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Research Article

FLOURIDE ANALYSIS OF SOIL IN CULTIVATED AREAS OF THOVALAI CHANNEL IN KANYAKUMARI DISTRICT, TAMILNADU, INDIA: CORRELATION WITH PHYSICO-CHEMICAL PARAMETERS

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ABSTRACT
In order to study the accumulation of fluoride in soil, samples were collected from eight villages near the bank of Thovalai Channel in Kanyakumari District, Tamilnadu. The concentration of fluoride was estimated by SPADNS Spectrophotometric Method. The result showed that fluoride content of the soil varied from 1.0 to 3.2 ppm. The high concentrations of fluoride were found in red soil, alluvial soil, black soil, and laterite soil indicating the binding capacity and soil type. Application of phosphate fertilizers over long periods of time had increased the concentrations of fluoride in both soil and ground water. As the area is free from industrial activity, heavy use of DAP fertilizer and soil profile may be the most likely sources of elevated ground water fluoride in the area. Fluoride is a persistent and non-degradable toxin that is accumulating in soils, plants, wildlife, and humans. Many farmers are unaware of the hidden presence of this highly toxic substance. The physico-chemical characteristics like pH, bulk density (g/cc), particle density (g/cc), porosity (g/cc), electrical conductivity (mhos/cm), and water holding capacity (%) were studied. The level of calcium, sodium, potassium, chloride, magnesium, phosphate, and fluoride (ppm) were also studied. These parameters have been detected by standard methods.

Keywords: *Fluoride; Correlation; Soil Leaching*

INTRODUCTION
Soil is one of the most significant ecological factors, on which plants depend for their nutrients, water, and mineral supply. Soil is a product of weathering in which environmental factors have been imposed upon a parent material over a period of time (Sharma, 2001; Adriano, 1986). Very common soil minerals, such as biotite, muscovite, and hornblende may contain a higher percentage of fluoride and therefore, it would result in the accumulation of fluoride in soil. However, Bowen (Bowen, 1979) believed that micas, apatite, and tourmaline in the parent materials were the original source of fluoride in soil. It appears, therefore, that the fluoride content of soil is largely dependent on the mineralogical composition of the soil inorganic fraction. Fluoride is usually present in soils in the form of the following minerals: Fluorite - CaF_2; Fluoroapatite - $Ca_{10}(PO_4)_6F_2$; and Cryolite - Na_3AlF_6. These minerals are sparingly soluble in water, so that only small amounts of fluoride are taken up by plants. The content of total fluoride in normal soils is usually in the range from 150 to 400 mg/Kg. Values that exceed 1000 mg/Kg have been registered in some heavy clayey soils. Artificial sources of soil pollution with fluoride are: aluminium smelters, phosphorus fertilizer factories, ceramic and glass industry, and combustion of coal. This halogen element is also introduced into soil through the application of phosphorus fertilizers, sewage sludge, and some pesticides (Blagojevic *et al.*, 2002; Elrashidi *et al.,* 1986; Weast, 1986). Phosphate fertilizers are the major sources of fluoride contamination of agricultural soils. They are manufactured from rock phosphates, which generally contain around 3.5% fluoride (Hart *et al.,* 1934). However, during the manufacture of phosphate fertilizers, part of the fluoride is lost into the atmosphere due to acidulation process, and the concentration of fluoride in the final fertilizer is lowered further through dilution with sulphur (super phosphates) or ammonium ion (ammoniated phosphates); the final product commonly contains 1.3 - 3.0% fluoride (McLaughlin *et al.*, 1996).

The uses of fluoride-containing pesticides as well as the fluoridation of drinking-water supplies also contribute to the release of fluoride from anthropogenic sources (Low *et al*., 1988). Fluoride levels in terrestrial biota tend to be increased in areas with high fluoride levels due to both natural and anthropogenic sources. Lichens have been used extensively as biomonitors for fluorides. Davies and Notcutt (Davies *et al*., 1988) sampled lichens from the slopes of the Mount Etna volcano in 1985 and 1987 and found fluoride levels ranging from 2 to 141 mg/Kg (lichen from control sites contained <2 mg fluoride/Kg). Similarly, Davies and Notcutt (Davies, 1989) found that lichens growing in the Canary Islands accumulated fluorides from minor volcanic eruptions.
Fluoride at high concentrations in soils can cause various forms of toxicity to plants and grazing animals who feed in such soils (Jezierska-Madziar *et al*., 2003; Clark *et al*., 1976; Loganathan *et al.*, 2001). The fluoride content in the soils ranged from 219.26 to 1163.01mg/Kg (Abugri1 *et al*., 2011). In general, clays contain a high amount of fluoride, whereas sand and silts are enriched with much or less fluoride (Madhavan *et al*., 2002).

