Research Inventy: International Journal of Engineering And Science
Vol.6, Issue 8 (September 2016), PP -12-24
Issn (e): 2278-4721, Issn (p):2319-6483, www.researchinventy.com

Comparative study of fluoride with chemical parameters of brine solutions, salt and pan soil from salt pans located in the east coastal belts of Tamil Nadu, India

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Abstract: *Variations in the fluoride content of saline water, salt and pan soil from nine different salt pans located at the East Coast belt of Tamil Nadu have been documented. Fluoride which is non-degradable and persists in the environment was estimated by Zirconyl-alizarin method. The fluoride level varied from 0.6 to 1.7 ppm. Fluoride level in the salt of Marakkanam (Bore well) was found to be slightly higher than other salt pans.The chemical parameters which are used to study the level of fluoride in saline waters included chloride, sulphate, sodium, magnesium, potassium and calcium.*
Keywords: *Fluorosis. Salt pan. Pan soil. Born-Haber cycle, Fluoride*

I. Introduction

Fluoride (F) is harmful when large doses are ingested extremely, and lower doses are taken continually [1,2]. The detrimental impact of fluoride (F) on plants, animals, and humans are well documented [3-5]. Many plants are sensitive to pollution especially F. Certain physiological processes like plant growth and chlorophyll content are known to decrease markedly decreased by F^- ion [6,7]. Demarcated opacities have a variable etiology: they may be associated with early childhood diseases, antibiotic therapy, and the toxic influence of dioxins on tooth germs [8,9]. However, it is often difficult to distinguish between F and non-F opacities, since the ameloblasts may respond to different types of injury in similar ways. Consequently, it is possible that the diffuse opacities can result from other systemic results, such as infections, or the antibiotics used to treat the infections [8,10].

Chronic fluoride (F) intoxication and fluorosis result in body pain, restricted movements of the joints, osteosclerosis, osteoporosis and other adverse effects [11]. Fluorosis is a worldwide health problem and is endemic in areas where the F content in drinking water is high. Its primary manifestations in humans and mammals are mottling of teeth and osteosclerosis of the skeleton (Fig. 1) [12].

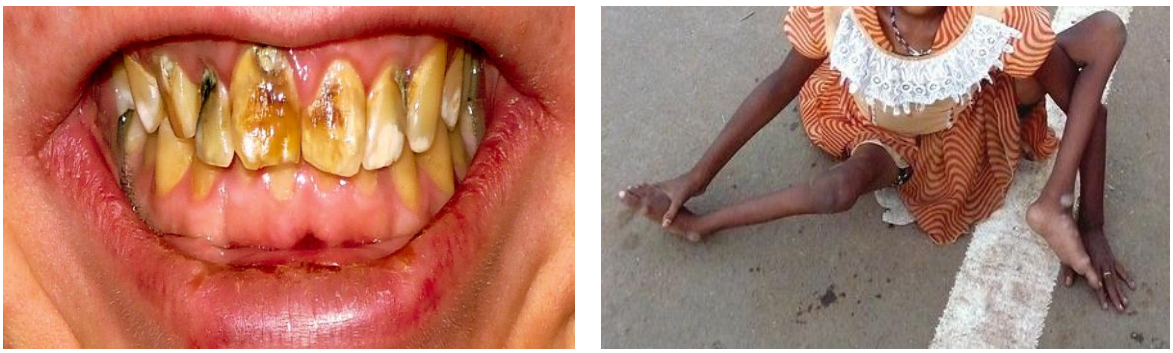

Fig.1 Fluorosis in humans

Excess intake of fluoride (F), apart from causing dental and skeletal abnormalities, can inhibit the activities of many enzymes [13]. In aquatic animals, F uptake occurs either through exposure to the surrounding water or feeding. Chronic exposure of fingerlings of Indian major carp to 15 mg NaF/l in water has been found to cause soft tissue damage [14]. Fluorosis originating from F in drinking water is of great concern in India. During the formation of sodium fluoride, sodium chloride is also crystallized predominantly. Both NaF and NaCl are having face centered cubic structures [15] (Fig.2). The number of atoms per unit cell in FCC arrangement is four.

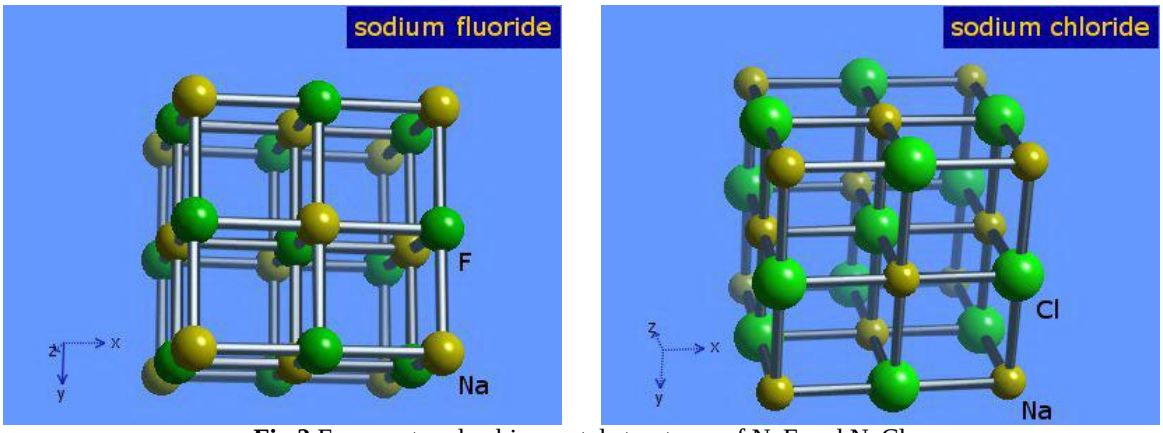

Fig.2 Face centered cubic crystal structures of NaF and NaCl

It has been reported hypo to hyper-endemic in more than fifteen states in India, viz., Andhra Pradesh, Bihar, Delhi, Gujarat, Haryana, Jammu & Kashmir, Karnataka, Kerala, Madhya Pradesh, Maharashtra, Orissa, Punjab, Rajasthan, Tamil Nadu and West Bengal [16,17].

II. Materials And Methods

2.1. The study area

The study area which includes Puthalam (Kanyakumari District), Kovalam (Kanyakumari District), Thoothukudi (Thoothukudi District), Veppalodai (Thoothukudi District) Ramanathapuram (Ramanathapuram District), Vedaranyam (Nagapattinam District), Parangipettai (Cuddalore District), Marakkanam I and II (Villupuram District) are displayed in the Tamil Nadu map (Fig 3). It includes more salt pans throughout Tamil Nadu.

