

COMMON COMPOSITION CHARACTERISTICS OF FLUORIDE BEARING GROUNDWATERS

V.V. JAGANNADHA SARMA and A. NARAYANA SWAMY

Dept. of Geophysics, Andhra University, Waltair - 530003, India

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Abstract. During routine groundwater surveys of the Visakhapatnam basin, concentrations of fluoride ions above the permissible limit of 1 to 1.5 mg l⁻¹ have been detected near the village Jaggayyapalem. The fluoride bearing groundwaters of the area were compared with fluoride bearing groundwaters from different parts of the world. It is observed that they contain meager amounts of Ca and Mg and large amounts of Na and bicarbonate. Linear statistical relationships are obtained between fluoride and Ca plus Mg, and bicarbonate.

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1. Introduction

The existence of fluoride in groundwater and its effect on tooth enamel was recognized around 1930 (Hem, 1959). It is observed that waters having fluoride ion concentration of more than 1 mg l⁻¹ (Handa, 1975) to 1.5 mg l⁻¹ (Todd, 1959) cause dental defects and retardation of bone growth. It is also observed (Dregne, 1967) that not only the concentration of fluoride in the waters but also the total amount of water consumed determines the effect on health. A detailed investigation regarding the occurrence of fluoride in the groundwater and its relationship with other ions was conducted for a small region, Jaggayyapalem situated in Visakhapatnam basin of Andhra Pradesh State in India. The available data from other parts of the world are also considered in the present investigation to generalize the characteristics of fluoride bearing groundwaters.

2. Survey Program

A regular survey of the groundwater resources of Visakhapatnam basin of the Andhra Pradesh State in India has been carried out by the Geophysics Department of Andhra University since 1974. Groundwater samples from the area are analyzed for Ca, Mg, and Na cations and chloride, bicarbonate, and sulphate anions in the manner prescribed by Taylor (1958). The water samples are also analyzed for fluoride ion using the Scott-Sanchis method (World Health Organization, 1958).

3. Results and Discussion

3.1. CONCENTRATION OF VARIOUS IONS

Water samples collected from 11 observation wells near and around Jaggayyapalem village in Visakhapatnam are observed to contain high amounts of fluoride ions (greater

