 - 7.6 meq/1 was next in abundance to that of HCO_3^- and was followed by SO_4^{-2}. The CO_3^{-2} content was negligible in all samples.

Table 1a Composition of Ground water with different fluoride concentrations in wells and bore wells of Visakhapatnam

Sl. No.	LOCATION/AREA	No.of Samples	pH	E.C mmho/ cm	Yearwise concentration of fluoride, mgL-1					
					1990		1991		1992	
					Av	Range	Av	Range	Av	Range
1	A.K.PALEM, LALITHANAGAR	12	7.50	1.05	1.03	0.90-1.10	1.04	0.95-1.10	1.05	0.96-1.12
2	GURUDWAR, SEETHAMPETA	10	7.26	1.20	1.03	0.78-1.22	1.05	0.75-1.18	1.06	0.80-1.17
3	M.V.P.COLONY	26	7.65	1.45	1.10	0.78-2.10	1.35	0.25-4.30	1.00	0.35-2.23
4	RISHIKONDA	05	8.04	1.30	1.08	1.05-1.15	1.09	1.06-1.12	1.10	1.05-1.15
5	ESKATHOTA, SHIVAJIPALEM	16	7.46	1.26	0.98	0.85-1.20	0.99	0.83-1.25	1.02	0.88-1.30
6	WALTAIR, E.POINT & L. BAY	18	7.58	1.14	1.05	0.92-1.25	1.10	0.95-1.30	1.12	0.78-1.28
7	POLICE QTRS. INDIRANAGAR	10	7.05	0.980	1.20	1.08-1.32	1.16	1.07-1.26	0.21	1.14-1.32
8	MADHAVADHARA	07	7.46	1.22	0.71	0.60-0.92	0.76	0.62-1.02	0.77	0.60-0.78
9	MADHURAWADA	09	6.94	0.86	0.76	0.48-1.08	0.77	0.45-1.30	0.77	0.41-1.08
10	MURALINAGAR	15	7.58	1.08	1.00	0.65-1.25	1.00	0.64-1.25	1.03	0.68-1.25
11	DONDAPRTHI, NEW COLONY	10	7.36	1.16	0.86	0.65-1.04	0.91	0.68-1.10	0.92	0.65-1.20
12	DABAGARDENS, M.R. PETA	11	7.22	1.36	1.11	0.84-1.32	1.16	0.87-1.38	1.19	0.88-1.34
13	GNANAPURAM, K.PALEM	11	7.18	1.12	0.72	0.52-0.92	0.77	0.62-0.95	0.79	0.65-0.95
14	GOPALAPATNAM	12	7.25	0.908	0.69	0.24-1.15	1.69	0.28-1.25	0.72	0.34-1.28
15	KAILASAPURAM, T.PALEM	14	7.16	0.840	0.95	0.80-1.20	0.98	0.83-1.25	1.00	0.85-1.25
16	MARRIPALEM	10	7.23	0.978	1.10	1.03-1.28	1.16	1.05-1.25	1.16	1.08-1.26
17	H.B.COLONY, V. PALEM	10	7.68	0.890	1.17	1.11-1.25	1.20	1.15-1.28	1.21	1.10-1.28
18	SEETHAMMA DHARA	12	7.20	0.880	0.77	0.55-1.12	1.19	0.58-0.95	0.79	0.55-1.02
19	OLD POSTOFFICE	14	7.28	0.96	0.97	0.85-1.10	1.97	0.80-1.12	0.98	0.82-1.15
20	DRIVERS COLONY	06	7.34	1.30	1.03	0.92-1.10	1.02	0.98-1.05	1.03	0.95-1.10
21	GAJUWAKA	20	7.18	1.28	1.16	0.91-0.45	1.16	0.86-1.45	1.20	0.85-1.51
22	JAGGAYYAPALEM, S.NAGAR	30	7.90	2.50	4.52	1.38-8.10	4.03	1.43-8.33	4.53	1.48-8.35
23	VENKATAPURAM	14	7.30	1.06	0.42	0.24-0.62	0.44	0.30-0.65	0.51	0.31-0.75
24	DIBBAVARAM, GANGAVARAM	18	7.60	1.26	1.12	0.87-1.50	1.05	0.96-1.21	1.10	0.80-1.28
25	SABBAVARAM, PENDURTHI	15	7.40	1.10	0.97	0.74-1.31	1.00	0.57-1.30	1.04	0.80-1.35