MATERIALS AND METHODS

Study Area

The high rainfall zone of Tamilnadu includes Kanyakumari District (K.K. Dist), located in the southern tip of the peninsular India, between 77.05^{o} and 77.36^{o} longitude and 8.03^{o} and 8.35^{o}N latitude. It is bordered by Tirunelveli District of Tamilnadu in the north and north-east, and Kerala State in the north-west, and sea in the west and the south. Kanyakumari District is divided into four taluks *viz*. Agasteeswaram, Thovalai, Kalkulam, and Vilavancode with Nagercoil town as the district headquarter. There are nine development blocks and four municipalities in the district. Thovalai and Nanchilnadputhanar Channels are the major sources of irrigation in the taluks of Agasteeswaram. Mixed types of red and alluvial soil are predominant in Agasteeswaram and Thovalai blocks. The soil pH generally ranges from 4.5 to 8.0.

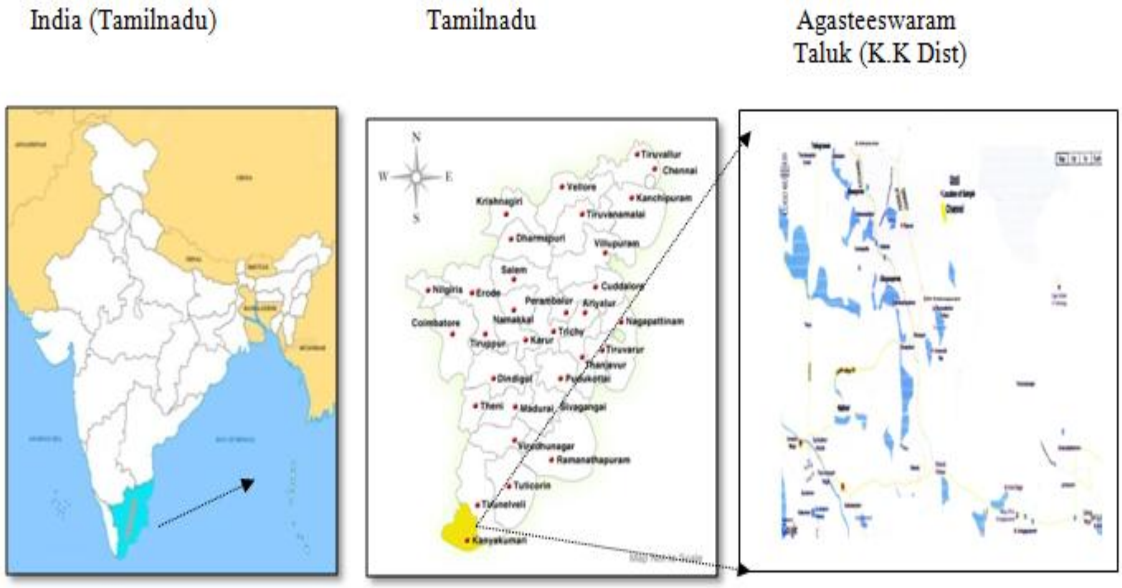

Figure 1: Maps representing location sites

Sample Collection

Sixteen soil samples were collected from croplands which are often used for the cultivation of most common crops in the area. The samples were taken within a depth range of 10 to 30.0 cm during June - September 2011 at some selected villages near the bank of Thovalai Channel in Agasteeswaram Taluk, Kanyakumari District (Figure 1). The surface of each soil sample was examined carefully to ensure that no stocks, remains of plants, or other debris were present. The soil samples were obtained by digging vertically and collecting from distinct horizons. The samples were kept in plastic bags and transported to the laboratory and air dried for at least 3 hours. The soils were ground to fine particles and sieved with mesh size of less than 2 mm.