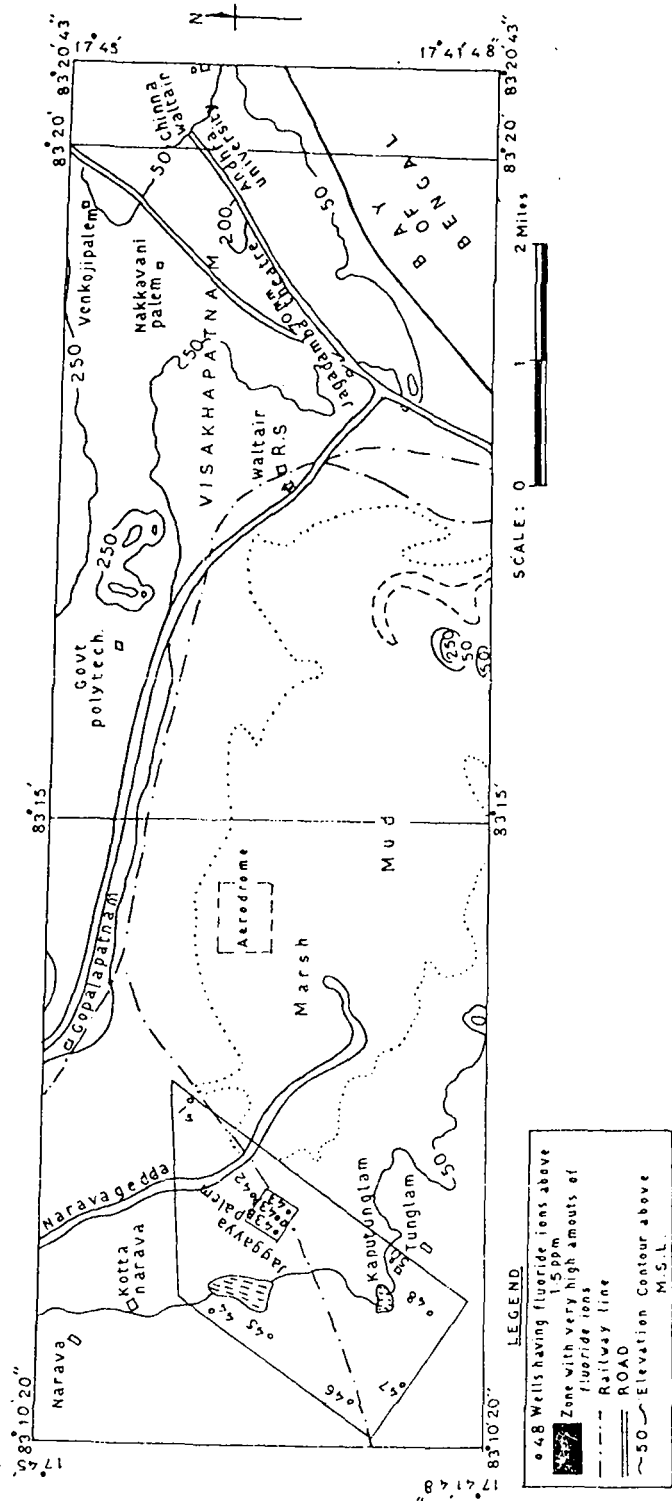


Fig. 1. Location map of fluoride bearing groundwater region near visakhapatnam.

than 1 mg l^{-1}). fluoride ion in the results of the 11 observations the months of October to represent high fluoride. The ionic concentration per liter (mg l^{-1}) Adsorption Ratio (RSC) as observed that the higher conductivity (1979) referred to the geology of the area.

Handa (1975) shows the ionic points out that readily soluble water has been fluoride bearing.

The areal distribution is plotted in figure respectively. From drop and $[\text{HCO}_3^-]$ $[\text{Ca}^{2+}] + [\text{Mg}]$ gives the computed 3b. From the Figure linear correlation between $[\text{F}^-]$

To verify the parts of the well different parts (Follett, 1974) 4b present the the waters mentioning these figures $[\text{HCO}_3^-]$ and $[\text{Ca}^{2+}] + [\text{Mg}]$ those obtained environment of Jaggayyapalem rocks whereas

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than 1 mg l^{-1}). Figure 1 shows the location of the region affected by the existence of fluoride ion in the groundwaters with amounts greater than 1 mg l^{-1} . Table I presents the results of the chemical analyses carried out for the groundwaters collected from all the 11 observation wells around Jaggayapalem village in Visakhapatnam basin during the months of October 1974 and February 1975. These sampling months are selected to represent high and low water table conditions from respective rainy and dry periods. The ionic concentrations of the anions and the cations are expressed in both milligrams per liter (mg l^{-1}) and milliequivalents per liter (meq l^{-1}). Table I also presents Sodium Adsorption Ratio (SAR), Soluble Sodium Percentage (SSP), Residual Sodium Carbonate (RSC) as given by Eaton (1950) and Electrical Conductivity. From Table I it is observed that the groundwater samples collected in the wet period (October) show higher conductivities than the samples from the dry period (February). Sarma *et al.