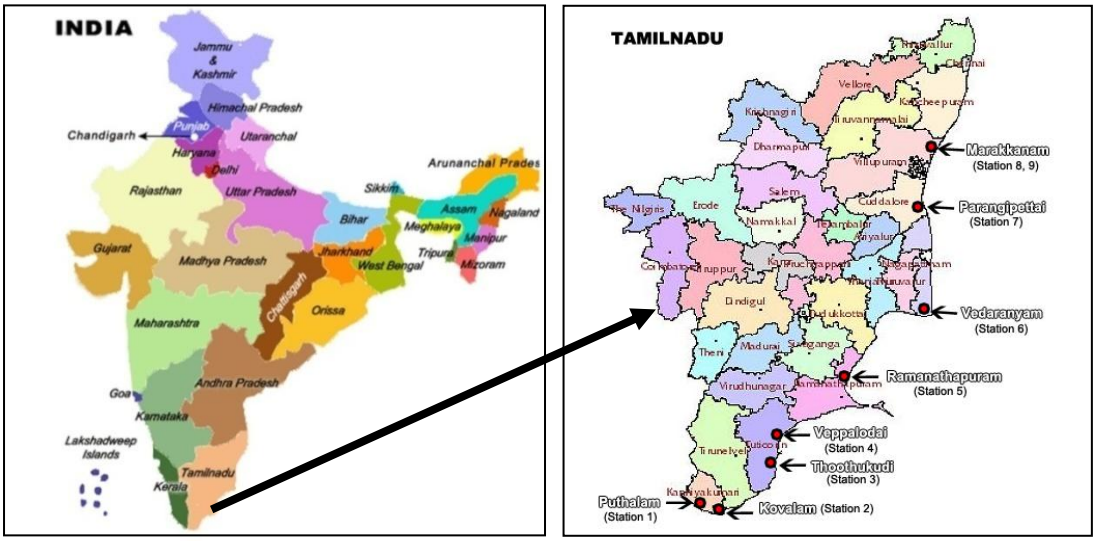

Fig.3. Station location map of salt pans in Tamil Nadu.

The area experiences hot summer and general dryness during the months of March, April and May. Among the salt pans, many of them (Kovalam, Thoothukudi, Veppalodai, Vedaranyam, Parangipettai, Marakkanam - I) receive saline water from the sea. Other salt pans (Ramanathapuram, Marakkanam - II) gain brine solutions from the bore wells. Few salt pans like Puthalam use both these solutions. Salt pans from Marakkanam to Thoothukudi mainly receive saline water from Bay of Bengal, but Kanyakumari District salt pans get saline water from Arabian Sea. Initially, the saline water is pumped into the reservoir. Later, it becomes a concentrated solution, and it can be transferred into the condenser ponds. Then it is channalised to the crystallizer ponds. After a few days, the concentrated brine solution present in the crystallizer pond gets crystallized into fine salt. The main purpose of this study was to highlight the fluoride level in brine solutions, salt and pan soil in the salt pans of the selected study area.

2.2. Sampling and sample preparation

2.2.1. Collection of brine samples

The saline water samples were collected from the crystallizer ponds of each salt pan daily for a period of seven days during the year 2011and 2012 summer. The samples were collected in 1 litre capacity sampling polythene bottles. The sampling bottles were cleaned thoroughly with water, rinsed with de-ionized water for two to three times before collecting the brine solution for estimation. Due to evaporation, the concentration of the saline water in the salt pan gradually increased, and finally salt was crystallized on the seventh day. The perfect crystallized salt was also collected for the estimation of F^- ion. For the estimation of a saturated solution was made by dissolving 357 g salt in 1litre of the de-ionized water.

2.2.2. Collection of soil samples

The sampling of soil was obtained by inserting a PVC pipe of 2 feet depth into the salt pan crystallization ponds. After crystallization the PVC pipe was removed, and soil samples collected for estimation from the nine salt pans were analyzed by dissolving 470 g of the pan soil in 1 litre of the de-ionized water.

2.3. Analytical methods and materials

Natural saline water contains many elements including fluoride. For the support of change in fluoride ion concentration during crystallization, along with fluoride, other anions such as chloride, iodide, sulphate, and cations such as sodium, magnesium, potassium, calcium were also estimated.

Fluoride was estimated by Zirconyl-alizarin method [18]. Mohr's titration method was employed for chloride estimation [19-21]. Turbidimetric method was adopted for the estimation of sulphate [21]. Sodium and potassium were estimated by flame emission photometric method [22]. For the estimation of calcium and magnesium in saline water, complexometric titration using ethylene diamine tetra acetic acid (EDTA) as the titrant and EBT as an indicator were used [23].

III. Results And Discussion

The data on fluoride ion distribution in brine solutions, salt and pan soil samples on the Eastern Coastal belts of Tamil Nadu are presented in Table 1.

Table 1: Amount of fluoride and other ions in the salt pans of study area

Salt Pans	Days in the crystallizer pond	Parameters						
		Fluoride (mg/l)	Chloride (g/l)	Sulphate (g/l)	Sodium (g/l)	Magnesium (g/l)	Potassium (g/l)	Calcium (g/l)
Station 1 Puthalam	1	0.6	45.38	11.53	28.55	14.86	3.91	6.01
	5	0.8	226.90	26.18	72.26	44.96	14.08	11.02
	7	0.7	191.45	18.54	56.05	34.64	10.44	7.82
	Salt (10)	0.7	187.90	9.61	60.69	2.43	2.82	4.01
	pan soil (10)	1.0	194.99	30.26	54.28	14.58	5.01	8.02
Station 2 Kovalam	1	0.9	67.36	19.93	32.81	6.08	4.50	6.01
	5	1.2	241.79	45.15	40.62	19.44	6.49	13.23
	7	0.8	207.04	36.99	36.32	15.80	5.71	10.42
	Salt (10)	0.8	198.54	9.61	35.63	2.43	3.56	4.01
	pan soil (10)	0.6	203.85	24.98	54.28	38.89	2.31	6.01
Station 3 Thoothukudi	1	0.9	233.99	17.05	36.00	36.46	8.13	8.02
	5	1.2	280.08	41.07	51.06	93.57	15.56	10.42
	7	1.0	262.35	36.02	40.28	81.42	13.29	8.22
	Salt (10)	1.0	255.26	9.61	39.50	2.43	2.82	6.41
	pan soil (10)	0.6	251.71	35.06	23.27	40.10	3.56	8.02
Station 4 Veppalodai	1	1.2	138.27	33.14	46.23	7.29	9.46	8.02
	5	1.7	283.62	39.87	107.68	30.38	14.08	14.03
	7	1.2	265.90	33.62	80.26	26.74	11.96	8.22
	Salt (12)	1.0	198.54	9.61	75.61	3.65	2.15	7.41
	pan soil (12)	1.0	202.08	15.85	29.98	34.03	4.97	6.01
Station 5 Ramanathapuram	1	1.0	152.45	12.49	43.73	8.51	5.94	6.61
	5	1.6	255.26	33.14	104.56	23.09	11.96	13.23
	7	1.2	244.62	31.22	94.90	19.44	11.03	11.22
	Salt (10)	1.0	177.26	9.61	77.52	2.43	2.85	9.42
	pan soil (10)	1.2	230.44	12.49	43.73	11.18	6.73	6.41
Station 6 Vedaranyam	1	0.8	155.99	12.97	37.20	10.94	4.85	6.21
	5	1.2	251.71	35.06	111.13	26.74	9.66	14.03
	7	1.0	237.53	32.66	94.93	20.05	8.48	11.82
	Salt (10)	1.0	235.76	11.05	87.71	3.65	2.66	9.42
	pan soil (10)	0.8	134.72	18.73	38.53	15.80	5.98	10.42

