SEASONAL VARIATION OF FLUORIDE IN SURFACE AND GROUND WATER IN SOME OF THE VILLAGES OF AGASTEESWARAM TALUK, K.K DISTRICT, TAMILNADU

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ABSTRACT

In order to study the seasonal variation of fluoride in surface and ground water, samples were collected from eighteen villages near the bank of Thovalai and Nanchilnadu Puthanar Channel in Kanyakumari District, Tamilnadu. The period of study was divided into three seasons (Southwest monsoon, Northeast monsoon and Summer) for two years. The concentration of fluoride was estimated by Ion Selective Electrode method. Fluoride intake may be associated with a number of adverse health effects. Dental fluorosis and effects on bones (increased fragility and skeletal fluorosis) are the two well documented adverse effects of fluoride intake. However, it is considered to be beneficial in the prevention of dental caries (tooth decay). Fluoride is a persistent and non-degradable toxin that is accumulating in water, soils, plants and wildlife. The emerging picture from all risk assessments conducted on fluoride is that there exists a narrow margin between the recommended intakes for the prevention of dental caries and the upper limits of exposure. The result showed that fluoride content of surface water ranged from a minimum of 0.10 mg/L during southwest monsoon to a maximum of 0.72 mg/L during summer. Similarly, the ground water showed the fluoride content ranged from 0.25 mg/L during southwest monsoon to 3.97 mg/L in bore well water collected from Nalloor village during summer season. The study revealed low fluoride concentration during monsoon seasons compared to summer season; this may be due to dilution with rain water. All the surface water samples were found to exhibit fluoride contents well within permissible limit prescribed by WHO (0.5 -1.0 mg/L). However, most of the ground water samples were found to have these values well above the permissible limit and hence unsuitable for drinking purpose. Overall ground water quality was found unsatisfactory for drinking purpose without any prior treatment.

Key words: Fluoride, Surface and Ground Water.

INTRODUCTION

Fluoride is a naturally occurring element[1]. Though it is not considered to be essential for human growth and development, it is considered to be beneficial in the prevention of dental caries (tooth decay). As a result, intentional fluoridation of drinking water and the development of fluoride containing oral care products (toothpastes and mouth rinses), foods (fluoridated salts), and supplements (fluoride tablets) have been employed since the early 20th century in several parts of the world as a public health protective measure against tooth decay. Additional exposure to fluoride comes from naturally occurring water (tap and mineral), beverages, food, and to a lesser extent, from other environmental sources.

Environmental transport, distribution, and transformation of fluoride are shown in Figure 1.1.