* (1979) referred to this variation by relating the position of the watertable with hydrogeology of the area.

Handa (1975) has indicated that high fluoride bearing groundwaters generally contain low amounts of Ca and high amounts of bicarbonate. Table I shows this feature. It also shows the ionic concentration of Mg^{2+} as low and that of Na^+ as high. Hem (1959) points out that low concentration of Ca compared to Na may indicate the absence of readily soluble Ca minerals or the action of base exchange whereby Ca originally in the water has been exchanged for Na. This may be the significant feature taking place with fluoride bearing groundwaters.

The areal distribution of $[\text{Ca}^{2+}] + [\text{Mg}^{2+}]$, $[\text{F}^-]$, and $[\text{HCO}_3^-]$ in the groundwater is plotted in figures 2a and 2b for the periods of October 1974 and February 1975, respectively. From the figures it can be observed that as $[\text{F}^-]$ rises $[\text{Ca}^{2+}] + [\text{Mg}^{2+}]$ drop and $[\text{HCO}_3^-]$ rises. Figures 3a and 3b show the relation between $[\text{F}^-]$ and $[\text{Ca}^{2+}] + [\text{Mg}^{2+}]$, and $[\text{HCO}_3^-]$ for the wet and dry periods respectively. Table II gives the computed correlation coefficients for the relationships shown in Figures 3a and 3b. From the Figure 3 and Table II it can be concluded that there exists a good negative linear correlation between $[\text{F}^-]$ and $[\text{Ca}^{2+}] + [\text{Mg}^{2+}]$ and positive linear correlation between $[\text{F}^-]$ and $[\text{HCO}_3^-]$.