Station 7 Parangipettai	1	0.8	159.54	13.45	33.50	14.34	4.03	6.41
	5	1.2	227.61	24.98	60.74	29.17	6.76	15.83
	7	0.9	222.64	19.93	38.69	21.88	6.18	12.42
	Salt (10)	0.9	212.72	14.89	36.69	2.43	2.11	10.02
	pan soil (10)	0.9	216.26	15.85	36.67	19.44	4.61	12.22
Station 8 Marakkanam (Sea Water)	1	0.9	106.36	23.06	26.14	8.88	6.57	6.21
	5	1.4	241.08	36.02	67.48	35.24	12.67	10.42
	7	1.1	184.35	33.62	51.13	22.00	8.45	5.61
	Salt (8)	1.0	141.81	13.45	42.12	3.52	2.82	5.41
	pan soil (8)	1.0	198.54	23.06	43.73	26.74	6.37	4.01
Station 9 Marakkanam (Bore well)	1	1.0	134.72	12.49	26.85	13.37	3.25	2.41
	5	1.6	276.53	23.06	59.57	29.17	9.15	12.63
	7	1.2	244.62	16.33	50.07	23.70	7.94	9.02
	Salt (10)	1.2	191.45	11.53	49.52	2.31	2.85	4.61
	pan soil (10)	0.8	255.26	10.57	31.45	26.74	7.12	6.01

Samples 1, 5 and 7 are brine solutions collected from the crystallizer pond during 1st, 5th and 7th days
The salt and pan soil collection days are given in brackets.

3.1 Chemistry of metal halides (MX_n)

The amount of all the anions and cations were found to be very much less on the first day of sampling, and it gradually reached the highest value on the fifth day. The concentration of ions declined in the seventh sampling and in the salt sample also. During salt formation considerable amount of cations and anions leached into the soil including fluoride. By the use of Born-Haber cycle, lattice energies of various ionic compounds were calculated. Lattice energy was observed to increase with increasing ionic charges and decrease with decreasing ionic sizes. The Born-Haber cycle applies only to fully ionic solids such as certain alkali halides. Most compounds include covalent and ionic contributions to chemical bonding and to the lattice energy, which is represented by an extended Born-Haber thermodynamic cycle[24] (Fig. 4).

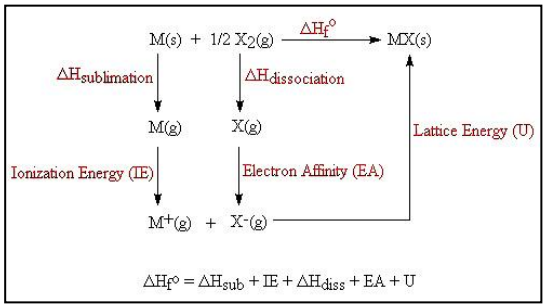

Fig. 4 Born-Haber cycle

Lattice energies (U) of various compounds [25] were tabulated (Table 2).

Table 2 Compounds and their lattice energies

Name of compound	Lattice energy (kJ/mole)
NaF	923
NaCl	786
NaBr	747
NaI	704
KF	821
KCl	715
MgF_2	2957
$MgCl_2$	2526
CaF_2	2635
$CaCl_2$	2258

Lattice energies of the given ionic compounds varied from 704 kJ/mole (NaI) to 2957 kJ/mole (MgF_2). During the estimation of all samples, it was found that the availability of sodium, potassium, calcium and chloride ions were more, and their compounds were formed predominantly. Compared to other halides, less availability of fluoride ions, its compounds (MF_n) were also formed. Lattice energy decreased while moving down a group in the periodic table. This is mostly due to the fact that while moving down a group in the periodic table the atomic radius increases. For example, while going down group VIIA of the periodic table from fluorine to iodine, the lattice enthalpies of their sodium salts (NaX) fall as the size of the negative ions increases [26] (Fig. 5).

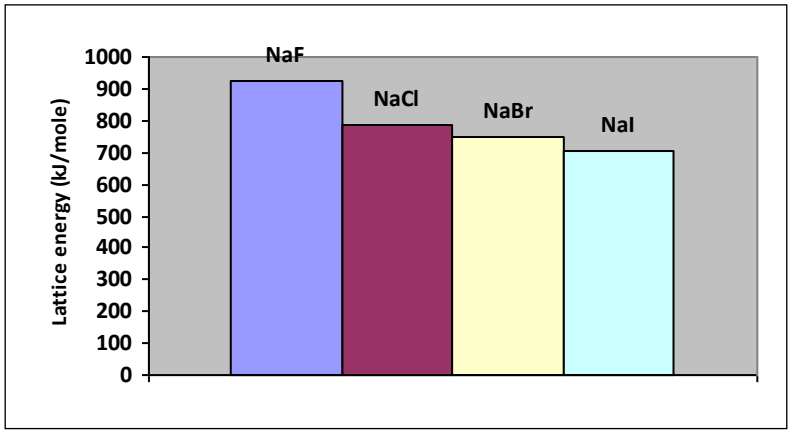

Fig.5 Lattice enthalpies of sodium halides

The electron gain enthalpy of Cl (348 kJ mol^{-1}) is higher than F (320 kJ mol^{-1}). The reason being due to small size of fluorine atom. The addition of an extra electron produces high electron density which increases strong electron – electron repulsion. The repulsive forces between electrons results in low electron affinity of F. Because of the high electron gain enthalpy of Cl, formation of sodium chloride is highly favoured than formation of sodium fluoride. More over the concentration of Cl^- ion is also very high compared to F^- ion.