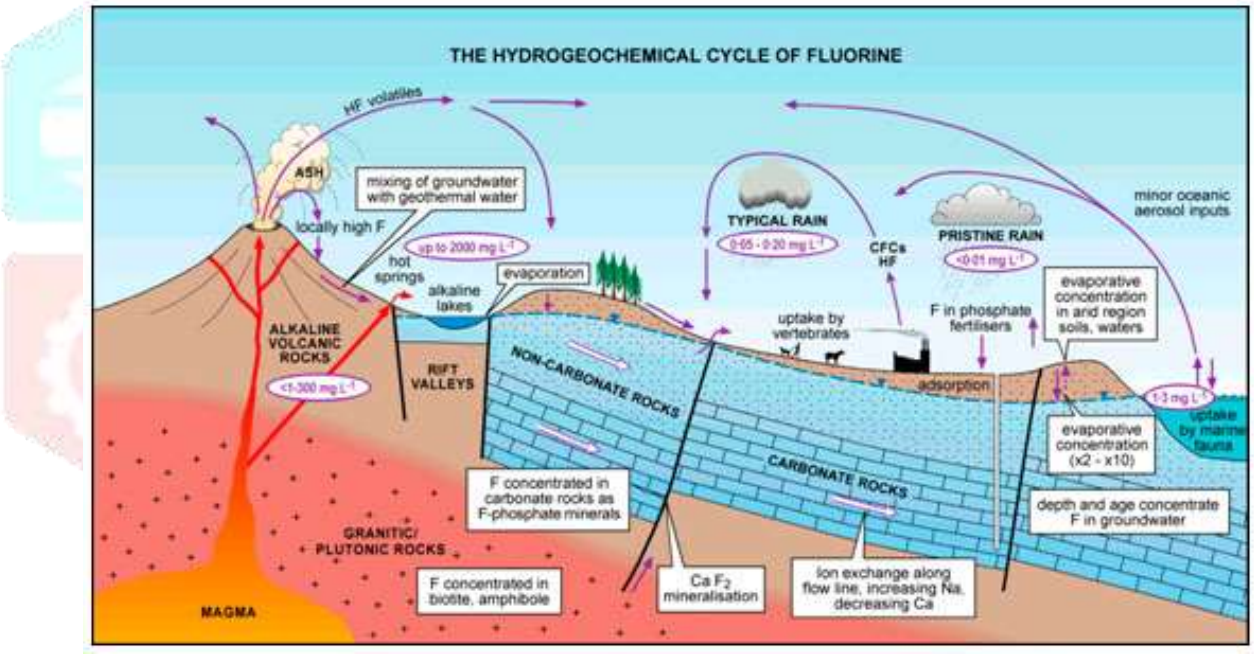


Figure 1 Schematic Diagram Showing the Hydrogeochemical cycle of Fluorine

Fluoride exists naturally in a number of different minerals. The most common minerals are sellaite (MgF_2), villiammite (NaF), fluorite (CaF_2), fluorapatite ($Ca_3F(PO_4)_3$), and cryolite (Na_3AlF_6). Fluorite (CaF_2) is common in granites, granitic gneiss, and pegmatite; while fluorapatite is more common in igneous and metamorphic rocks. Table 1.1 shows the percentage of fluoride in fluoride bearing minerals. Cryolite (used for the production of aluminium) and rock phosphates (used for the

production of fertilizers) have fluoride contents up to 54%. Most of this fluoride is insoluble and not biologically available.

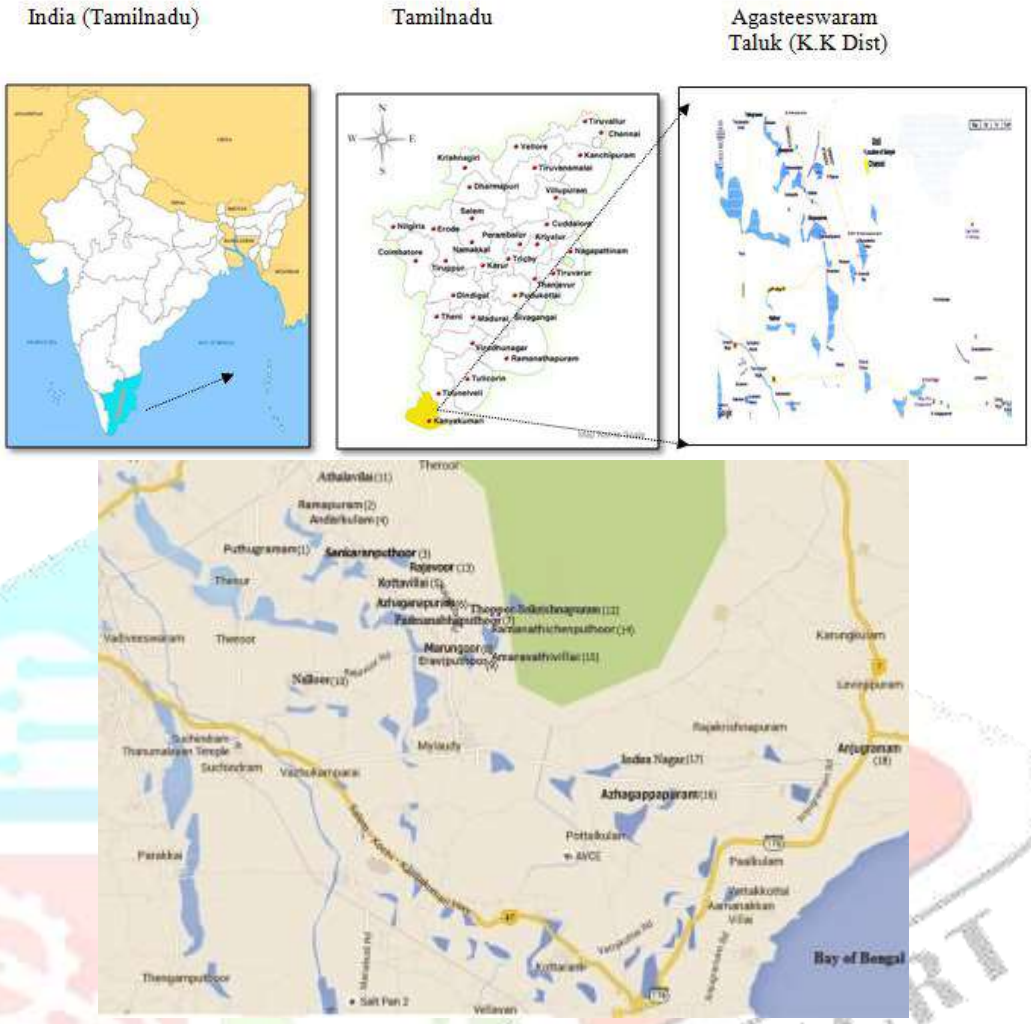
The main natural source of inorganic fluorides in soil is the parent rock. During weathering, some fluoride minerals (e.g., Cryolite) are rapidly broken down, especially under acidic conditions. Other minerals, such as fluorapatite and calcium fluoride are dissolved more slowly. The mineral fluorophlogopite (mica; $KMg_3(AlSi_3O_{10})F_2$) is stable in alkaline and calcareous soils. However, its solubility is affected by pH and the activities of silicic acid (H_4SiO_4), aluminium ion (Al^{3+}), potassium ion (K^+), and magnesium ion (Mg^{2+}) *etc*. Fluoride intake may be associated with a number of adverse health effects. Dental fluorosis and effects on bones (increased fragility and skeletal fluorosis) are two well documented adverse effects of fluoride intake. Systemic effects following prolonged and high exposure to fluoride have also been reported and more recently effects on the thyroid, developing brain and other tissues, and an association with certain types of osteosarcoma (bone cancer) have been reported[2].