To verify these relationships for fluoride bearing groundwaters belonging to different parts of the world, the chemical analysis data of fluoride bearing groundwaters from different parts of India (Handa, 1975), Brazos and Burleson Counties, Texas, U.S.A. (Follett, 1974) and Manitoba, Canada (Charron, 1974) are considered. Figures 4a and 4b present the variation of $[\text{HCO}_3^-]$ and $[\text{Ca}^{2+}] + [\text{Mg}^{2+}]$ ions with $[\text{F}^-]$ ion of all the waters mentioned above along with those belonging to Jaggayapalem area. Interestingly these figures also exhibit linear positive correlation ($r = 0.30$) between $[\text{F}^-]$ and $[\text{HCO}_3^-]$ and a linear negative correlation ($r = -0.37$) between $[\text{F}^-]$ and $[\text{Ca}^{2+}] + [\text{Mg}^{2+}]$. The existence of low correlation coefficients when compared to those obtained for Jaggayapalem can be explained as due to the differences in geological environment from which the groundwater samples are collected. In the case of the Jaggayapalem area all of the water samples are collected from the khondalitic suite of rocks whereas the data presented by Handa (1975) itself were collected from different

TABLE I

Results of chemical analyses of fluoride bearing groundwaters of Jaggayyapalem, India

Well No.	Conductivity in micromhos at 25 °C	Chloride		Bicarbonate		Sulphate		Ca		Mg		Na		Fluoride		SAR ^a	SSR ^b	RSC ^c
		mg l ⁻¹	meq l ⁻¹	mg l ⁻¹	meq l ⁻¹	mg l ⁻¹	meq l ⁻¹	mg l ⁻¹	meq l ⁻¹	mg l ⁻¹	meq l ⁻¹	mg l ⁻¹	meq l ⁻¹	mg l ⁻¹	meq l ⁻¹			
<i>October, 1974</i>																		
41	4177	1500	42.300	390.4	6.4025	175	3.6400	88	4.3911	150.8	12.3940	817.8	35.5570	1.2	0.0632	12.3	67.9	-
42	1907	350	9.870	733.0	12.0047	40	0.8320	4	0.1995	31.6	2.5990	457.9	19.9080	3.0	0.1579	16.8	87.7	9.2
43	1371	140	3.948	756.4	12.4049	30	0.6239	4	0.1995	9.7	0.7996	367.5	15.9780	5.0	0.2632	22.6	94.1	11.4
43A	1125	56	1.551	829.6	13.6054	15	0.3119	4	0.1995	9.7	0.7996	332.8	14.4690	6.0	0.3158	20.5	93.5	12.6
43B	1096	65	1.833	732.0	12.0050	15	0.3119	4	0.1995	17.0	1.3993	288.7	12.5510	5.0	0.2632	14.0	88.7	10.4
44	1309	205	5.780	488.0	8.0031	40	0.8320	32	1.5967	53.5	4.3980	198.3	8.6213	1.2	0.0632	5.0	57.0	2.0
45	1462	210	5.923	573.4	9.4040	50	1.0399	16	0.7983	14.6	1.1994	330.5	14.3680	1.6	0.0842	14.4	87.8	7.4
46	1154	170	4.794	451.4	7.4030	45	0.9359	36	1.7963	24.3	1.9990	214.8	9.3374	1.4	0.0737	6.8	71.1	3.6
47	1392	220	6.204	585.6	9.6040	40	0.8320	40	1.9959	29.2	2.3990	281.6	12.2450	1.2	0.0632	8.3	73.6	5.2
48	675	60	1.692	341.6	5.6022	65	1.3520	32	1.5967	34.0	2.7990	97.8	4.2510	1.0	0.0526	2.9	49.2	1.2
50	797	150	4.230	341.6	5.6022	15	0.3119	48	2.3951	63.2	5.1980	58.7	2.5513	0.6	0.0316	1.3	25.2	-
<i>February, 1975</i>																		
41	3377	1600	45.120	244.0	4.0015	209	4.1600	28	1.3971	158.1	12.9900	894.5	38.8900	1.8	0.0947	14.5	73.0	-
42	1266	360	10.150	744.2	12.2048	40	0.8320	8	0.3991	24.3	1.9990	478.2	20.7900	6.0	0.3158	19.0	89.7	9.8
43	1091	130	3.666	976.0	16.0060	50	1.0400	6	0.2993	20.7	1.6990	430.4	18.7140	8.0	0.4210	18.7	90.4	14.0
43A	975	80	2.256	805.2	13.2050	20	0.4160	5	0.2594	13.9	1.1394	333.0	14.4780	7.0	0.3684	17.3	91.2	11.2
43B	709	65	1.833	799.1	13.1050	15	0.3119	6	0.2993	20.7	1.6990	304.8	13.2520	6.0	0.3158	13.3	86.9	11.1
44	887	155	4.370	414.8	6.8030	35	0.7280	40	1.9959	60.8	4.9980	112.9	4.9100	1.6	0.0842	2.6	41.2	5.2
45	972	210	5.922	671.0	11.0040	60	1.2480	4	0.1995	17.0	1.3990	381.2	16.5750	1.8	0.0947	18.5	91.2	9.8
46	815	170	4.794	457.5	7.5030	35	0.7280	8	0.3991	36.5	2.9990	221.4	9.6270	1.6	0.0842	7.4	73.9	4.1
47	709	115	3.243	549.0	9.0035	35	0.7280	6	0.2993	35.3	2.8990	224.9	9.7760	1.6	0.0842	7.7	75.4	5.8
48	645	95	2.679	512.4	8.4033	65	1.3520	16	0.7983	40.1	3.2990	191.8	8.3370	1.6	0.0842	5.8	67.1	4.3
50	507	150	4.230	341.6	5.6022	25	0.5199	56	2.7943	57.2	4.6980	65.8	2.8600	1.2	0.0632	1.5	27.6	-

