MONITORING OF FLUORIDE CONCENTRATION IN GROUND WATER OF KADAYAM BLOCK OF TIRUNELVELI DISTRICT, INDIA: CORRELATION WITH PHYSICO-CHEMICAL PARAMETERS

G. Alagumuthu* and M.Rajan [a]
Department of Chemistry, Research Centre, Sri Paramakalyani College,
Alwarkurichi – 627 412, Tamilnadu
* Email: alagupathi@yahoo.co.in.

ABSTRACT
Hydrological investigation has been carried out in Kadayam block of Tirunelveli district, Tamilnadu, India. The fluoride concentration in ground water was determined, where it is the only source of drinking water. Various other water quality parameters such as pH, electrical conductivity, total hardness, and total alkalinity as well as calcium, magnesium, carbonate, bicarbonate and chloride concentrations were also measured. A systematic calculation of correlation coefficients among different Physico-chemical parameters was performed. Few samples do not comply with Indian as well as WHO standards. The fluoride concentration in the ground water of these villages varied from 0.73 to 3.02 mg/l, causing dental fluorosis among people especially children of these villages. Overall water quality was found unsatisfactory for drinking purposes without any prior treatment except few villages.
Keywords: *Correlation; Fluoride; Fluorosis; Ground water; Hydrochemistry, Isopleth.*

INTRODUCTION

One of the greatest challenges of the twenty-first century is to provide an adequate supply of safe – water for household consumption to everyone. But, the demand for water is constantly on the rise. On the other hand, the quality of the water resources, which are unevenly distributed over the earth's surface, is deteriorating due to the anthropogenic activities. Therefore, even countries with vast water resources could suffer from scarcity of water in the near future. Because of the rise in the amount of soil pollution by dumping of municipal wastes, industrial waste and heavy use of fertilizers in agriculture land, properties of ground water have also been simultaneously changing. Hence, it is essential to analyze the ground water to study the variation in quality parameters. Based on the physico-chemical parameters, quality could be rated for varies uses (Drinking, Agriculture, Industrial etc.) for the judicious and effective use and get documented for the further references.

Contamination of ground water also depends on the geology of the area where extensive cavern systems are below the water table[1]. The changes in quality of groundwater respond to the variation in physical, chemical and biological environments through which it passes[2]. Fluoride is one of the toxic elements in water and also it's an essential element in ground water. Small concentration of fluoride in drinking water has an enormous beneficial effect on human body if consumed in standardized quantity.

In this study, a thorough research on the correlation between fluoride and other physical parameters has done. A positive correlation coefficient of Sodium with fluoride in ground water has reported in Jabalpur district[3]. The ratio of total alkalinity and total hardness was higher if the fluoride concentration is more than 1.0 mg L^{-} [4]. The similar relationship was also reported at Udaipur[5]. They have prepared correlation matrixes for the relationship between physical and chemical parameters of ground water. They have focused on boron concentration in ground water to classify the irrigation water for various types of crops in the Damman and Kawait group of aquifers, Kuwait[6].

Variation of ground water quality in an area is a function of physical and chemical parameters that are greatly influenced by geological formations and anthropogenic activities. The geological information systems (GIS) have represented and understand the spatial variation of various geochemical elements in

Panvel Basin, Maharastra, India[7]. The fluoride concentration of ground water using Isopleth techniques in Krishanagiri and Palacode blocks of Dharmapuri District[8].

In the present investigation, the analysis of ground water samples of Kadayam block of Tirunelveli District is presented. The Kadayam block has 23 panchayt, with more than 8,86,253 inhabitants and is one of the most densely populated area (inhabitants/km^2) in the western part of the Tirunelveli district. Using this as a starting point, the researchers decided to test the quality of the ground water distributed in Kadayam block. They have studied the correlation analysis of the Physicochemical parameters, pH, EC, TH, TA, Ca^{2+}, Mg^{2+}, Cl^-, CO_3^{2-}, HCO_3^- and F^- measured in 35 samples collected from all over Kadayam block.