Sample Analysis

Water Holding Capacity (WHC) can be determined as the amount of maximum water present in saturated solids. The electrical conductivity of the soil was determined in 1:5 soils: water suspension with the help of a conductivity meter. The pH of the soil was determined in 1:5 soils: water suspension with the help of a pH meter. Bulk density, particle density, and porosity were determined by standard calculation methods. Calcium and magnesium were determined by complexometric titration method (Medley *et al.,* 1995). The chloride present in the samples was determined in 1:5 soils: water suspension by argentometric method. Sodium and potassium were determined by flame photometer.
Phosphate of soil content was determined by spectrophotometric method (Samira *et al*., 2009; Saroj Mahajan *et al.,* 2014). The fluoride present in the sample was determined in 1:5 soils: water suspension by SPANDS method on UV spectrophotometer (Apambire *et al*., 1997).

RESULTS AND DISCUSSION

Different parameters of the soil from some villages near the bank of Thovalai Channel in Kanyakumari District have been studied. The samples collected from selected communities (Table 1) were found to have high fluoride concentration in their groundwater sources based on previous studies (Abugri *et al.,* 2011; Jackson, 1973; Chhatwal *et al.,* 1989; APHA, 2000). The correlations of fluoride with other physicochemical parameters are also shown in Table 2. The analysed chemical and physical properties that show the wide variation range especially in alluvial soils and red soil. The results revealed that the pH ranged from 6.2 to 8.3. Minimum pH 6.2 was observed in Anjugramam village, and maximum pH 8.3 in Athalavilai village. The values of electrical conductivity ranged from 181 to 1456 mhos/cm. Higher EC indicate accumulation of salts in the soil (Shaikh *et al.,* 2013). The minimum 181 mhos/cm and maximum 1456 mhos/cm of EC were reported from the villages Amaravathivilai and Azagappapuram respectively. EC (r = 0.8477) pH (r = 0.2383) and were positively correlated with fluoride (Figure 2a & 2c). This means that the fluoride content increases with soil EC and pH respectively. Similar findings have been reported by Abugri *et al*., (2011). Bulk density ranged from 1.5 to 1.8 (g/cc), particle density varied from 1.08 to 2.92 (g/cc) and porosity 0.52 to 1.48 g/cc. Also WHC varied from 50 to 65 (%) in this study. Bulk density (r = 0.1501) and porosity (r = 0.3333) were positively correlated with fluoride (Figure 2d & 2f). Particle density (r = -0.2709) and WHC (r = -0.4195) were negatively correlated with concentration of fluoride (2b & 2d). The results indicate that concentration of fluoride decreases with particle density and WHC of soil.
Fluoride concentrations in soil varied from 1 to 3.3mg/Kg which affects the growth of crops. It also causes dental and traces of skeletal fluorosis in inhabitants consuming these crops. In the present study, the minimum (1mg/Kg) and maximum (3.5mg/Kg) concentrations of fluoride were observed in villages Amaravathivilai and Azagappapuram respectively.
Calcium and magnesium ranged from 62 to 82 mg/Kg and from 61 to 137 mg/Kg in the samples collected from Rajavoor, Azagappapuram, Amaravathivilai, and Azagappapuram respectively. In the present study, the calcium (r = 0.0847) and magnesium (r = 0.402) showed a positive correlation with fluoride (Figure 2g & 2k). This result may be due to the presence of some minerals like fluorite (CaF_2), fluorapatite [$(3Ca_3(PO_4)_2.CaF_2)$] and magnesium fluoride (MgF_2) in the soil. The main natural source of inorganic fluorides in soil is the parent rock (WHO, 1984). During weathering, some fluoride minerals (e.g., cryolite or Na_3AlF_6) are rapidly broken down, especially under acidic conditions (Fuge *et al.,* 1989). Other minerals, such as fluorapatite [$(3Ca_3(PO_4)_2.CaF_2)$] and calcium fluoride, are dissolved more slowly (Kabata-Pendias *et al*., 1984).
Sodium ranged from 99 to 149 mg/Kg and a minimum concentration (98 mg/Kg) had been observed from the samples collected in Rajavoor and maximum (149 mg/Kg) has been observed from Azagappapuram. Sodium showed a moderate positive correlation with fluoride (r = 0.6820) (Figure 2h). The positive correlation between the alkalinity and fluoride levels might be due to the accumulation of Cryolite (Shekhar *et al.,* 2006) (Na_3AlF_6) mineral in soil. The concentration of potassium varied from 16 (Ramanachinpudur) to (Srikrishnapuram) 62 mg/Kg. Fluoride had significant positive relationship with potassium (r = 0.6618) (Figure 2i). The positive correlation of fluoride with potassium was due to the use of potassium fertilizers used for agriculture purpose.