mg l⁻¹ = milligrams per liter.meq l⁻¹ = milli equivalents per liter.

$$^a \text{ Sodium adsorption ratio} = \frac{(\text{Na}^+)}{\sqrt{\frac{(\text{Ca}^{2+}) + (\text{Mg}^{2+})}{2}}}$$

$$^b \text{ Soluble sodium percentage} = \frac{(\text{Na}^+)}{(\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+)} \times 100$$

$$^c \text{ Residual Sodium Carbonate} = (\text{HCO}_3^-) - (\text{Ca}^{2+} + \text{Mg}^{2+})$$

(In all cases ionic concentrations expressed in meq l⁻¹)

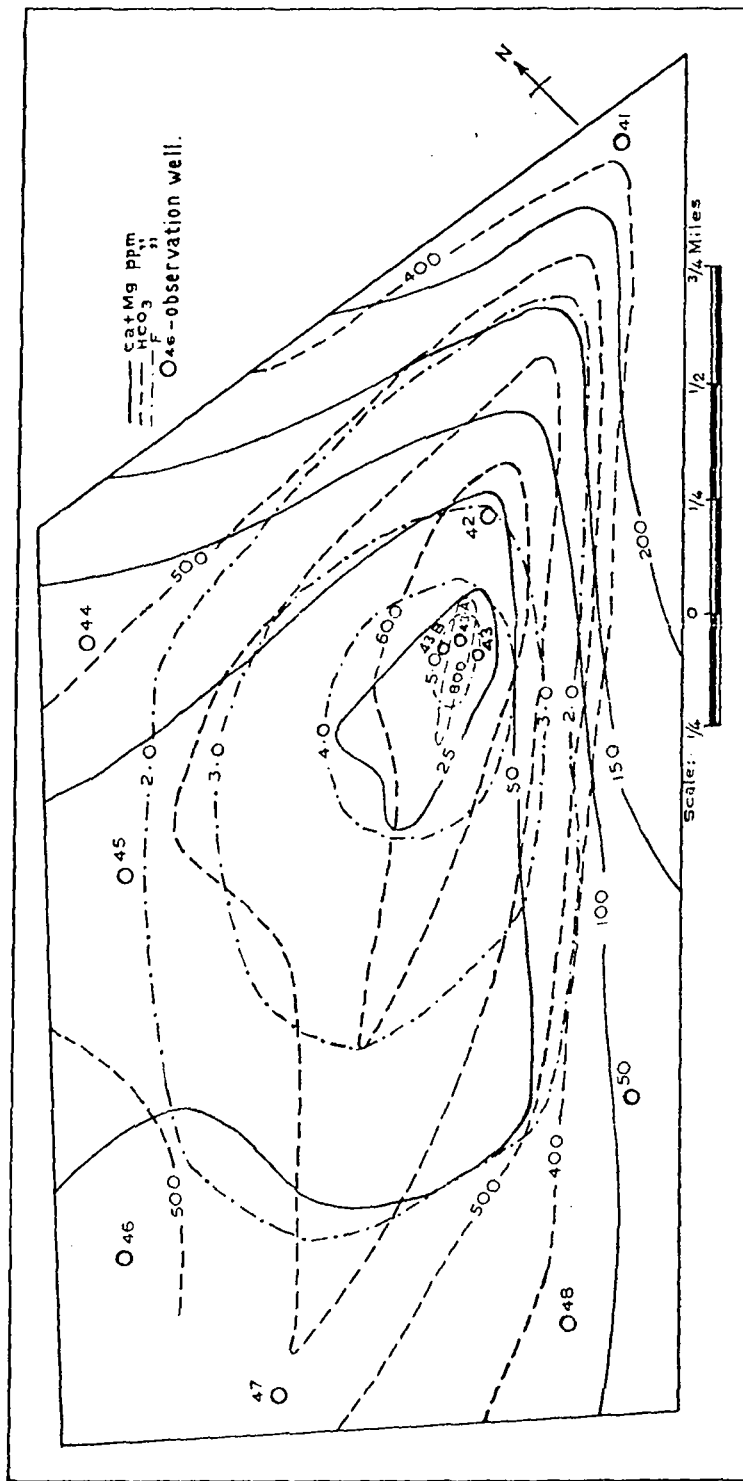


Fig. 2a. Distribution of fluoride, Bi-carbonate and Ca plus Mg ions in October, 1974.

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

Multiple-sulfate percentage
 $(Ca^{2+} + Mg^{2+} + Na^+) \times 100$

$\sqrt{(Ca^{2+} + Mg^{2+})}$

(In all cases ionic concentrations expressed in meq l⁻¹)