MATERIALS AND METHODS

Collection of Water Samples

Study area consists of 18 villages [Puthugramam, Ramapuram, Sankaranputhoor, Andarkulam, Kottaivillai, Azaganapuram, Padmanabhaputhoor, Marungoor, Eraviputhoor, Nalloor, Athalavilai, Thoopor-Srikrishnapuram, Rajavoor, Ramanathichenputhoor, Amaravathivillai, Azagappapuram, Indira Nagar, and Anjugramam] near the bank of Thovalai and N.P Channel in Agasteeswaram Taluk, Kanyakumari District (K.K Dist), Tamilnadu[3]. The district lies between 77º15′ and 77º36′ of the eastern longitudes and 8º03′ and 8º35′ of the northern latitudes. It is bordered by Tirunelveli district of Tamilnadu in the north and northeast, and Kerala State in the northwest, and sea in the west and the south (Figure 1).

Figure 1: Maps representing the location sites



The period of study (in water, soil, and vegetation) was divided into three seasons for two years (2011-12 and 2012-13)

1. The southwest monsoon (SWM) between June and September
2. The northeast monsoon (NEM) between October and December
3. The summer season (SS) between March and May

Totally 70 water samples per season were collected from ground water [hand pump (HP), bore well (BW), open well (OW)] surface water [river water (RW) and pond water (PW)].Collected samples were stored in plastic containers at room temperature in a dark place until the analysis was carried out.

Determination of Fluoride

The concentration of fluoride in water samples was determined by using Fluoride ion Selective Electrode. An Elico L1 126 was used for this purpose. This instrument had fluoride ion selective electrode along with reference electrode (all Elico make) for the measurement of fluoride ion. By adding a suitable buffer solution, which is a decomplexing agent and at the same time controlling the pH and the total ionic strength, the background is prevented from interfering with the fluoride ion by complexation. For our samples, sodium citrate buffer is very effective.

The addition of a highly concentrated salt solution to a sodium fluoride solution causes the potential (to compare with slope) to shift extensively. Another such condition, however of a small size, hardly changes the potential anymore. This effect is made use of by the initial addition of the sodium citrate buffer to the sample before the initial determination and standard addition. The buffer gives the sample a high total ionic strength. Additions of a small amount of standard fluoride solution do not significantly change this system. It also controls the pH and the most important, it effectively makes or ties up the interfering ions as mentioned, thus releasing the bound fluoride. The reference electrode with a standard solution of silver chloride, as filling solution was used. TISAB was added to the standard as well as the samples before measurement of fluoride. The instrument was calibrated with four standard fluoride solutions, so chosen that the concentration of one is 10 times the concentration of the other and also that the concentration of the unknown falls between those four standards. The concentration of the unknown was directly read from the digital display of the meter.

RESULTS AND DISCUSSION

The results of fluoride analysis in surface and ground water around eighteen villages in three seasons of Kanyakumari District are presented in Table 1.

Table 1 Fluoride (mg/L) content in Ground Water (HP, BW, OW) and Surface Water (PW, RW)

S.No	Villages	Sources	Study year	Southwest Monsoon	Northeast Monsoon	Summer
1	Puthugramam	HP	2011-12	2.00	2.10	2.50
			2012-13	2.60	2.20	2.60
		BW	2011-12	1.52	1.65	1.60
			2012-13	1.65	1.70	1.65