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Table 1: Sample Analysis of Soil Obtained from Thovalai Channel

Sl	Village	Source	P^H	WHC %	Electrical Conductivity mhos/cm	Bulk Density g/cm^3	Particle Density g/cm^3	Porosity g/cm^3	Ca^{2+} mg/kg	Na^+ mg/kg	K^+ mg/kg	Cl^- mg/Kg	Mg^{2+} mg/kg	PO_4^{3-} mg/kg	Fluoride mg/kg
1	Athalavilai	UC	8.3	54	290	1.6	2.61	0.61	64	184	56	14	86	24	2.4
		LC	7.0	60	345	1.7	2.85	0.59	82	140	33	18	120	21	2.6
2	Thoppor–Sri Krishna Puram	UC	8.1	50	756	1.5	2.86	0.52	65	218	62	12	121	31	3.1
		LC	6.8	61	900	1.7	2.92	0.58	89	99	24	16	190	29	3.2
3	Rajavoor	UC	7.9	57	190	1.5	2.75	0.54	62	98	22	12	161	13	1.9
		LC	6.9	60	210	1.6	2.85	0.56	70	125	32	16	210	23	2.1
4	Ramanadhichan Pudhoor	UC	7.2	56	280	1.5	2.62	0.57	79	135	19	15	119	18	1.7
		LC	6.9	62	291	1.7	2.68	0.63	82	138	32	19	147	21	1.8
5	Amaravathi vilai	UC	7.1	61	181	1.6	2.85	0.56	69	99	25	15	105	17	1.0
		LC	6.5	65	195	1.7	2.87	0.59	78	198	53	18	90	13	1.5
6	Azhagappa Puram	UC	8.0	50	1182	1.6	1.08	1.48	70	192	62	16	193	52	3.2
		LC	7.0	60	1456	1.7	2.90	0.58	82	321	85	18	201	33	3.3
7	Indiranagar	UC	7.9	52	880	1.6	2.65	0.60	69	192	58	15	92	21	2.5
		LC	6.8	61	930	1.8	2.75	0.65	71	215	70	18	160	30	3.0
8	Anjugramam	UC	7.1	62	345	1.8	2.80	0.64	80	141	34	22	121	19	2.0
		LC	6.2	60	423	1.7	2.86	0.59	86	102	41	16	195	14	2.2

LC - Lower Crust UC - Upper Crust

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Table 2: Correlation Matrix

	F^-	pH	WHC	EC	BULK DENSITY	PARTICLE DENSITY	POROSITY	Ca^{2+}	Na^+	K^+	Cl^-	Mg^{2+}	PO_4^{3-}
F^-	1												
pH	0.238	1											
WHC	-0.419	-0.847	1										
EC	0.847	0.150	-0.346	1									
BULK DENSITY	0.150	-0.629	0.666	0.181	1								
PARTICLE DENSITY	-0.270	-0.433	0.556	-0.351	0.186	1							
POROSITY	0.333	0.283	-0.418	0.421	0.002	-0.973	1						
Ca^{2+}	0.084	-0.761	0.575	0.121	0.588	0.238	-0.104	1					
Na^+	0.547	0.202	-0.221	0.694	0.141	-0.118	0.148	-0.107	1				
K^+	0.616	0.200	-0.285	0.728	0.222	-0.216	0.267	-0.178	0.922	1			
Cl^-	-0.044	-0.581	0.642	0.056	0.868	0.063	0.0904	0.621	0.13	0.072	1		
Mg^{2+}	0.45	-0.322	0.094	0.427	0.148	-0.185	0.279	0.302	-0.002	0.07	0.069	1	
PO_4^{3-}	0.761	0.368	-0.515	0.777	0.008	-0.719	0.762	-0.103	0.492	0.550	-0.009	0.413	1