Based on the findings from the above samples, it was felt to analyse the water for its quality rating for drinking, which will provide the basic information for the water resources management. Correlation between parameters will be measured for closeness of relationship with chosen dependent and independent variables. Based on the fluoride content of water samples the fluoride endemic villages of Kadayam block were identified. Mapping of these fluoride endemic villages was done using *the Isopleth technique*, a statistical method. The results obtained are presented and discussed in this paper.

EXPERIMENTAL

Study Area

Kadayam block is in the southwest corner of the Tirunelveli district, Tamilnadu and occupies an area of 64.5 sq.km shown in Fig 1.

Water analysis

Water samples were from all the available sources of the villages, belonging to the Kadayam block of Tirunelveli district of Tamilnadu in South India. They were collected in clean, high density polyethylene bottles in January 2008.The samples were analyzed for determining the water quality parameters, Viz.., pH, Electrical Conductivity (EC), Total Alkalinity (TA), Total Hardness (TH), Chloride (Cl^-), Carbonate (CO_3^{2-}), Bicarbonate (HCO_3^-), Calcium (Ca^{2+}) and Magnesium (Mg^{2+}). Chemical analysis was carried out as per the standard methods. All the chemicals used were Analar Grade. Fluoride ion concentration was determined by ion-selective electrode (Model: Eutech-cyberscan 2100). The mapping of fluoride endemic area was presented by using *Isopleth technique*. The correlation coefficient for the ten Physico chemical parameters was determined. Let X and Y be any two variables (that is physico chemical parameters in our case) and (X_i, Y_i) be n pairs of the observed values of these variables (i= 1, 2,…..n). Then the correlation coefficient between these variables X and Y is given by the well known relation[9]:

$$r = \frac{\sum XY - \bar{X}\Sigma Y}{\left[\left(\Sigma X^2 - \bar{X}\Sigma X\right)\left(\Sigma Y^2 - \bar{Y}\Sigma Y\right)\right]^{0.5}} \quad \text{…….. (1)}$$

Where, the summations are taken from 1 to n (number of observations), the value of empirical parameters *a* and *b* was calculated with the help of equations 2 and 3:

$$b = \frac{\sum XY - \bar{X}\Sigma Y}{\Sigma X - \bar{X}\Sigma X} \quad \text{……. (2)}$$

$$a = \bar{Y} - b\bar{X} \quad \text{……... (3)}$$

Where $\bar{X} = \left(\Sigma X / n\right);\ \bar{Y} = \left(\Sigma Y / n\right)$ …….(4)

Keeping the above observations in mind a linear relationship is proposed:

$$Y = a + bX \quad \text{……(5)}$$

Simple regression analysis was done to determine the nature of correlation and significance of the quality parameters on fluoride content.

RESULTS AND DISCUSSION

The results revealed that the pH ranged from 6.7 to 7.6. Minimum pH 6.7was observed in Muthaliyarpatty village and maximum pH 7.6 in Arunachalapuram and Angapuram village (Fig 2). The value of pH showed the positive correlation with most of the other parameters (Table 1). A positive correlation (r =0.57) was observed between F^- and pH. The relationship between pH and fluoride ion concentration is showed in fig 3. According to (WHO 1996), the permissible limit for pH is 6.9 to 9.2.

EC is numerical expression ability of an aqueous solution to carry electric current. USPH recommended permissible limit for electrical conductivity (EC) is 300 μmhos/cm. The values of EC ranged from 0.81 to 3.58 mmhos/cm were noticed. The Minimum 0.81mmhos/cm and maximum 3.58 mmhos/cm of EC were reported from the villages Govinthaperi and Arunachalapuram respectively. EC in all water samples are within the permissible limit. The EC has also showed the positive correlation with other parameters. A significant positive correlation has showed EC with Chloride (r = 0.87) and positive correlation with fluoride (r = 0.12). Total alkalinity ranged from 125 to 520 mg/L was observed from Angapuram, Naraiyappapuram, Pulavanoor and A.P.Nadanoor, Madathur respectively. In the present studies, the total Alkalinity showed a negative correlation with Fluoride (r = -0.71).This is presented in fig 4. The same negative correlation is also reported[10]. The positive correlation has been showed with TA and F^- as earlier reported[11]. The solubility of CaF_2 increases with the increase in TA in the ground waters[12, 13]. According to the following reactions