Table 1b

S.No.	LOCATION / AREA	Na^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{-2}	HCO_3^-	SSP	RSC
1	A.K.PALEM, LALITHANAGAR	4.365	3.226	1.634	4.868	0.970	4.970	47.32	0.400
2	GURUDWAR, SEETHAMPETA	4.762	3.250	1.812	5.108	1.080	5.180	48.47	0.118
3	M.V.P.COLONY	5.132	2.634	3.361	5.785	1.240	6.460	46.12	0.465
4	RISHIKONDA	4.693	2.580	2.603	5.332	1.150	5.624	47.52	0.441
5	ESKATHOTA, SHIVAJIPALEM	4.720	2.310	2.216	5.214	0.935	5.330	51.05	0.804
6	WALTAIR, E.POINT & LAWSONS BAY	4.800	3.490	1.430	5.012	0.976	5.050	49.38	0.130
7	POLICE QUARTERS, INDIRANAGAR	3.989	2.652	0.897	4.305	0.843	4.200	52.92	0.651
8	MADHAVADHARA	4.669	3.184	1.654	4.996	0.998	4.960	49.11	0.122
9	MADHURAWADA	3.432	2.849	0.953	3.776	0.869	3.900	47.44	0.098
10	MURALINAGAR	4.742	3.132	1.772	4.972	1.05	5.080	49.16	0.176
11	DONDAPRTHI, NEW COLONY	4.420	2.765	1.932	5.078	0.830	4.800	48.48	0.103
12	DABAGARDENS, MAHARANI PETA	4.803	2.185	3.920	5.316	0.740	5.40	44.03	-
13	GNANAPURAM, KANCHARAPALEM	4.213	2.861	2.024	4.732	0.590	5.123	46.31	0.238
14	GOPALAPATNAM	3.818	2.689	1.756	4.187	0.460	4.740	46.20	0.295
15	KAILASAPURAM, T.PALEM	3.340	2.537	1.388	3.656	0.390	4.100	45.97	0.175
16	MARRIPALEM	3.163	2.132	1.659	4.255	0.500	3.980	45.48	0.189
17	H.B.COLONY, VENKOJI PALEM	3.723	3.084	1.953	3.978	0.370	4.130	42.50	-
18	SEETHAMMA DHARA	3.486	2.783	1.854	3.892	0.320	4.650	42.91	0.013
19	OLD POSTOFFICE	3.791	2.954	1.883	4.146	0.430	5.840	43.93	1.003
20	DRIVERS COLONY	4.892	2.239	2.481	5.023	0.960	6.20	50.89	1.480
21	GAJUWAKA	4.65	3.657	0.890	4.830	0.850	6.05	50.55	1.503
22	JAGGAYYAPALEM, SHEELANAGAR	13.70	2.860	2.801	7.635	1.850	8.280	70.76	2.62
23	VENKATAPURAM	4.568	2.793	1.186	4.625	0.768	4.530	53.44	0.551
24	DIBBAVARAM, GANGAVARAM	4.864	3.050	1.184	5.056	0.942	4.800	53.46	0.566
25	SABBAVARAM, PENDURTHI	4.786	2.891	1.230	4.895	0.865	4.650	53.73	0.524

Note: All values express in meq. L-1; SSP=Soluble Sodium Percentage = $\dfrac{Na^+}{(Ca^{2+} + Mg^{2+} + Na^+)} \times 100$

RSC = Residual Sodium Carbonate = $(HCO_3^-) - (Ca^{2+}+Mg^{2+})$

Table-2 shows year wise mean chemical composition of ground waters with different fluoride concentrations at Jaggayyapalem and Sheelanagar areas. In Table-3 the correlation coefficient values for various sets of combinations amongst the parameters analysed were given. From Table-1 and Table-2 it was evident that high fluoride waters had invariably high concentrations of bicarbonate and sodium and low concentrations of calcium and magnesium. This fact is evident from Table-3, wherein a high positive correlation was observed between bicarbonate vs. Fluoride and that negative correlation for calcium vs. Fluoride, Low concentration of calcium and magnesium in high fluoride waters is due to very low solubility of CaF_2 ($Ksp = 1 \times 10^{-10.57}$ at 25°C). Though solubility of MgF_2 is much higher than CaF_2 ($Ksp = 7.0 \times 10^{-9}$) its precipitation in high fluoride waters cannot be ruled out. High concentrations of fluoride along with high sodium content shows high degree of mineralisation and also a source for its occurrence in groundwater. In fact most of the ground waters having fluoride concentrations above 2.0 mg/L had sodium percentage above 70. This has been observed in other parts of India. Though fluoride concentrations increasing with E.C. (Electrical Conductivity) values, it is not necessary that ground waters with low E.C. values may not have high concentration of fluoride. Low concentrations of calcium compared to sodium in Jaggayyapalem and Sheelanagar area indicated that the absence of readily soluble calcium minerals or the action of base exchange where by calcium originally in the water has been exchanged

for sodium. The bicarbonate rich water in this area causes precipitation of calcium and magnesium compounds in soil resulting in high RSC and SSP values. This fact is evident from table- 1a, lb and table -4.