In our selected study area of nine different salt pans in Tamil Nadu, the fluoride levels in brine solutions and salt samples ranged from 0.6 mg/l to 1.7 mg/l. The maximum value of fluoride in the brine sample was found at Veppalodai salt pan (1.7 mg/l), and lower value was at Puthalam salt pan (0.6 mg/l). The salt samples also contained a considerable amount of fluoride varying from 0.7 to 1.2 mg/l. The peak value (1.2 mg/l) was observed at Marakkanam (Borewell) salt pan, and the minimum value (0.7 mg/l) was observed at Puthalam Salt pan. From the results of an estimation of brine solutions and salt of Veppalodai salt pans, Thoothukudi District, Tamil Nadu, India, the fluoride values ranged between 1.2 mg/l to 1.7 mg/l [27]. In another study at Parangipettai, Cuddalore District, Tamil Nadu, India, proved the value of fluoride in the brine solutions and salt which was ranged between 0.8 mg/l to 1.2 mg/l [28]. The study of soil samples revealed the available fluoride in the range from 0.6 mg/l to 1.2 mg/l. Maximum fluoride level was observed in the pan soil of Ramanathapuram salt pan (1.2 mg/l), and the minimum fluoride level was at Kovalam and Thoothukudi salt pans (0.6 mg/l) The variations in fluoride ion concentration were estimated and reported in Fig. 6.

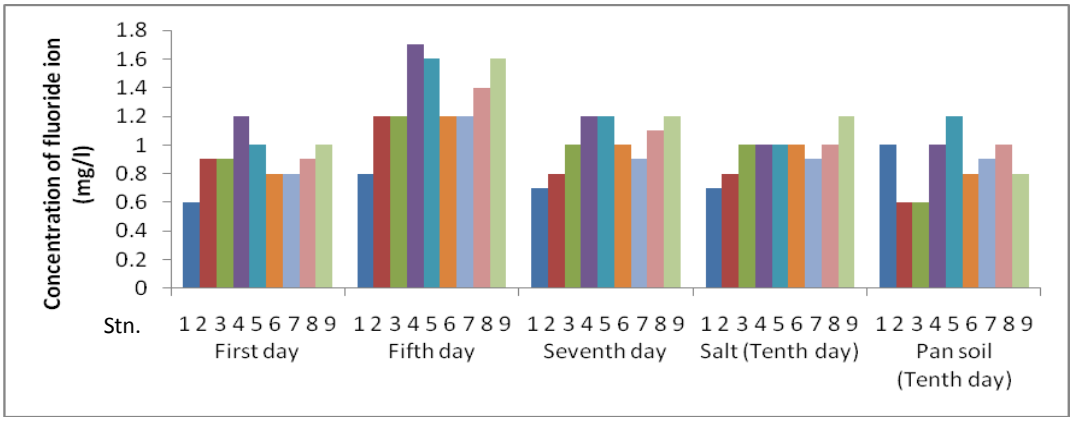

Fig. 6 Fluoride in the brine solutions, salt and pan soil of nine different stations

[1,2,3,4,5,6,7,8,9 represent salt pans of Puthalam, Kovalam, Thoothukudi, Veppalodai, Ramanathapuram, Vedaranyam, Parangipettai, Marakkanam (Sea water) and Marakkanam (Bore well) respectively]

Previous fluoride studies reveals that of an estimation of ground water used for drinking and irrigation purpose in Belora region, Nandgaon (Khandeshwar) Taluk, Amravati district, Maharashtra State had in India fluoride concentration from 0.93 mg/l to 2.11 mg/l [29]. In another study, it was reported that the amount of fluoride in ground and surface water used for drinking and irrigation purposes in Mysore Taluk, Karnataka State of India ranged from 1.5 to 3 mg/l [30].

The saline waters of Marakkanam, Villupuram District, Tamil Nadu, India, have high level of fluoride initially but on crystallization the salt proceeds to process only limited content of fluoride making it conducive for human consumption and avoid fluorosis from health view point [31]. Brine solutions of Thoothukudi, Thoothukudi District, Tamil Nadu, India, salt pan contained high levels of fluoride initially (1.2 mg/l) but after crystallization its level declined (1.0 mg/l) [32].

During the crystallization of NaCl, NaF was also co-crystallized, since both are iso structural (FCC). The distribution of chloride ions in 9 salt pans were estimated accordingly. On the first day it was less (45.38 g/l) at Puthalam Salt pan, and its values were maximum (283.62 g/l) at Veppalodai salt pan on the fifth day in the crystallizer pond. These variations in chloride ion concentration estimated are reported in Fig. 7.

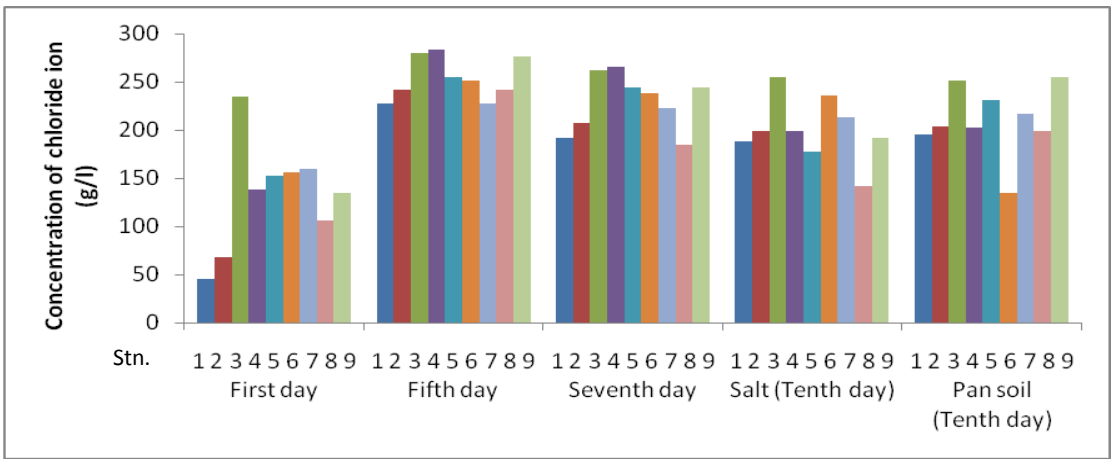

Fig.7 Chloride in the brine solutions, salt and pan soil of nine different stations

[1,2,3,4,5,6,7,8,9 represent salt pans of Puthalam, Kovalam, Thoothukudi, Veppalodai, Ramanathapuram, Vedaranyam, Parangipettai, Marakkanam (Sea water) and Marakkanam (Bore well) respectively]

The concentration of iodide in the salt was also estimated. The amount of iodide in this salt pan was found to be very less (60 ppb). For human health, considerable amount of iodine is required. Deficiency of iodine causes goiter (Fig 8).