$$CaF_2 + CO_3^{2-} \rightarrow CaCO_3 + 2F^-$$

$$CaF_2 + 2HCO_3^- \rightarrow CaCO_3 + 2F^- + H_2O + CO_2$$

But in this present case, a negative relationship of TA with F^- (Table 3) suggests that $CaCO_3$ and $CaHCO_3$ have increased. But CaF_2 has decreased in the type of geological formation.

Total hardness of Minimum 310 mg/L and Maximum 1120 mg/L were reported from Madathur and Angapuram Villages respectively. But WHO has recommended the safe permissible limit for hardness i.e. 100 - 500 mg/L. In ground water, hardness is formed mainly due to carbonate, bicarbonate, and Chloride of Ca^{2+} and Mg^{2+}. Total hardness is higher in 74% of the villages; 26% of the samples contain TH within the optimum limit. In this study, hardness has showed a moderate positive correlation with Fluoride (r = 0.34). The trend is given in fig 5. Calcium hardness (Ca-H) ranged from 84 to 510 mg/L and minimum CaH, 84mg/L has been observed from Mela Ambur and Maximum CaH 510 mg/L has been observed from Angapuram. Magnesium hardness (MgH) ranged from 34 to 225 mg/L. The Minimum (34 mg/L) and maximum (225 mg/L) values were reported Adachani and Angapuram respectively. Chloride contents of ground water samples are 114 mg/L ranging upto 823 mg/L. Chloride showed a positive correlation with Fluoride (r = 0.20). Total Hardness, Calcium, Magnesium and Chloride data's are shown in Fig 6.

Fluoride (F^-) ion varied from 0.73 mg/L to 3.02 mg/L. This is given in Table 2. The results are shown in Fig 7. Minimum 0.73 mg/L and Maximum 3.02 mg/L concentration of F^- were observed from Kelakadayam and Arunachalapuram villages respectively. Most of the samples are above the permissible limits. Out of 35 ground water samples 23 samples have above the permissible limits i.e.65.7 %.

An overall correlation analysis is almost a positive correlation between the concentration of fluoride ion with pH, Total Hardness, Ca^{2+}, Mg^{2+} and Chloride. However Total Alkalinity, Carbonate and Bicarbonate correlated negatively with fluoride concentration. The carbonate and Bicarbonate the correlation coefficient are (r = -0.26) and (r = -0.68) respectively. Out of several parameters, the researcher has considered, only a few linear regression analyses. The pairs are: (a) Fluoride and pH, (b) Fluoride and Total Alkalinity, (c) Fluoride and Total Hardness and (d) Fluoride and Bicarbonate. The developed linear relationships for fluoride with pH, Total Alkalinity, Bicarbonate and Total Hardness are given in the equation;

(a). $\mathbf{F} = -7.357 + (1.264 * \mathbf{pH})$

(b). $\mathbf{F} = 2.496 - (0.00280 * \mathbf{TA})$

(c). $\mathbf{F} = 0.984 + (0.000994 * \mathbf{TH})$

(d). $\mathbf{F} = 2.550 - (0.0111 * \mathbf{HCO_3^-})$

In the equation ***a***, and ***b*** reveal the linear regression having moderate negative "r" value, ***c*** and ***d*** having a positive "r" Values.

Isopleth Mapping of fluoride areas:

Based on the results of the fluoride levels of the water samples, a fluoride *Isopleth map* of the region was prepared which is shown in fig 8. Fluoride zone regions with high fluoride levels in their drinking water were identified and distinguished by different shades depicting the fluoride levels. Geochemical maps such as this can be used to plan strategies for health protection in a geological context.