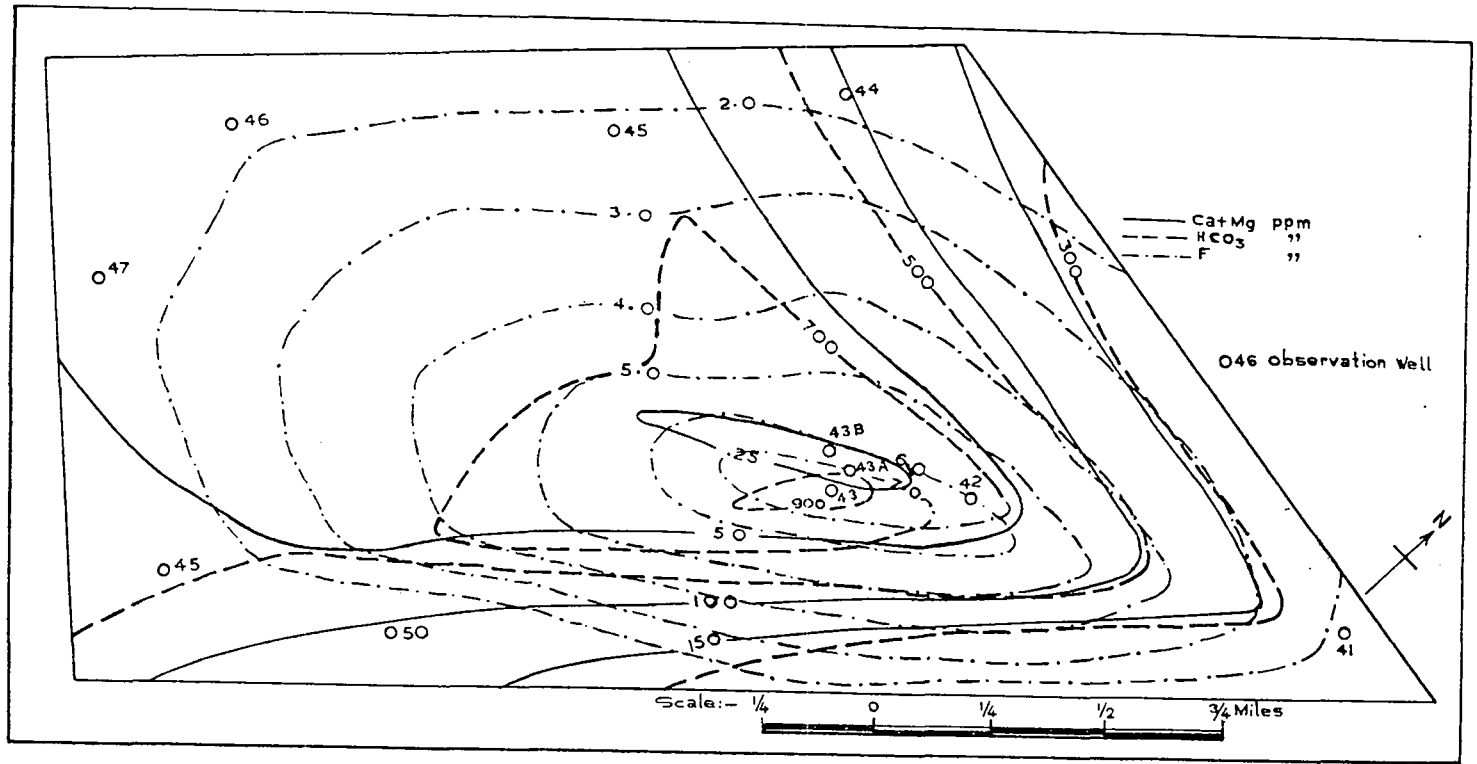


Fig. 2b. Distribution of fluoride, Bi-carbonate and Ca plus Mg ions in February, 1975.

Ca + Mg (ppm)

Fig. 3. Variatio

Ion:

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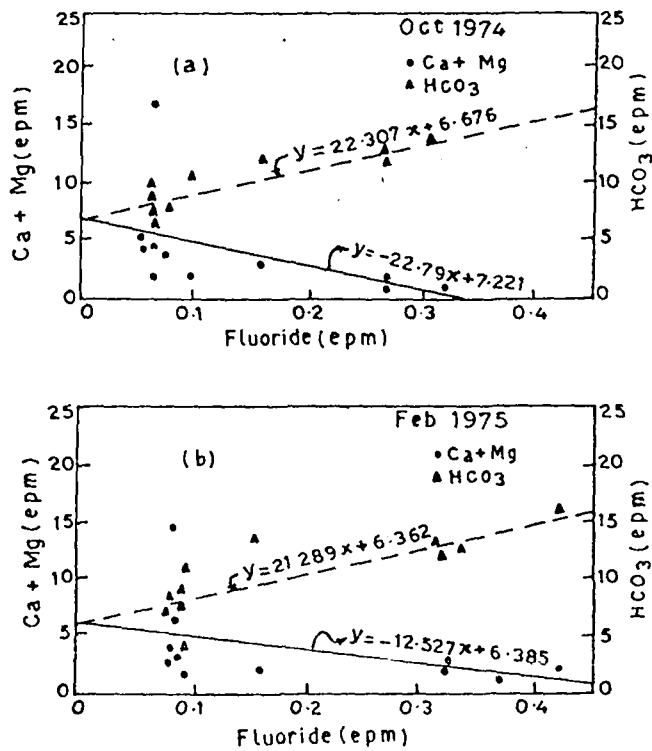


Fig. 3. Variation of Ca plus Mg and bicarbonate with fluoride in fluoride bearing groundwaters of Jaggayapalem.

TABLE II

Correlation coefficient (r) values of various relationships

Ions	October, 1974	February, 1975
	(r)	(r)
(F ⁻) vs (Ca ²⁺) + (Mg ²⁺)	-0.750	-0.600
(F ⁻) vs (HCO ₃ ⁻)	+0.863	+0.833

geological environments of Rajasthan, Andhra Pradesh, West Bengal, Gujarat and Tamilnadu States of India. Similarly data collected from Texas and Manitoba are also from different geological environments.

Hem (1959) points out that the solubility of calcium fluoride probably limits the concentration of fluoride in waters that have more than about 10 mg l^{-1} of Ca in solution. However, Handa (1975) puts forward a solution-evaporation-base exchange hypothesis to explain the genesis of the fluoride bearing groundwaters.