		PW	2011-12	0.72	0.64	0.65
			2012-13	0.70	0.62	0.68
2	Ramapuram	OW	2011-12	0.25	0.28	0.68
			2012-13	0.56	0.32	0.70
		BW	2011-12	1.68	1.72	1.80
			2012-13	1.80	1.75	1.85
		RW	2011-12	0.15	0.13	0.15
			2012-13	0.15	0.13	0.14
3	Sankaranputhoor	HP	2011-12	1.50	1.60	2.20
			2012-13	2.20	1.80	2.32
		BW	2011-12	1.00	1.03	1.50
			2012-13	1.55	1.10	1.65
		RW	2011-12	0.10	0.13	0.14
			2012-13	0.10	0.13	0.15
4	Andarkulam	HP	2011-12	1.50	1.60	1.70
			2012-13	1.60	1.70	1.75
		BW	2011-12	1.20	1.30	1.30
			2012-13	1.35	1.35	1.31
		PW	2011-12	0.30	0.40	0.45
			2012-13	0.30	0.40	0.45
5	Kottavillai	OW	2011-12	2.65	2.77	2.91
			2012-13	2.95	2.80	2.95
		BW	2011-12	0.66	0.66	1.07
			2012-13	1.20	0.67	1.08
		RW	2011-12	0.40	0.45	0.38
			2012-13	0.20	0.25	0.30
6	Azhaganapuram	HP	2011-12	1.60	1.70	1.70
			2012-13	1.70	1.75	1.70
		BW	2011-12	1.75	1.83	1.90
			2012-13	1.75	1.86	1.85
		RW	2011-12	0.45	0.46	0.50
			2012-13	0.35	0.36	0.35
7	Padmanabhaputhoor	OW	2011-12	1.00	1.00	1.20
			2012-13	1.20	1.20	1.25
		BW	2011-12	0.72	0.90	1.00
			2012-13	0.92	0.96	1.20
		PW	2011-12	0.10	0.17	0.20
			2012-13	0.10	0.17	0.18
8	Marungoor	OW	2011-12	1.15	1.30	1.60
			2012-13	1.65	1.35	1.65
		BW	2011-12	1.35	1.50	1.60
			2012-13	1.65	1.60	1.70
		PW	2011-12	0.15	0.17	0.25
			2012-13	0.15	0.18	0.19
9	Eraviputhoor	OW	2011-12	0.65	0.65	0.85
			2012-13	0.93	0.76	0.91
		BW	2011-12	0.90	1.00	1.12
			2012-13	0.92	1.05	1.15
		RW	2011-12	0.20	0.19	0.18
			2012-13	0.20	0.19	0.20
10	Nalloor	HP	2011-12	1.55	1.70	1.80
			2012-13	1.85	1.75	1.85
		BW	2011-12	1.56	1.60	3.90
			2012-13	2.80	1.68	3.97
		PW	2011-12	0.18	0.27	0.29
			2012-13	0.20	0.26	0.30
11	Athalavilai	HP	2011-12	1.50	1.57	1.60
			2012-13	1.55	1.62	1.65
		OW	2011-12	0.85	0.97	1.10
			2012-13	0.98	0.98	1.20
		BW	2011-12	0.95	1.02	1.40
			2012-13	1.00	1.12	1.50
		PW	2011-12	0.15	0.25	0.26

			2012-13	0.15	0.25	0.30
12	Thoppor – Srikrishnapuram	OW	2011-12	1.25	1.46	1.50
			2012-13	1.35	1.48	1.55
		BW	2011-12	1.69	1.77	1.80
			2012-13	1.70	1.79	1.85
		PW	2011-12	0.20	0.38	0.40
			2012-13	0.20	0.38	0.40
13	Rajavoor	OW	2011-12	0.53	0.53	1.10
			2012-13	0.65	0.62	1.30
		BW	2011-12	1.65	1.60	1.70
			2012-13	1.70	1.65	1.75
		PW	2011-12	0.10	0.15	0.17
			2012-13	0.15	0.16	0.18
14	Ramanathichen Puthoor	OW	2011-12	1.00	1.00	1.80
			2012-13	1.01	1.10	1.78
		BW	2011-12	0.90	0.84	1.00
			2012-13	0.95	0.96	1.05
		PW	2011-12	0.10	0.15	0.21
			2012-13	0.20	0.25	0.26
15	Amaravathivillai	OW	2011-12	1.65	1.70	1.65
			2012-13	1.70	1.75	1.68
		BW	2011-12	0.40	0.40	0.60
			2012-13	0.45	0.38	0.80
		PW	2011-12	0.35	0.40	0.45
			2012-13	0.35	0.40	0.48
16	Azhagappapuram	OW	2011-12	0.75	0.851	1.21
			2012-13	0.80	0.78	1.32
		BW	2011-12	1.78	1.89	2.10
			2012-13	1.80	1.90	2.30
		PW	2011-12	0.20	0.40	0.42
			2012-13	0.30	0.45	0.45
17	Indira Nagar	BW	2011-12	1.65	1.78	1.80
			2012-13	1.70	1.81	1.85
		OW	2011-12	1.78	1.82	1.85
			2012-13	1.75	1.84	1.9
		PW	2011-12	0.25	0.30	0.40
			2012-13	0.15	0.16	0.18
18	Anjugramam	HP	2011-12	1.05	1.18	1.19
			2012-13	1.08	1.16	1.10
		BW	2011-12	0.65	0.8	0.85
			2012-13	1.00	1.15	1.17
		PW	2011-12	0.10	0.20	0.25
			2012-13	0.10	0.15	0.16