Ground water Management

Incidences of the harmful effects of Fluoride on health are on the increase, not only due to the widespread occurrence of fluoride bearing minerals in the earth's crust, but also due to the impact of environmental factors and human activities[14, 15, 16, 17]. Therefore, a sustainable management plan on fluorosis is long overdue and is required for the study area. For formulating a sound management plan in the area, the following recommendations were made for the supply of high-quality groundwater with safe concentrations of Fluoride:

- High fluoride concentration waters should be discouraged through regulation such as the provision of protected water – supply schemes and the control of ground water usage for drinking purposes with effective monitoring.
- Food rich in calcium and phosphorous are recommended, as the rate of accumulation of fluoride in the human body decreases when these are consumed.
- The adoption of an activated alumina adsorption techniques is recommended for defluoridation, to reduce the fluoride content in water.
- Recharging the underground aquifer through the harvesting at appropriate locations can reduce the fluoride content significantly through dilution.
- Environmental awareness of the health implication of fluoride should be emphasized though education of the public and community participation.

CONCLUSIONS

Fluoride distribution is associated with pH, Calcium, Magnesium and Chloride. Positive correlations are observed in the parameters like pH, EC, Total Hardness, Chloride, Calcium and Magnesium with Fluoride. Negative correlations are observed in the parameters like Total Alkalinity, Bicarbonate and Carbonate with Fluoride. The linear correlation is very useful to get fairly accurate idea of the quality of the drinking water or the nature of water.

1. This study reveals that the fluoride concentration of some village ground water samples analysed are more than 1.5 mg/L and ranging upto 3.02 mg/L which is much above the permissible limits prescribed by ICMR, WHO, and ISI. Dental fluorosis and Skeletal is noticed in some villages.
2. Total hardness of village ground water samples are more than 310 mg/L and ranging upto1120 mg/L which is much above the permissible limits prescribed by ICMR.
3. Chloride contents of ground water samples are 114 mg/L ranging upto 823 mg/L within the limits prescribed by ICMR.
4. The pH and EC are found to be within limits prescribed by ICMR and other parameters are more or less within the permissible limits.
5. A ground water management program is suggested.

ACKNOWLEDGEMENTS

Financial support of the author by the University Grant Commission (UGC), Government of India, New Delhi Under the major research project F.No. 32-296/2006(SR) is gratefully acknowledged.

REFERENCES

1. K.P. Singh, Environmental effects of industrialization of groundwater resources, Bangkok, E6 E6-7, (1982).

2. Mandeep Singh, Samanpreet Kaur, S.S. Sooch, *J. IPHE*, **2**, 29-31, (2003).
3. Shikha Saxena, Nidhi Jaih, R.K,Shrivastava, *Poll Res*, **24 (4)**, 831-834, (2005).
4. R.K.Bhargava, S.C. Saxena, V.P. Thergonkar, *Indian J. Environ. Health*, **20,** 290-302, (1978),
5. S.Gupta, *Indian J. Environ. Health*, **23**, 195-207, (1981).
6. A.Saleh, F.Ai-Ruwaih, M.Shehata *J Arid Environ*, **42** ,195-209(1999).
7. S.Anbazhagan, A.M.Nair, *India. J. Environ Geol*, **45**, 753 – 761(2004).
8. G.Karthikeyan, A.Shunmugasundarraj, *Fluoride***, 33,** 121-127 (2008).
9. R.K. Trivedy, P.K.Goel, Chemical and Biological methods for pollution studies, Environmental Publications, Karad. (1984).
10. P.Mariappan, V.Yengnaraman, T.Vasudevan, *IJEP*, **20(3)**, 182-187(1999).
11. N.Subba Rao, *Environ Geol*, **43,** 419-431, (2003).
12. N.V.Ramamohan Rao, K.Suriyaprakasa Rao, R.D.Schuiling, *Environ. Geol*, **21**, 84-89 (1993).
13. V.K.Sexena, S.Ahemd, *Environ. Geol*, **40**, 1084-1087 (2001).
14. B.K.Handa, *Ground water*, **13**, 275-281 (1975).
15. B.K.Wodeyar, G.Sreenivasan, *Current Sci*, **70**, 71-74 (1996).
16. N.Subba Rao, *Environ. Geol*, **41**, 552-562 (2002).
17. N.Subba Rao, A.T. Rao, *Appl. Geochem*, **5**, 94-100 (2003).