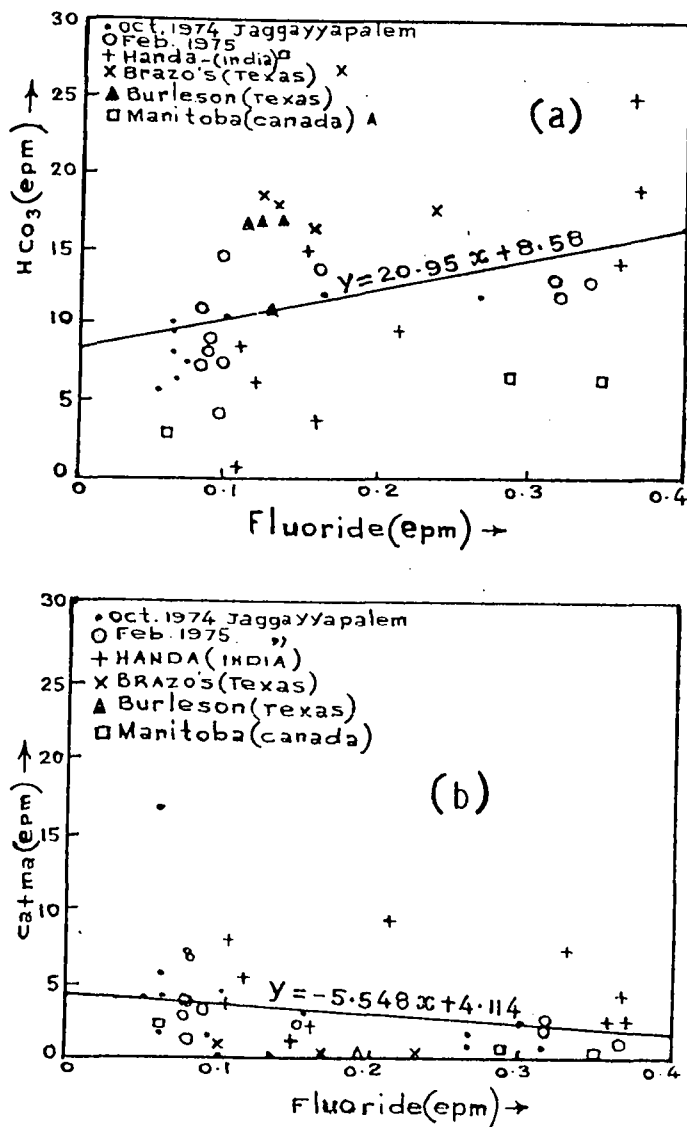


Fig. 4a. Variation of bicarbonate with fluoride (for all regions combined). (b) Variation of Ca plus Mg with fluoride (for all regions combined).

3.2. CLASSIFICATION OF FLUORIDE BEARING GROUNDWATERS

The fluoride bearing groundwaters from different parts of the world (as referred in Section 3.1) are classified using the Sodium diagram (Figure 5) given by Wilcox (1958). From the figure it can be observed that in general most of the waters are classified as high to very high Na waters.

In addition, the fluoride bearing groundwaters are also classified according to U.S. Salinity Laboratory Staff (1954) as shown in Figure 6. It can be seen from the figure

that barring few hazardous waters. of Residual So prescribed by

- (a) In general, [Ca²⁺] + [Mg²⁺] ions in high flu
- (b) Most of Na and are cla
- (c) The RSC of 2.5 meq l⁻¹

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Sodium (meq/L) ↑

Fig

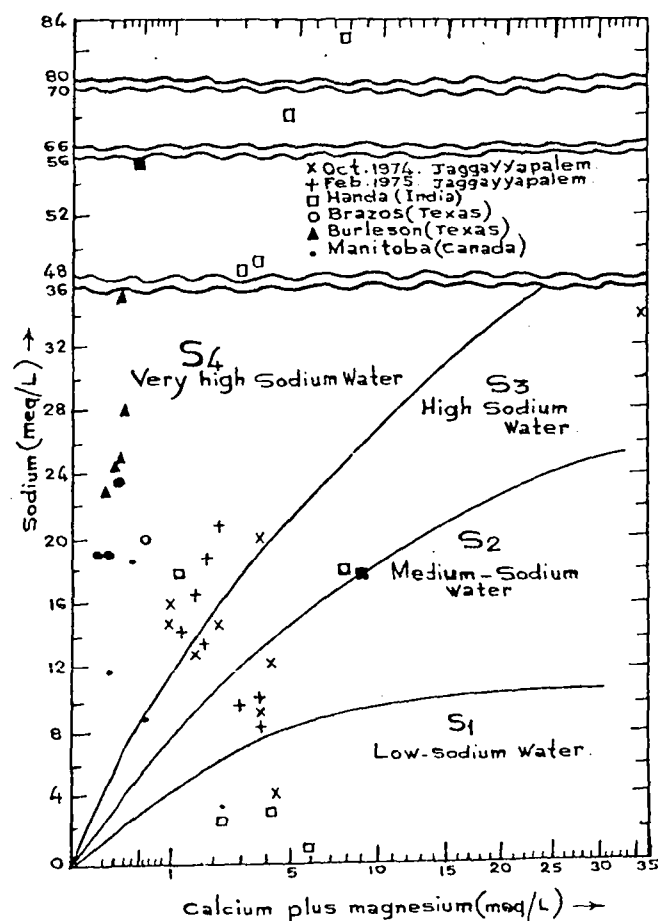


Fig. 5. Classification of fluoride bearing groundwaters using Na diagram.

that barring few exceptions all the waters are classified as high and very high alkali hazard waters. It is also observed that almost all the waters contain very high amounts of Residual Sodium Carbonate (RSC) exceeding the maximum value of 2.5 meq l^{-1} as prescribed by U.S. Salinity Laboratory Staff (1954) for irrigational purpose.