* BW-Bore Well, HP- Hand Pump, OW-Open Well, PW-Pond Water, RW-River Water

Table 1 shows fluoride content in surface and ground water at three seasons (Southwest monsoon, Northeast monsoon and Summer) in two study periods (2011-12 and 2012-13). The fluoride content of surface water ranged from a minimum of 0.10 mg/L [PW; Padmanabhaputhoor, Rajavoor, Ramanathichenputhoor, Anjugramam; southwest monsoon; 2011-12] to a maximum of 0.72 mg/L [PW, Puthugramam, southwest monsoon; 2011-12]. Similarly, the groundwater showed the fluoride content ranged from 0.25 mg/L in Ramapuram [OW, southwest monsoon; 2011-12] to 3.97 mg/L in bore well water collected from Nalloor during summer 2011-12), respectively. All the surface water samples were found to exhibit fluoride contents well within permissible limit prescribed by WHO (0.5 -1.0 mg/L)[4]. However, most of the ground water samples were found to have these values well above the permissible limit.

Figure 2.a-c revealed that the limitation of fluoride content in water samples (ground and surface). Green line (0 - 1.0 ppm) indicates protected villages, green line to red line (1-2.5 ppm) indicates dental fluorosis prone villages, and above red line (2.5 ppm) indicates skeletal fluorosis prone villages.