Table-1:Value of correlation coefficient of water samples collected from villages.

Parameters	pH	EC	TA	TH	CO_3^-	HCO_3^-	Cl^-	Ca^{2+}	Mg^{2+}	F^-
pH	1.00									
EC	0.21	1.00								
TA	-0.21	0.25	1.00							
TH	0.39	0.41	-0.17	1.00						
CO_3^-	-0.16	-0.07	0.29	-0.35	1.00					
HCO_3^-	-0.21	0.23	0.91	-0.08	0.25	1.00				
Cl^-	0.22	0.87	0.14	0.51	-0.07	0.13	1.00			
Ca^{2+}	0.42	0.49	-0.11	0.70	-0.13	0.01	0.54	1.00		
Mg^{2+}	0.26	0.17	-0.25	0.51	-0.41	-0.19	0.19	0.46	1.00	
F^-	**0.57**	0.12	**-0.71**	**0.34**	-0.26	**-0.68**	0.20	0.31	0.21	1.00

Table-2: Fluoride contents of the water samples collected from the villages

S.No	Villages	Fluoride (ppm)	S.No	Villages	Fluoride (ppm)
1	Mylappapuram	0.94	19	Pulavanoor	2.89
2	Pungampatty	1.82	20	Mettur	1.64
3	Katttaripatty	1.25	21	Vekkalpatty	1.00
4	Servaikaranpatty	1.82	22	Thergumadur	1.83
5	Arunachalapuram	3.02	23	Kelayappapillaiyur	2.04

6	Kelakadam	0.73	24	Keela Ambur	1.89
7	Muthaliarpatty	0.92	25	Mela ambur	1.91
8	Thurimalaiappapuram	0.98	26	Sivasailam	1.57
9	Pottalpudur	1.52	27	Govinthaperi	1.26
10	Pappankulam	1.06	28	Sammankulam	1.93
11	A.P.Nadanoor	1.52	29	Settykulam	1.63
12	Adaichani	2.07	30	Manthiyur	1.44
13	Anjankattalai	1.63	31	Virasamutram	1.53
14	Vengatampatty	1.73	32	Vagaikulam	1.89
15	Kadayamperumpathu	1.45	33	Dharmamadapuram	1.12
16	Kalyanipuram	1.74	34	Madathur	0.87
17	Angapuram	2.08	35	Thuppakudi	1.08
18	Naraiyappapuram	2.34			