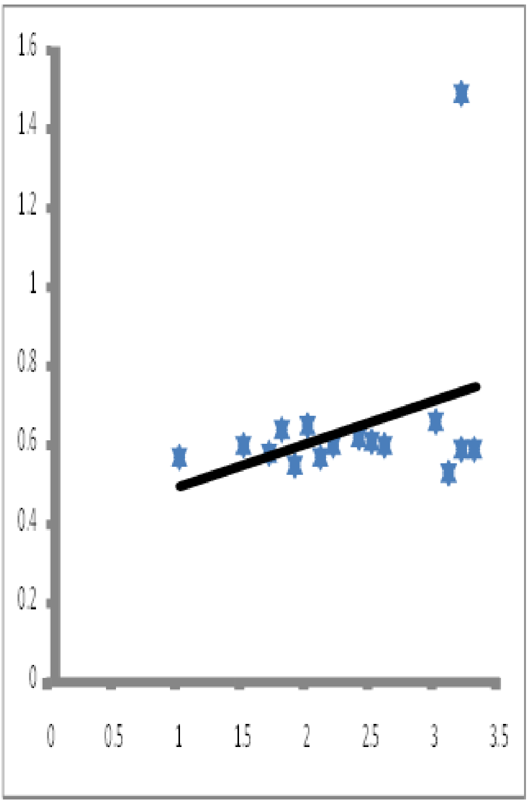

Figure 2a: F$^-$ Vs pH r = 0.1494

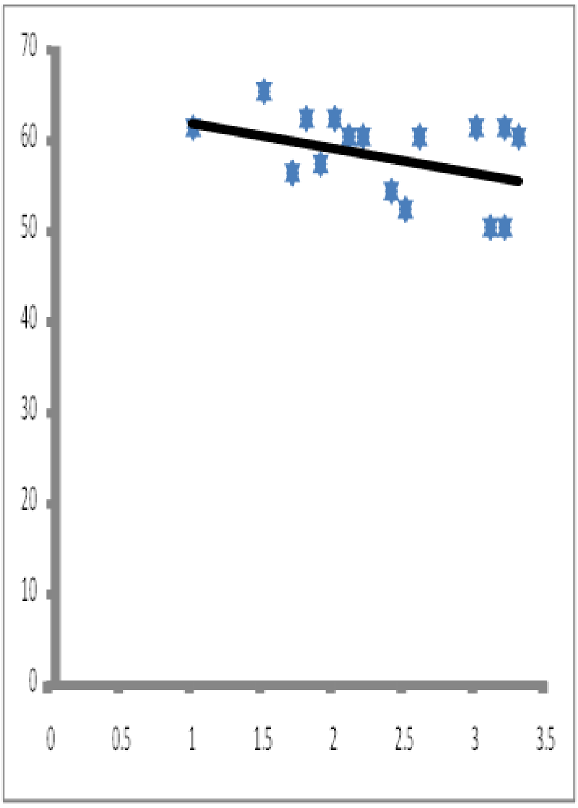

Figure 2b: F$^-$ Vs WHC r = -0.4195

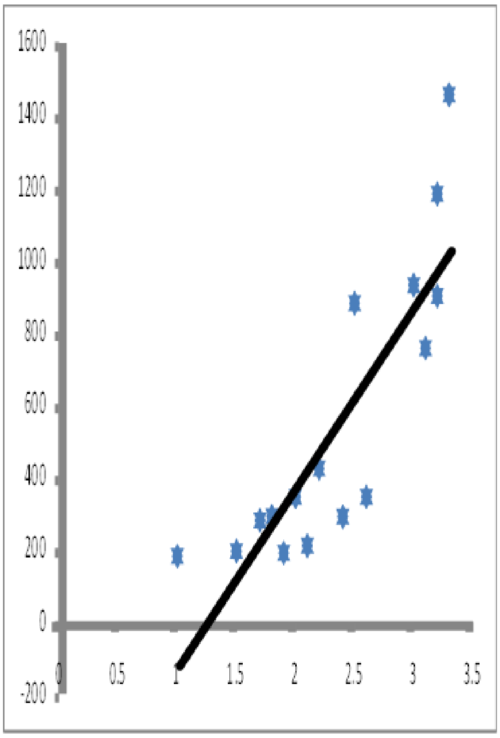