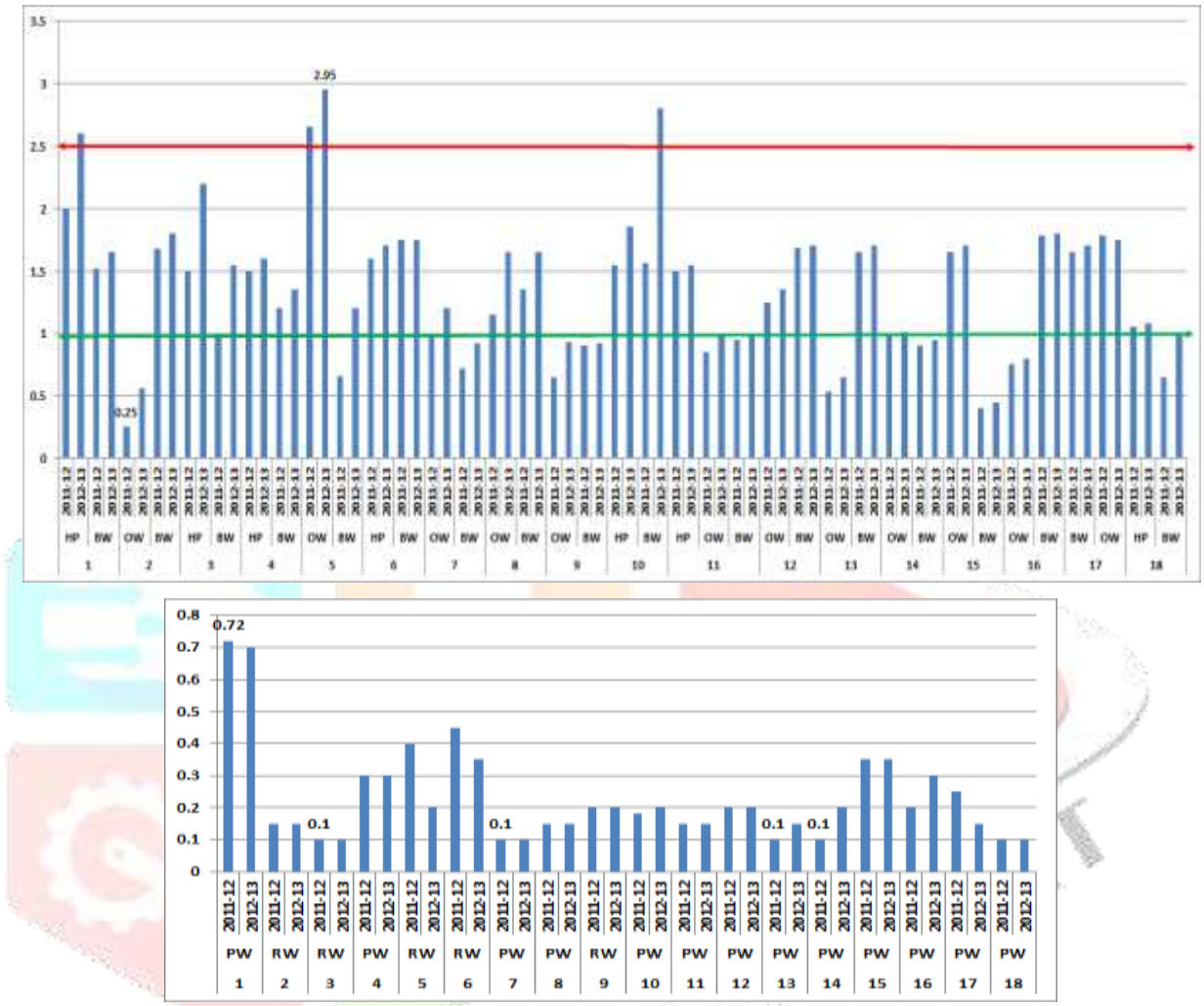
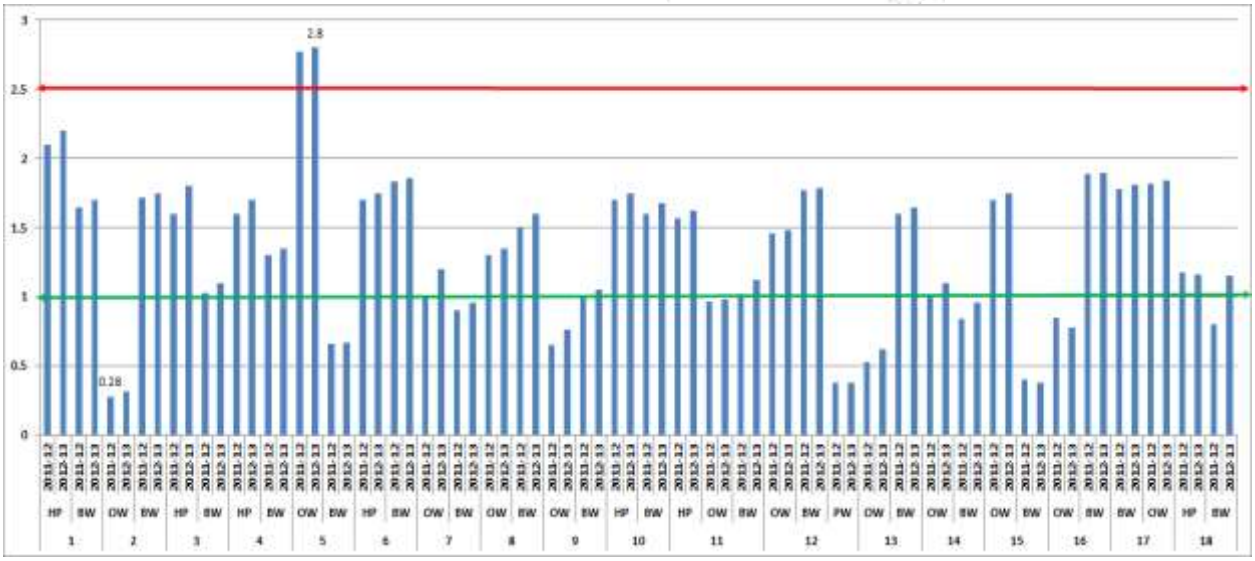


Figure 2.a Fluoride Content (in ppm) in (i) Ground and (ii) Surface Water Samples for Southwest Monsoon



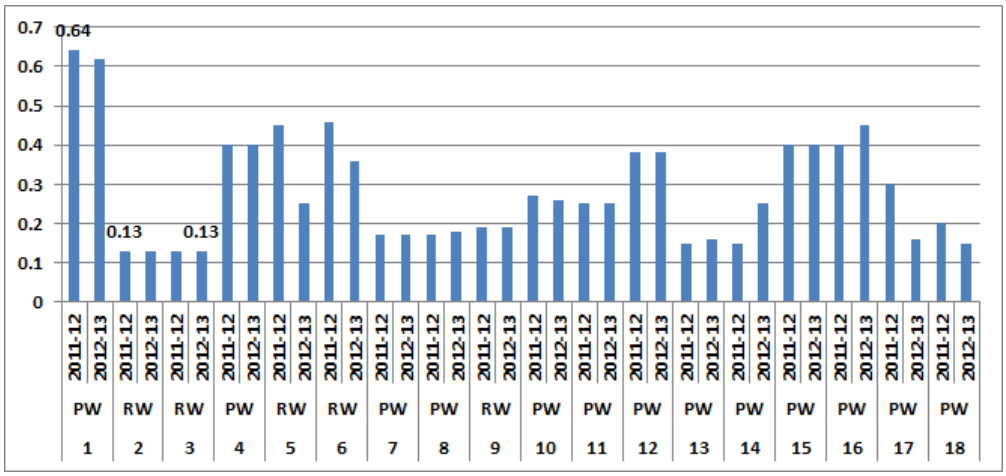


Figure 2.b Fluoride Content (in ppm) in (i) Ground and (ii) Surface Water Samples for Northeast Monsoon