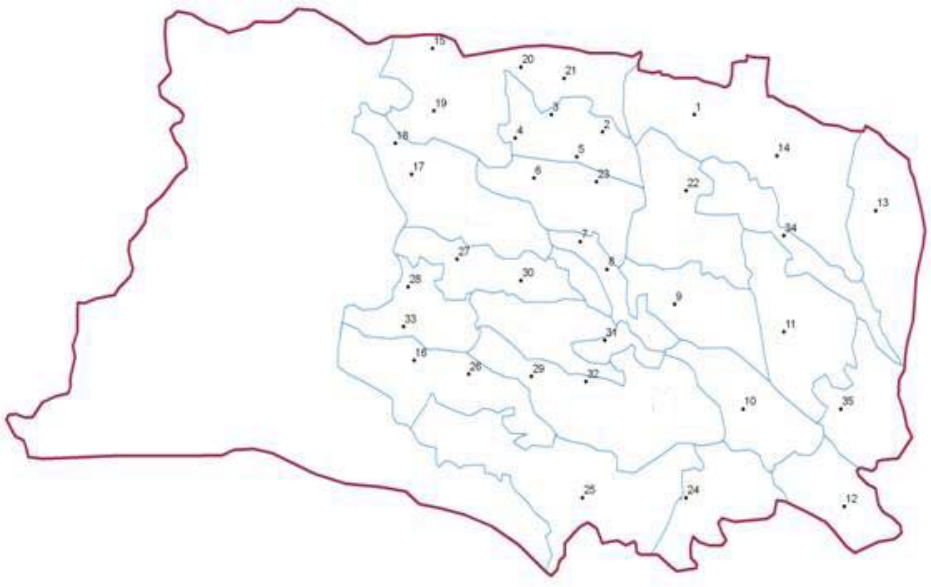

Fig.1. Site map of Kadayam block

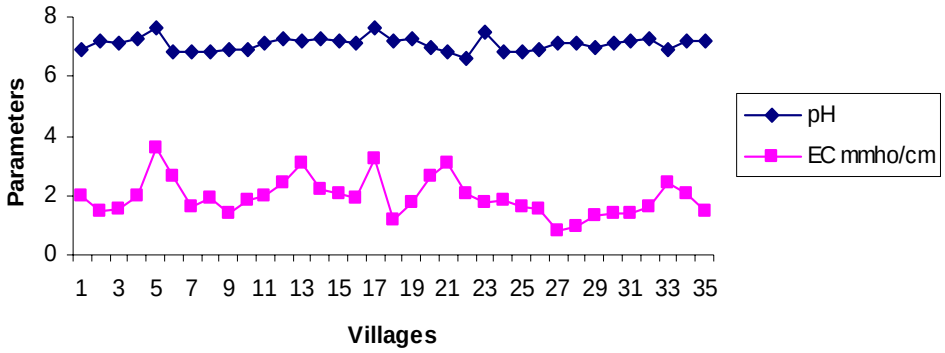

Fig.2. The pH and EC levels of Kadayam block.