Figure 2c: F$^-$ *Vs* EC r = 0.847

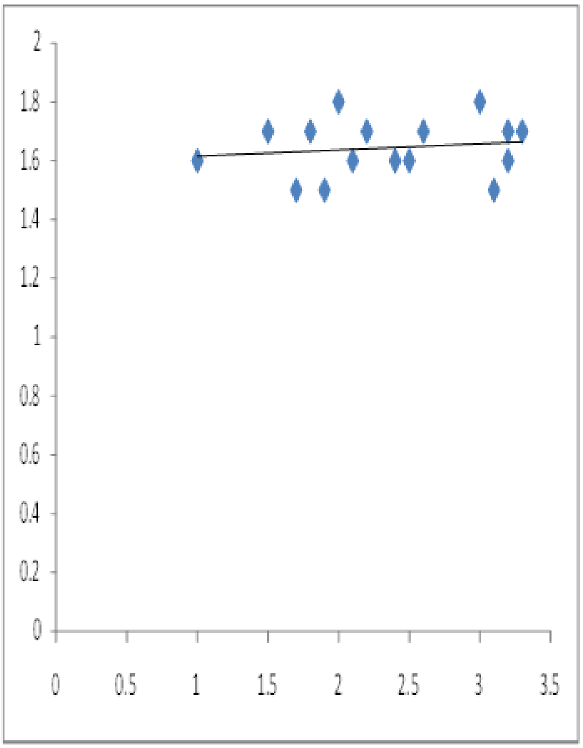

Figure 2d: F$^-$ *Vs* Bulk Density r = 0.150

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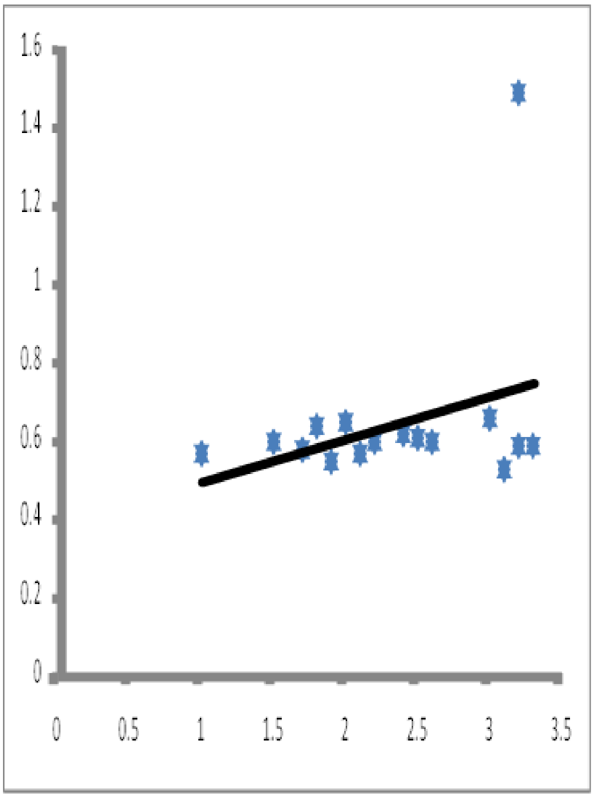