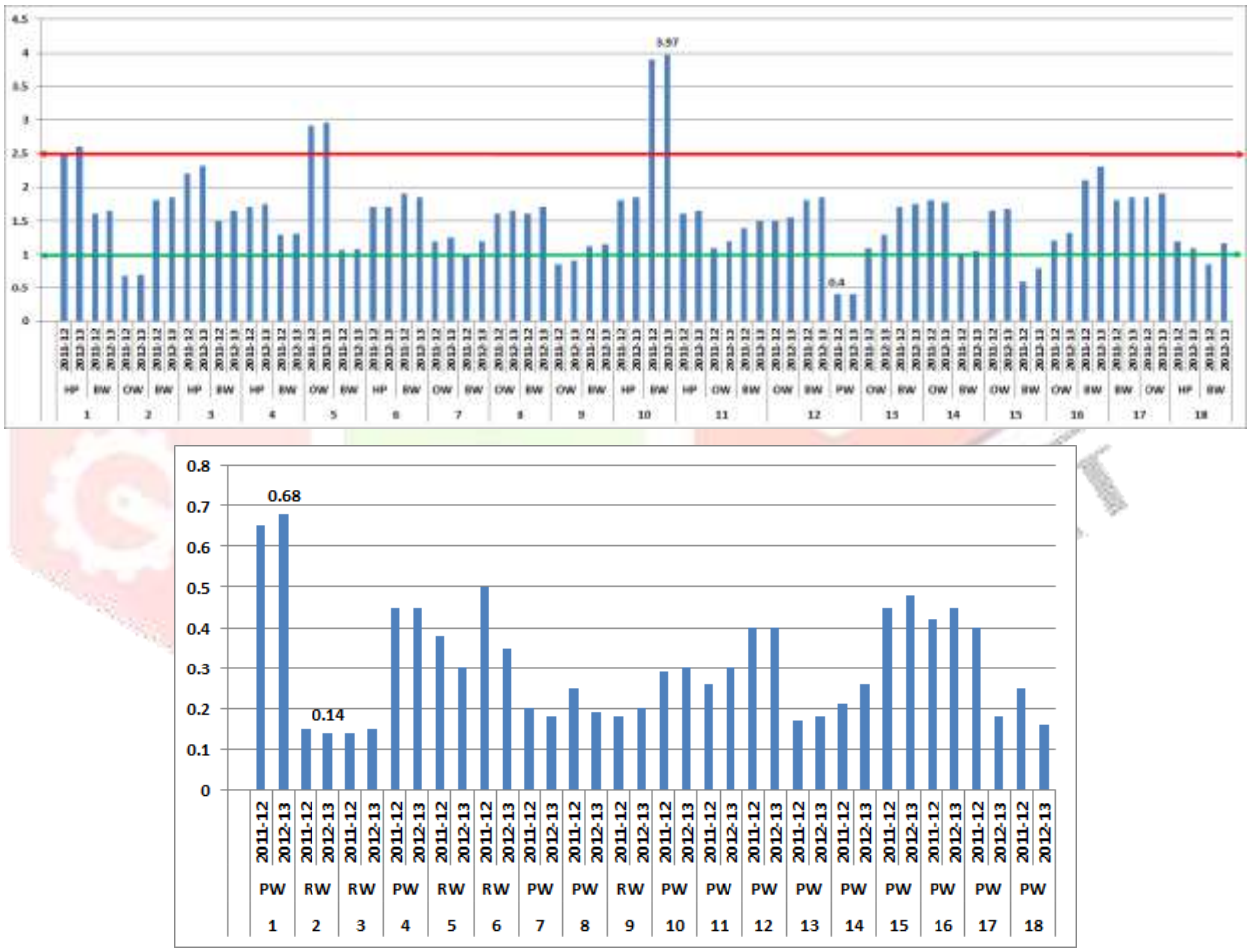


Figure 2.c Fluoride Content (in ppm) in (i) Ground and (ii) Surface Water Samples for Summer