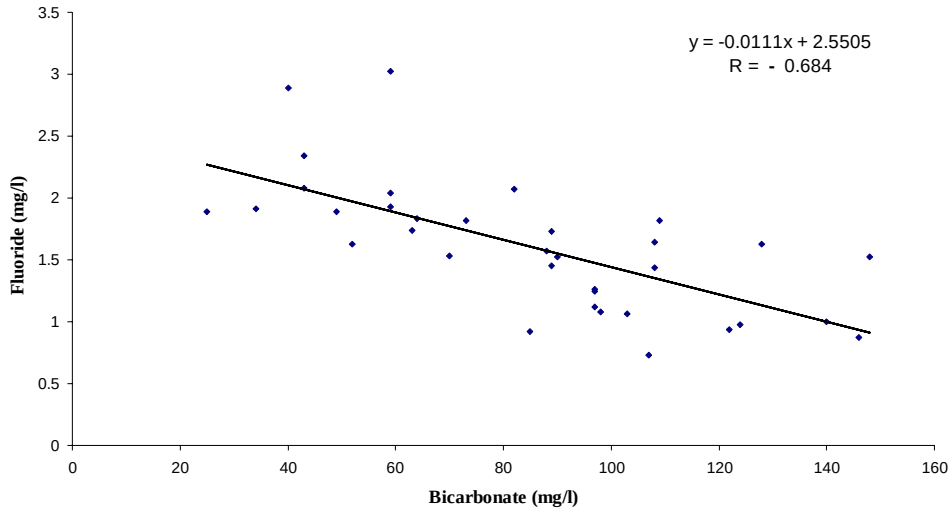

Fig 3.Relationship between Fluoride and pH

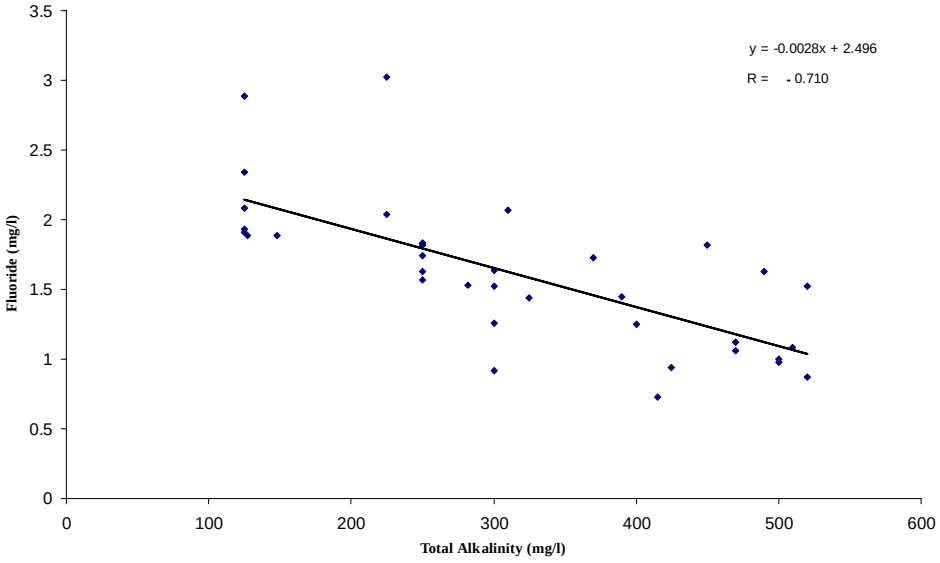

Fig 4.Relationship between Fluoride and Total Alkalinity

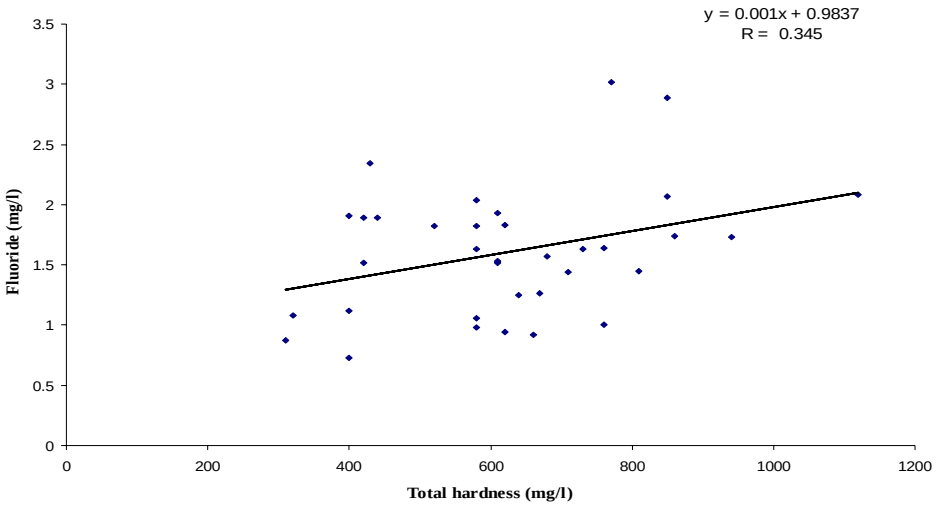

Fig 5.Relationship between Fluoride and Total Hardness

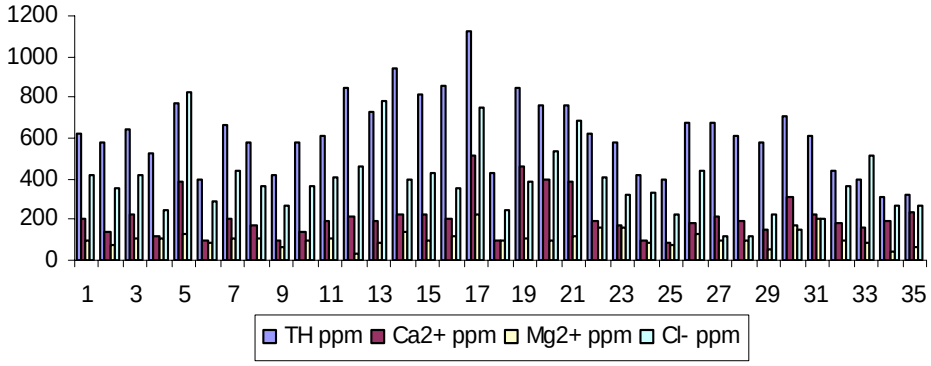

Fig 6. TH, Calcium, Magnesium and Chloride levels of Kadayam block.