Figure 2e: F^- *Vs* Particle Density r = -0.270

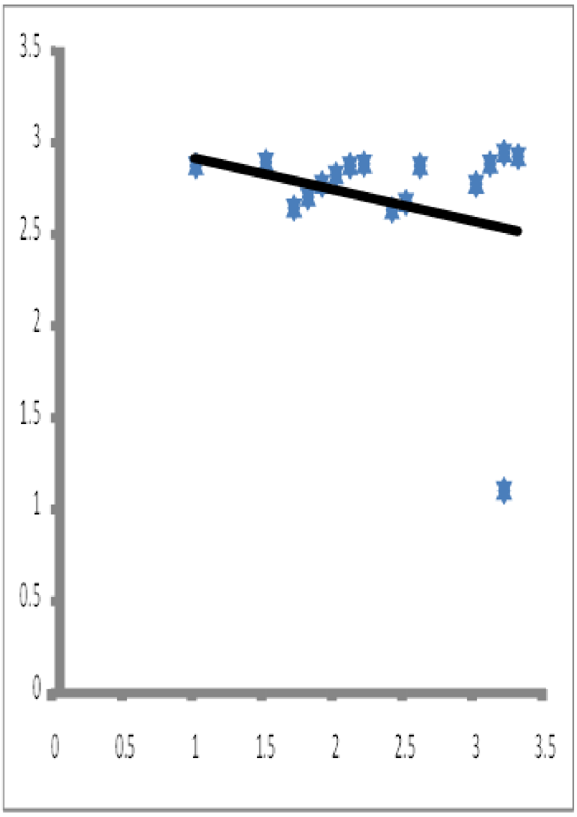

Figure 2f: F^- *Vs* Porosity r = 0.333

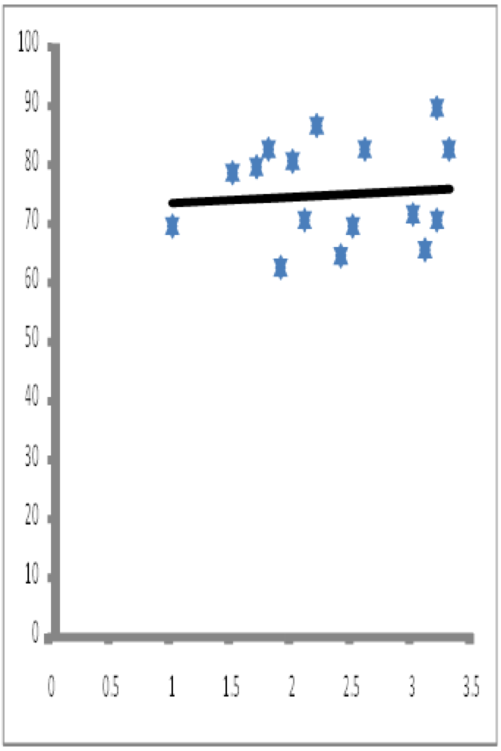

Figure 2g: F^- *Vs* Ca^{2+} r = 0.008

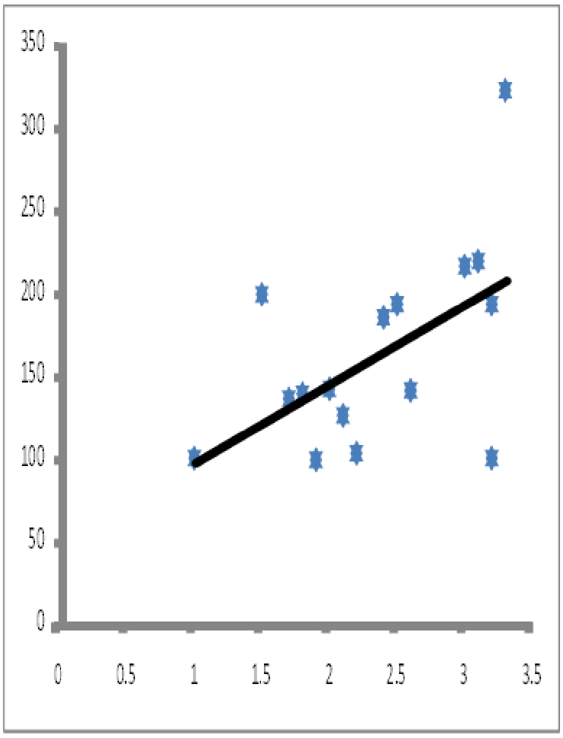

Figure 2h: F^- *Vs* Na^+ r = 0.457

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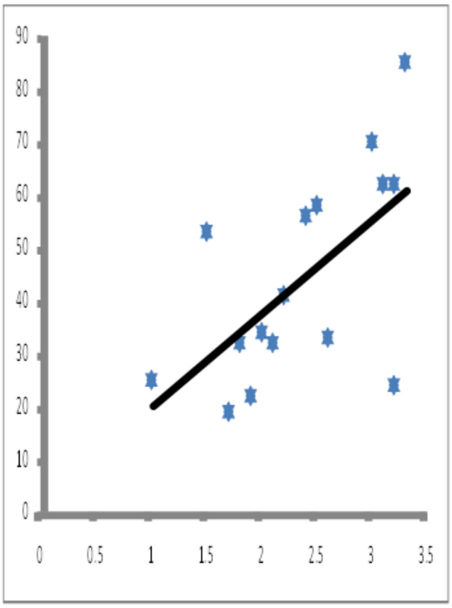