Table 2 Chemical Composition of Ground Waters in Jaggayyapalem and Sheelanagar Areas (year wise)

S. No.	Parameter	1990		1991		1992	
		Av.	Range	Av.	Range	Av.	Range
1	pH	7.90	7.6-8.18	7.91	7.68-8.20	7.86	7.58-8.06
2	E.C	2.50	0.820-3.76	2.43	0.786-3.80	2.58	0.860-3.92
3	Bicarbonate	502	260-830	5.40	240-780	495	250 -730
4	Fluoride	4.52	1.38-8.10	4.03	1.43-8.33	4.53	1.48-8.35
5	Chloride	271	106-340	260	119-356	265	130-370
6	Sulphate	86	45-180	90	35-176	95	56-184
7	Sodium	313	110-430	294	96-415	320	115-420
8	Potassium	26	8-36	33	9.52	35	12-45
9	Hardness	262	168-390	280	170-440	296	180-430
10	Calcium	48	32-78	54	39-90	56	48-95
11	Magnesium	44	24-62	45	35-66	52	38-84

Note : All values express in mg. L-1 except pH and E.C.

E.C = Electrical Conductivity expressed in m.mho cm-1

AV = Average values of 25 samples

Table 3 Correlation Coefficient values for various sets of combinations yearwise (1990 - 1992)

YEAR	E.C. Vs. F-	E.C. Vs. Ca^{2+}	Ca^{2+} Vs. Hardness	F-Vs.Ca^{+2}	F-Vs.HCO_3^-
1990	0.313	0.114	0.589	-0.496	0.487
1991	0.305	0.128	0.530	-0.392	0.513
1992	0.321	0.139	0.465	-0.458	0.467

E.C. = Electrical Conductivity

From the various leaching techniques summarised in table 5 it is clear that water extracts only 15- 25% of the total fluoride in a non-exhaustive leaching on soils. In a parallel procedure, leaching with 0.lM HCI on the same soil sample, already leached with distilled water gave much higher extraction of fluoride (20 to 30% of additional) from soil. In this way it was clear that at least significant portion of fluoride present in soil was insoluble in water but soluble in dilute mineral acids, i.e. a possible calcium fluoride. The effectiveness of various leaching procedures were also tested by spiking soil samples with known standard highly soluble ammonium fluoride. It was found that only 20 to 30% of fluoride was leached with distilled water. Whereas with dilute hydrochloric acid and sodium hydroxide fusion techniques 50 to 60% and 75 to 80% of fluoride was leached respectively.

The present study revealed that out of 250 male and female subjects examined for degree of discoloration of teeth 45.18% and 40% males and females respectively showed moderate to severe symptoms. In the age group upto 8, 16 percent were normal and 9, 14, 45 and 18 percent of subjects exhibited very mild, moderate and severe symptoms respectively. 13 and 22 percent of subjects in the age group 13-22 exhibited moderate and severe symptoms respectively and rest were normal. Fifteen and 10 percent of subjects exhibited moderate and severe symptoms in 25-32 age group. In the age group 45 - 60, one out of 9 individuals examined exhibited severe symptoms. The incidence of fluorosis remains almost same in both sexes, the prevalence of severe form of fluorosis in the age group up to 8 was more in female than the males.

Table 4 Relative abundance of different Cations (O/. of the total Cations) and Different Anions (% of the total anions) in ground waters of Jaggayyapalem and Sheelanagar Areas

E.C	CATIONS				ANIONS		
u mho cm-1	Na^{+}	Ca^{+2}	Mg^{+2}	K^{+}	HCO_3^{-}	Cl^{-}	SO_4^{-2}
<1,000	51.6	38.50	7.83	2.6	65.39	23.4	6.9
1000-1500	54.8	26.0	11.38	4.6	66.1	26.3	7.3
1500-2500	59.2	22.4	13.0	4.8	62.35	29.34	8.1
>2500	71.6	11.1	14.8	2.8	58.1	31.4	9.9

E.C. = Electrical Conductivity

Table 5 Fluoride Concentrations in Soil Samples from Jaggayyapalem and Sheelanagar Areas

Location / Area	Depth (ft.)	Fluoride Concentration (ug/g) with different extracting techniques			
		Distilled Water	0.1M H Cl	Total Leachable	NaOH fusion (total)
Sheelanagar	3	10.4	22.4	37.2	33.8
Sheelanagar	5	12.8	26.8	41.4	37.6
Jaggayyapalem, near to well	3	22.4	34.5	57.9	65.5
Unhygenic surroundings	5	25.5	37.6	63.1	74.4
At the entrance of Jaggayyapalem	3	20.1	33.6	53.7	57.8
Village near Rly., track	5	21.8	34.8	56.6	62.5
Jaggayyapalem near Secondary School	3	23.4	36.4	59.8	68.6

Hence it can be concluded that very high fluoride (4.0 - 8.0 mg/L) concentrations were observed in certain wells of Jaggayyapalem and Sheelanagar area besides having lower values of calcium and magnesium. The abnormal fluoride levels could be due to the

local geology as is evident from high fluoride levels obtained in soil leaching studies. No other significant factor can be ascertained except for the natural occurrence of fluoride.

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