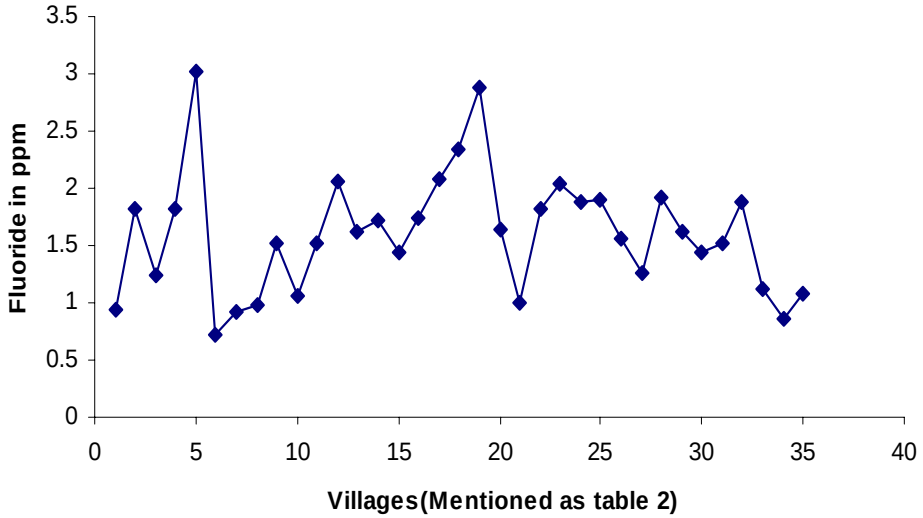

Fig 7. Fluoride variations in study area.

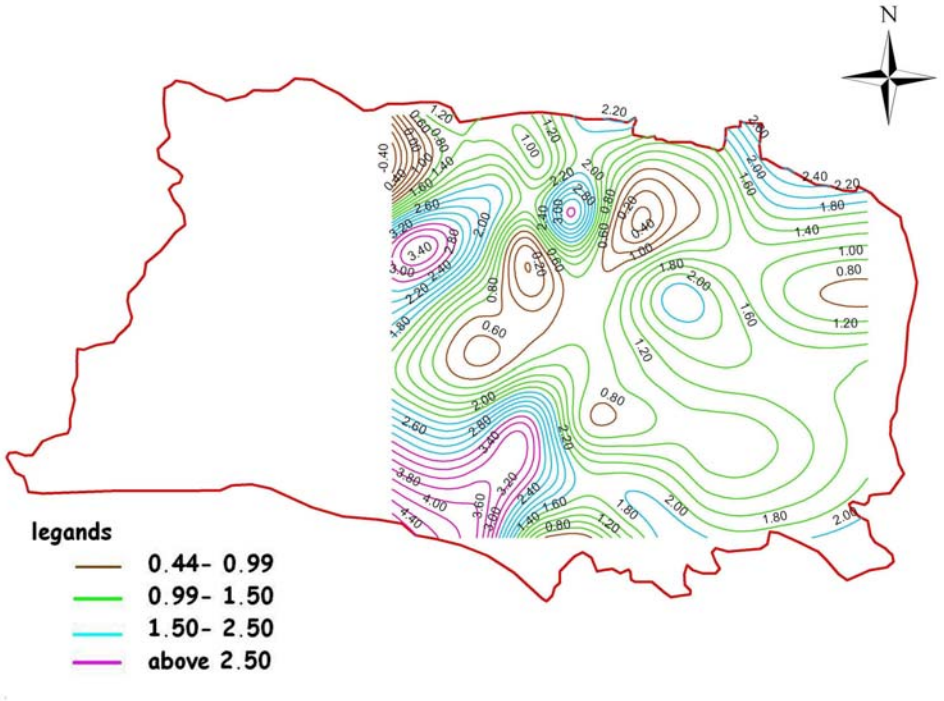

Fig 8. Fluoride zone of Kadayam block

(Received: 21 November 2008 Accepted: 30 November 2008 RJC-286)