Figure 2i: F^- *Vs* K^+ r = 0.616

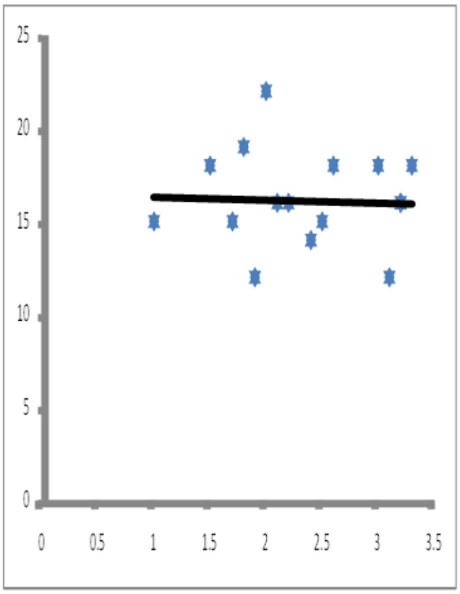

Figure 2j: F^- *Vs* Cl^- r = -0.044

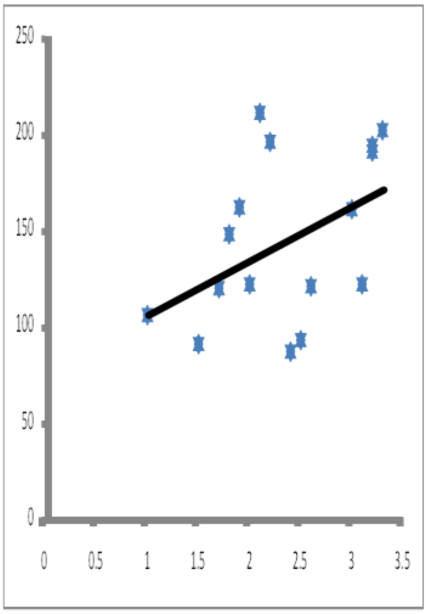

Figure 2k: F^- *Vs* Mg^{2+} r = 0.450

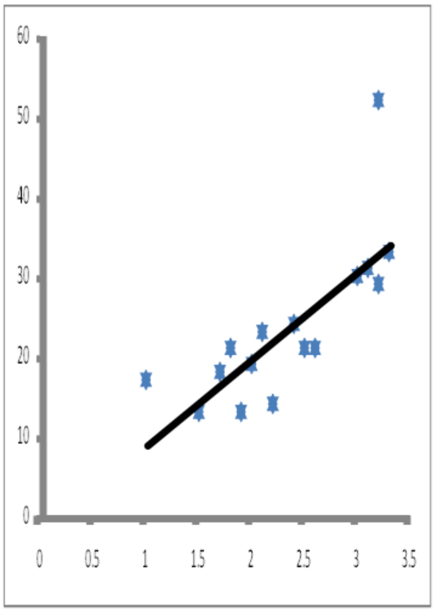

Figure 2l: F^- *Vs* PO_4^{3-} r = 0.761

The chloride content found in field soil from Athalavilai village and Rajavoor was 12 to 19 mg/Kg. Chloride has slightly positive correlation (r = 0.098) with fluoride (Figure 2j). Phosphate ranged from 13 to 31 mg/Kg. The minimum and maximum concentrations of phosphate were reported from Amaravathivilai and Azagappapurm respectively. Phosphate had a high correlation (r = 0.746) with fluoride (Figure 2l), as the farmers in the area have been using diammonium phosphate (DAP) fertilizer in their fields that releases fluoride into the soil environment. Phosphate fertilizer application to pastures increases topsoil fluoride concentration but seldom increases the fluoride concentration in the herbage (Loganathan, *et al.*, 2001). The fluoride content in these samples showed a significant positive correlation with the phosphate fertilizer used for agriculture and soil profile. There is no such relation with anthropogenic activities (Abida, 2008).

Conclusion

On the basis of the results obtained, the following important conclusions can be drawn. Most of the investigated soil samples have values for total fluoride exceeding maximum permissible value

(1.5mg/Kg). These soils have naturally high contents of fluoride. Chemical-intensive practices in agricultural systems develop and result in fluoride contamination and other pollution problems that exceed normal limits. Plants take up fluoride through fine hair rootlets and stems from the soil. More fluoride is absorbed from sandy soil than from clay soil. Application of phosphate fertilizer over long periods of time has increased the concentration of fluoride in both soil and ground water. As the area is free from industrial activity, heavy use of DAP fertilizer and soil profile may be the most likely sources of elevated ground water fluoride in the area (Abida *et al*., 2012). The high fluoride content in the cultivated soils during the rainy seasons are washed by rain water into the streams and irrigated dams where ingestion by aquatic plants and animals can occur. This could contribute to bioaccumulation of the fluoride ion in their systems (Abugri *et al.*, 2011).

It can be concluded that the fluoride is consumed by grazing animals and human beings through the plants from the soil with water. Prolonged excessive intake of fluoride will result in fluorosis. It is recommended that the organic manures have to be used for improvement in fertility of soil instead of chemical fertilizers and water analysis should be carried out from time to time to monitor the rate and kind of contamination. It is the need of awareness among the farmers to maintain the cleanliness of soil and water at their highest quality and purity levels to achieve a healthy life.

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