4. Conclusions

(a) In general, there exists a good linear negative relationship between $[\text{F}^-]$ and $[\text{Ca}^{2+}] + [\text{Mg}^{2+}]$ ions and linear positive relationship between $[\text{F}^-]$ and $[\text{HCO}_3^-]$ ions in high fluoride bearing groundwaters.

(b) Most of the fluoride bearing groundwaters contain high to very high amounts of Na and are classified as high to very high alkali hazard waters.

(c) The RSC in fluoride bearing groundwaters is very high from the maximum limit of 2.5 meq l^{-1} .

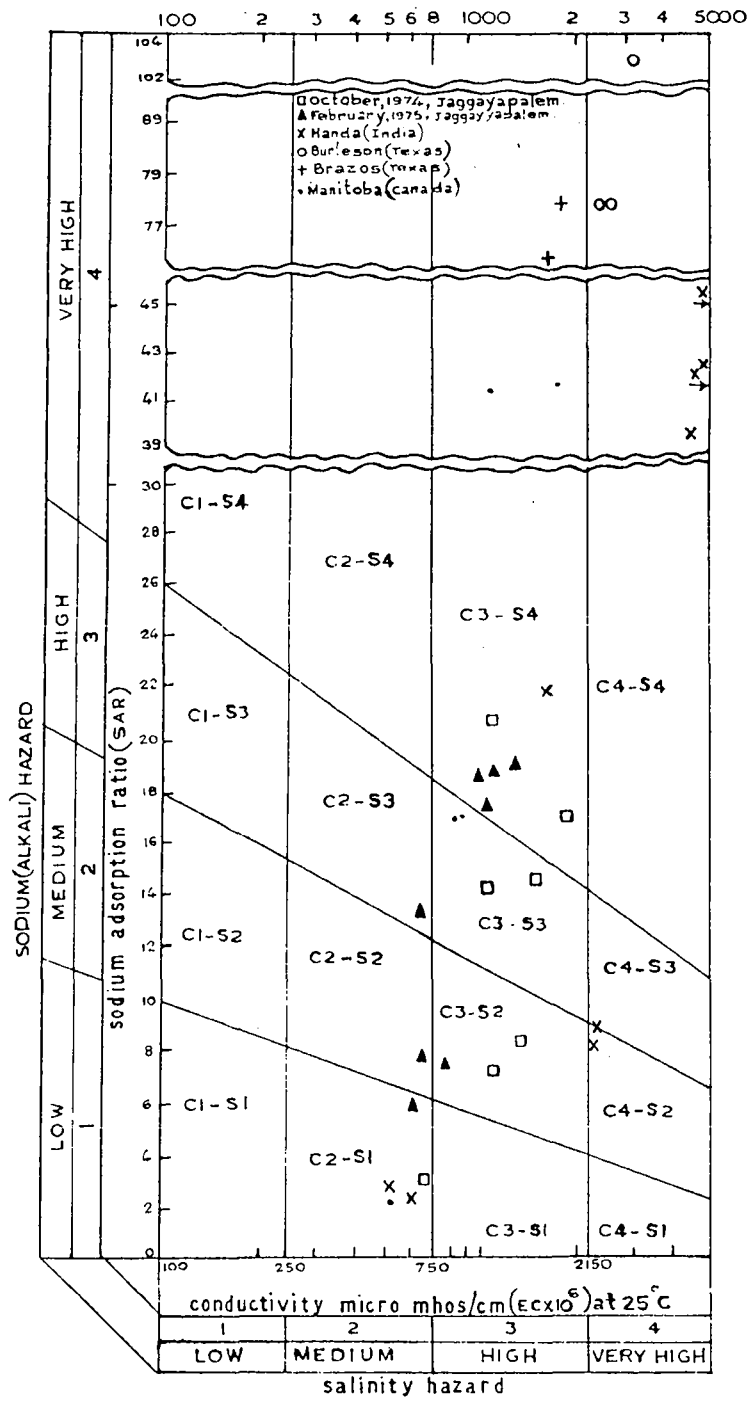


Fig. 6. Na (alkali) hazards of fluoride bearing groundwaters of all regions combined.

One of the authors of Scientific and Technical work.

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Acknowledgments

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