Fig. 8 Goiter in human

To avoid such kind of diseases, the concentration of iodine in salt was gradually increased in Switzerland. (3.75 mg/kg in 1952; 7.5 mg/kg in 1962; 15 mg/kg in 1980; 20 mg/kg in 1998 and 25 mg/kg in 2014) [33].

The variations of sulphate ion concentration estimated are presented in Fig. 9. The higher concentration of sulphate in saline water samples were found in Kovalam salt pan on the fifth day in the crystallizer pond (45.15 g/l), while the lower concentration was at Puthalam salt pan on the first day of collection (11.53 g/l). Here, the salt contained a high level (14.89 g/l) of sulphate in Parangipettai salt pan, and the low level (9.61 g/l)

was observed at Puthalam, Kovalam, Thoothukudi, Veppalodai and Ramanathapuram salt pans. The maximum amount of sulphate recorded was at the pan soil of Thoothukudi salt pan (35.06 g/l), and the minimum level (4.80 g/l) was at Kovalam salt pan.

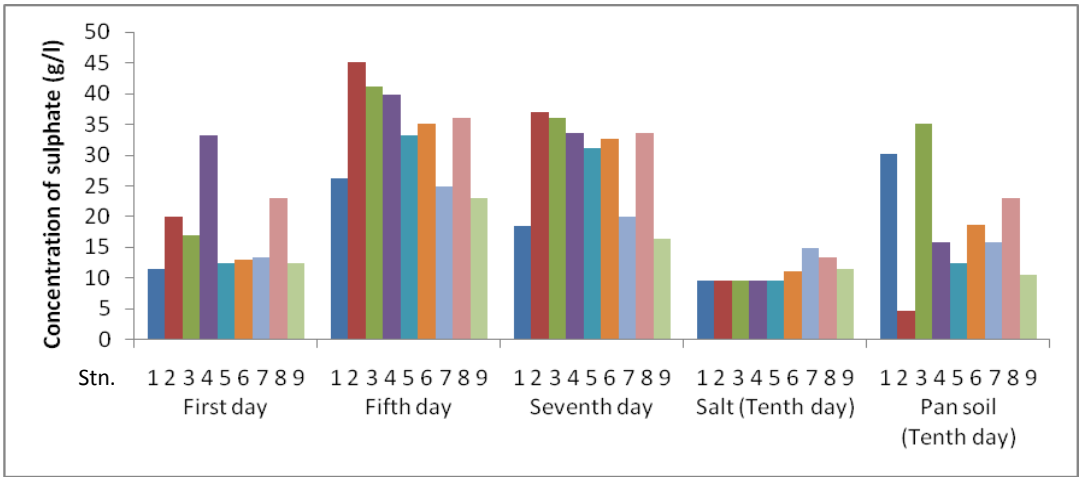

Fig.9 Sulphate in the brine solution, salt and pan soil of nine different stations

[1,2,3,4,5,6,7,8,9 represent salt pans of Puthalam, Kovalam, Thoothukudi, Veppalodai, Ramanathapuram, Vedaranyam, Parangipettai, Marakkanam (Sea water) and Marakkanam (Bore well) respectively]

The variations in the sodium ion concentration estimated are portrayed in Fig. 10. The concentration of sodium in the brine solutions of all the nine salt pans in the crystallizer ponds ranged from 26.14 g/l (Marakkanam - Sea water salt pan) to 111.13 g/l (Vedaranyam salt pan). In salt, the concentration of sodium was found to be 87.71 g/l in Vedaranyam salt pan, and 35.63 g/l at Kovalam salt pan. The level of sodium in the pan soil varied from 23.27 g/l (Thoothukudi salt pan) to 54.28 g/l (Puthalam and Kovalam salt pans).

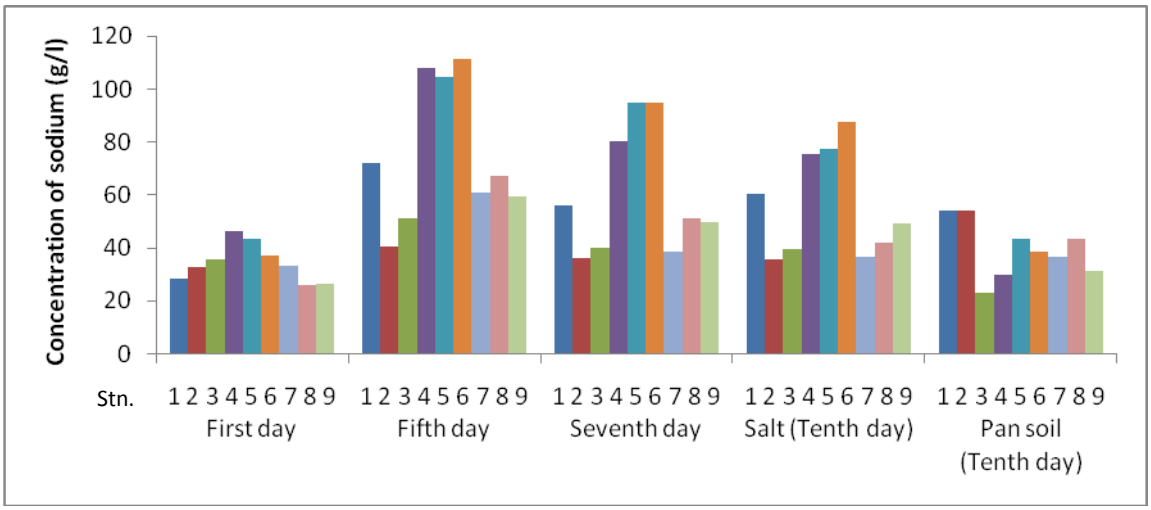

Fig.10 Sodium in the brine solutions, salt and pan soil of nine different stations

[1,2,3,4,5,6,7,8,9 represent salt pans of Puthalam, Kovalam, Thoothukudi, Veppalodai, Ramanathapuram, Vedaranyam, Parangipettai, Marakkanam (Sea water) and Marakkanam (Bore well) respectively]

The variations in magnesium ion concentration that were estimated are presented in Fig. 11. The amount of magnesium in brine solution was in the range of 6.08 g/l (Kovalam salt pan) to 93.57 g/l (Thoothukudi salt pan). The higher level was observed on the fifth day in the crystallizer pond. Large concentration of magnesium in salt was found in Vedaranyam and Veppalodai salt pans (3.65 g/l), and the lower amount was observed from Marakkanam (Bore well) salt pan (2.31 g/l). The higher amount of magnesium (40.10 g/l) in pan soil was recorded in Thoothukudi salt pan, and the lower amount (11.18 g/l) was recorded in Ramanathapuram salt pan.