The problem of high fluoride in groundwater has been reported by several researchers[5-8]. The results revealed that ground water samples contain the highest amount of fluoride. This may be due to the weathering of rocks containing fluoride minerals *viz*. amphiboles, hornblende, topaz, rock phosphates, *etc*., which

ultimately leads to the leaching of fluoride in the groundwater[9-11]. The high concentration of fluoride in groundwater bodies may also be due to recharge of groundwater with agricultural runoff contaminated with phosphate fertilizers. It is evident that superphosphate (2750 mg of F/Kg), potash (10 mg of F /Kg), and Nitrogen-Phosphorous-Potassium (NPK, 1675 mg of F/Kg) which are phosphate fertilizers contain remarkable amount of fluoride[12] Datta *et al.*[13] reported that if an agriculture field of 1 hectare receives 10 ml of irrigation water containing 10 mg/L of fluoride, and then the soil can obtain 10 mg/Kg of fluoride. This is considered as a potential threat for increase in fluoride concentration in soil and ground water.

The study revealed low fluoride concentration during monsoon seasons compared to summer season; this may be due to dilution with rain water. Rain water saturates the tiny spaces between alluvial materials (sand, gravel, silt, clay *etc*) or the crevices or fractures in rocks[14,15].

CONCLUSION

All the surface water samples were found to exhibit fluoride contents well within permissible limit prescribed by WHO (0.5-1.0 mg/L). However, most of the ground water samples were found to have these values well above the permissible limit. The results revealed that ground water samples contain the highest amounts of fluoride. This may be due to weathering of rocks containing fluoride minerals like amphiboles, hornblende, topaz, rock phosphates, *etc.*, which ultimately leads to the leaching of fluoride in the groundwater.

From the results and discussion presented it can be concluded that most of the water samples collected from some of the villages of Agasteeswaram Taluk, show a high concentration of fluoride in the ground water. Hence it is not suitable for consumption. Without any prior treatment high fluoride consumption leads to the fluorosis. The study also revealed low fluoride concentrations during monsoon seasons compared to summer season; this may be due to dilution effect with rain water.

REFERENCE

1. Mason B and Moore CB, Principles of geochemistry, Wiley, New York, (1982).

2. Scientific Committee on Health and Environmental Risks (SCHER), Critical review of any new evidence on the hazard profile, health effects, and human exposure to fluoride and the fluoridating agents of drinking water, Adopted this pre-consultation opinion at its 7th plenary on 18 May, (2010).

3. Tamilnadu website (Jan, 2015). http://www.tamilnadu.com.

4. WHO, International Standards for Drinking Water, 3rd ed., Geneva, (2008).

5.Msonda KW, Masamba WR,and Fabiano E,A study of fluoride groundwater occurrence in Nathenje, Lilongwe, Malawi, *Physics and Chemistry of the Earth*, 32(15-18):1178-1184, (2007).

6. Davraz A, Sener E, and Sener S, Temporal variations of fluoride concentration in Isparta public water system and health impact assessment (SW-Turkey), *Environmental Geology*, 56:159-170, (2008).

7. Desbarats AJ, An elevated fluoride and boron concentrations in ground waters associated with the Lake Saint-Martin impact structure, Manitoba, *Applied Geochemistry*, 24:915-927, (2009).

8. Keshavarzi B, Moore F, Esmaeili A, and Rastmanesh F, The source of fluoride toxicity in Muteh area, Isfahan, Iran, *Environmental Earth Sciences*, doi: 10.1007/s12665-009-0390-0, (2010).

9. Salve PR, Maurya A, Kumbhare PS, Ramteke DS, and Wate SR, Assessment of Groundwater Quality with Respect to Fluoride, *Bull Environ Contam. Toxicol*, 81:289- 293, (2008).

10. Chanderkar AV and Kamble RK, Groundwater fluoride in Rajura Tehsil in Chandrapur district, Maharashtra, *IJEP*, 30(10):823-831, (2010).

11. Reshma S and Prakasam VR, Portability of dug wells of Mayyanad panchayat, Kerala, *Indian J. Environ. Ecoplan*, 7(3):471-476, (2003).

12. Ramamohana Rao NV, Suryaprakasa Rao K, and Schuiling RD, Fluorine distribution in waters of Nalgonda District, Andhra Pradesh, India, *Environmental Geology*, 21:84-89, (1993).

13.Datta PS, Deb DL, and Tyagi SK, Stable isotope (180) investigations on the processes controlling fluoride contamination of ground water, *Journal of Contaminant Hydrology*, 24:85-96, (1996).

14. Sabal D and Khan TI, Fluoride contamination status of groundwater in Phulera Tehsil of Jaipur district, Rajasthan, *J. Environ. Biol*., 29:871-876, (2008).

15. Division of Minerals and Geology, Ground water in Colorada-A primer, *Rock Talk*, 5(4):1-16, (2000).