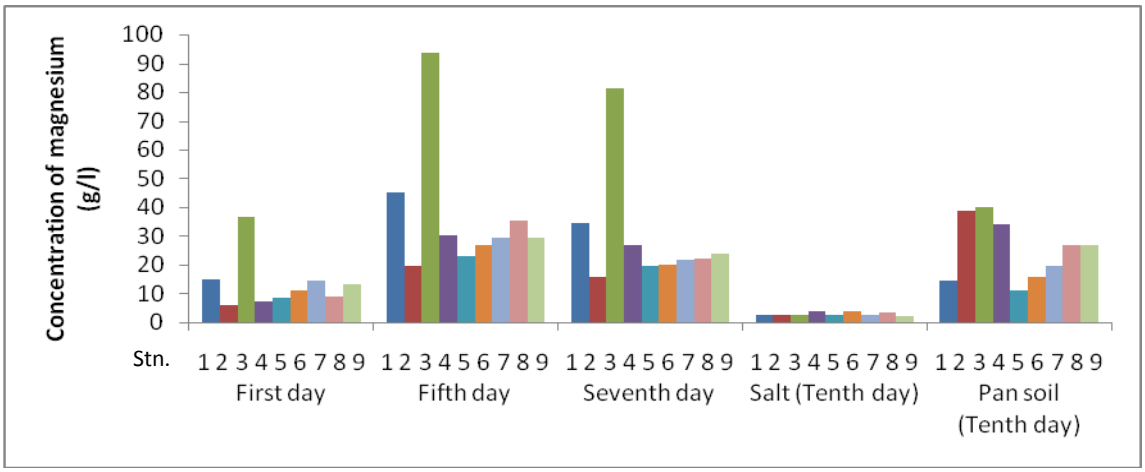

Fig.11 Magnesium in the brine solutions, salt and pan soil of nine different stations

[1,2,3,4,5,6,7,8,9 represent salt pans of Puthalam, Kovalam, Thoothukudi, Veppalodai, Ramanathapuram, Vedaranyam, Parangipettai, Marakkanam (Sea water) and Marakkanam (Bore well) respectively]

The variations in the potassium ion concentration were estimated, and are given in Fig. 12. The amount of potassium in saline water was high in the Thoothukudi salt pan (15.56 g/l) on the fifth day, and low at Marakkanam (Borewell) Salt pan (3.25 g/l) in the crystallizer pond. The amount of potassium in salt was low (2.11 g/l) in Parangipettai salt pan, and high (3.56 g/l) in Kovalam salt pan. The level of potassium from pan soil was low (2.31 g/l) in Kovalam salt pan, and high (7.12 g/l) in Marakkanam (Bore well) salt pan.

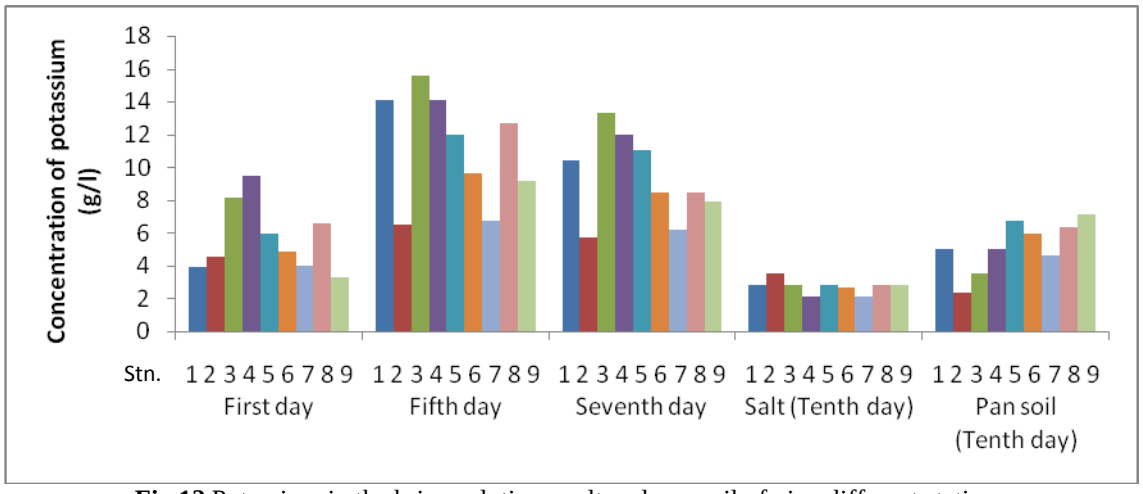

Fig.12 Potassium in the brine solutions, salt and pan soil of nine different stations

[1,2,3,4,5,6,7,8,9 represent salt pans of Puthalam, Kovalam, Thoothukudi, Veppalodai, Ramanathapuram, Vedaranyam, Parangipettai, Marakkanam (Sea water) and Marakkanam (Bore well) respectively]

The estimation of calcium in brine solutions showed a minimum value of 2.41 g/l at Marakkanam – bore well on the first day at the crystallizer pond. Its maximum value was 15.83 g/l at Parangipettai on the fifth day in crystallizer pond. The low calcium level (4.01 g/l) in salt was observed in Puthalam and Kovalam salt pans samples. High levels of calcium (10.02 g/l) were noted at Parangipettai salt pan. The low calcium value (4.01 g/l) was observed in pan soil of Marakkanam (Sea water) salt pan, while the high value (12.22 g/l) was recorded at in Parangipettai salt pan. The variations in calcium ion concentration estimated are presented in Fig. 13.

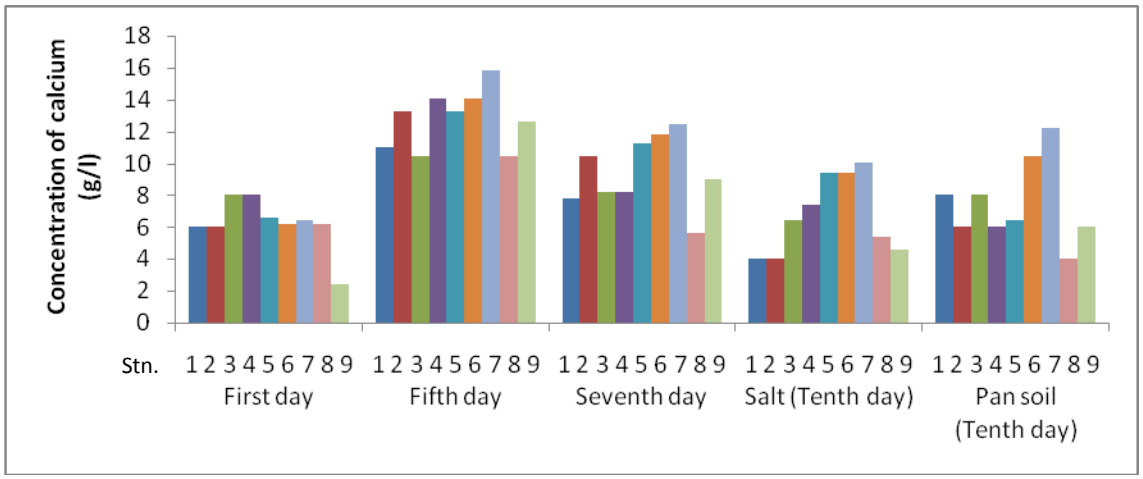

Fig.13 Calcium in the brine solutions, salt and pan soil of nine different stations

[1,2,3,4,5,6,7,8,9 represent salt pans of Puthalam, Kovalam, Thoothukudi, Veppalodai, Ramanathapuram, Vedaranyam, Parangipettai, Marakkanam (Sea water) and Marakkanam (Bore well) respectively]

3.1 Availability of cations and anions in various samples on different days at Thoothukudi salt pan

The variations in different cations and anions in the brine solutions, salt and pan soil were separately dealt taking Thoothukudi salt pan as prime example. The concentrations of various cations in brine solutions, salt and pan soil of Thoothukudi salt pans were estimated and presented in Table 3.

Table 3. Variations in different cation concentrations in brine solutions, salt and pan soil of Thoothukudi salt pans

Number of days.	Sodium (g/ l)	Magnesium (g/ l)	Potassium (g/l)	Calcium (g/l)
First day (brine solution)	36.00	36.46	8.13	8.02
Fifth day (brine solution)	51.06	93.57	15.56	10.42
Seventh day (brine solution)	40.28	81.42	13.29	8.22
Tenth day (salt)	39.50	2.43	2.82	6.41
Tenth day (pan soil)	23.27	40.10	3.56	8.02

On the first day, cations such as sodium (36.00 g/l) and magnesium (36.46 g/l) were approximately equal in the brine solution of crystallizer pond. Similarly potassium (8.13 g/l) and calcium (8.02 g/l) were approximately equal in amount. But during the fifth day magnesium reached the peak level (93.57 g/l). Next to this level, sodium (51.06 g/l) was available. Potassium and calcium were available in the range of 15.56 g/l, and 10.42 g/l respectively. During salt formation, considerable amount of cations got settled into the pan soil. These variations of cations are plotted in the chart (Fig.14).

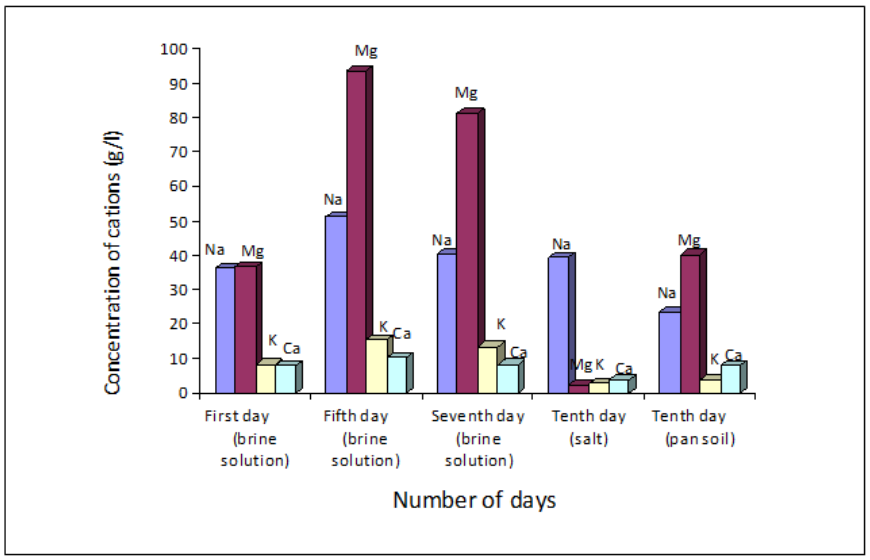

Fig. 14 Variations of different cation concentration in the crystallizer pond

The various anion concentration in brine solutions, salt and pan soil of Thoothukudi salt pans were estimated and portrayed in Table 4.

Table 4. Variation in different anion concentration in brine solutions, salt and pan soil of Thoothukudi salt pans

Number of days	Fluoride (mg/ l)	Chloride (g/ l)	Sulphate (g/l)
First day (brine solution)	0.9	233.99	17.05
Fifth day (brine solution)	1.2	280.08	41.07
Seventh day (brine solution)	1.0	262.35	36.02
Tenth day (salt)	1.0	255.26	9.61
Tenth day (pan soil)	0.6	251.71	35.06

On the first day, the amount of anions were less (Fluoride = 0.9 mg/l, Chloride = 233.99 g/l, and Sulphate = 17.05 g/l). On the fifth day, the anionic concentration emerged to a peak value (Fluoride = 1.2 mg/l, Chloride = 280.08 g/l, and Sulphate = 41.07 g/l). The concentration of fluoride, chloride and sulphate ions were less in the brine solution on the seventh day and salt on the tenth day because considerable amount of these ions leached into the pan soil. So anion concentration in the salt was very much reduced (Fluoride = 1.0 mg/l, Chloride = 255.26 g/l, and Sulphate = 9.61 g/l). The variations in fluoride ion are presented in Fig.15 while that of chloride and sulphate in Fig. 16. The amount of fluoride ion was maximum on the fifth day similar to chloride and sulphate ions.

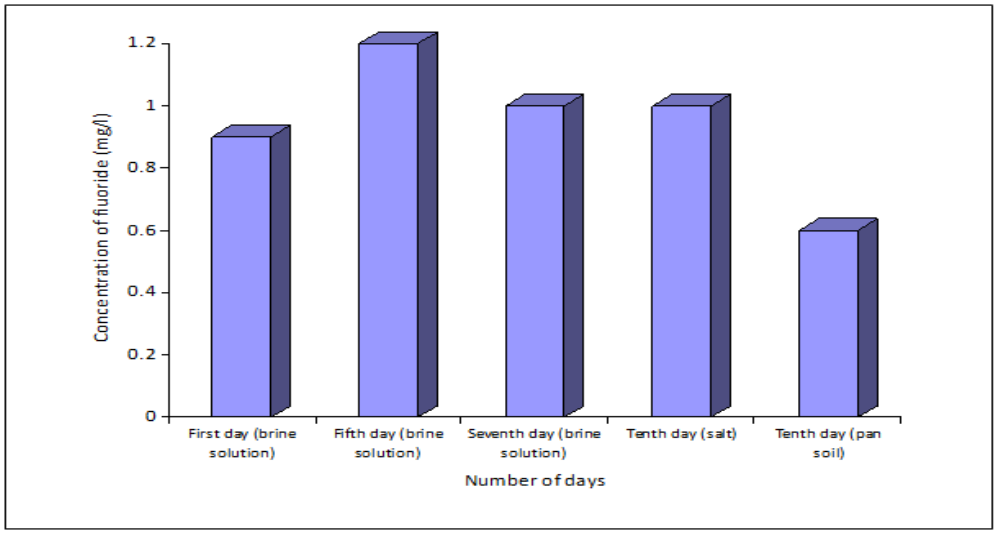

Fig 15. Variations of fluoride ion concentration in the crystallizer pond.
[Brine solutions (first three samples), salt (fourth sample) and pan soil (fifth sample)]

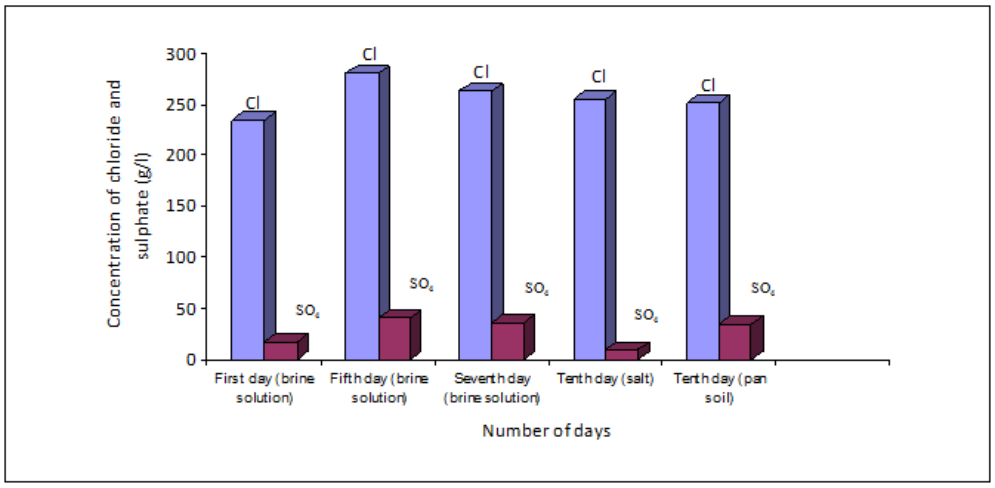

Fig.16. Amount of chloride and sulphate ions in the crystallizer pond
[Brine solution (first three samples), salt (fourth sample) and pan soil (fifth sample)]

3.2 Availability of cations and anions in the salt and pan soil on the tenth day at Thoothukudi salt pans.

The amount of various ions in the crystallizer pond on the tenth day were estimated and plotted in Table 5.

Table 5: Amount of various ions in the salt and pan soil of Thoothukudi salt pans

Salt and pan soil in the crystallizer pond	Fluoride (mg/l)	Chloride (g/l)	Sulphate (g/l)	Sodium (g/l)	Magnesium (g/l)	Potassium (g/l)	Calcium (g/l)
Salt (10^{th} day)	1.0	255.26	9.61	39.50	2.43	2.82	6.41
Pan soil (10^{th} Day)	0.6	251.71	35.06	23.27	40.10	3.56	8.02

Complete salt crystallization in the crystallizer pond took place on the tenth day in Thoothukudi salt pans. During the solidification of brine solution in Thoothukudi salt pans, considerable amount of anions and cations leached into the pan soil. Variations in fluoride ions in the salt and pan soil were reported in the form of par chart (Fig. 17).

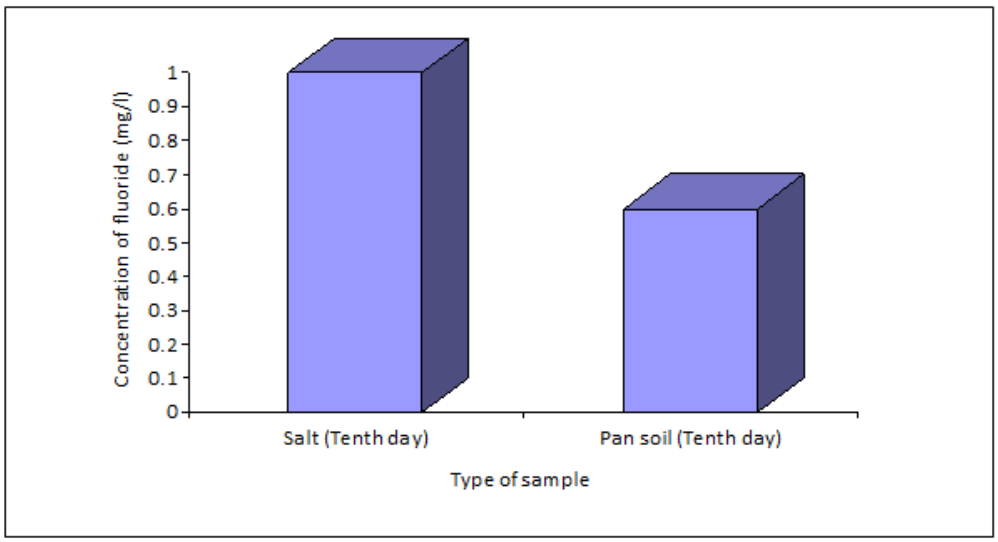

Fig.17. Amount of fluoride in the salt and pan soil

The level of fluoride in pan soil from a study at Ramanathapuram, Ramanathapuram District, India was found to be 1.2 mg/l [34]. Another study at Vedaranyam, Nagapattinam District, India also proved the amount of fluoride in the pan soil was found to be 0.8 mg/l [35].

Similar variations were obtained during the estimation of other anions and cations present in the salt and pan soil, and are portrayed in Figures 18 and 19.

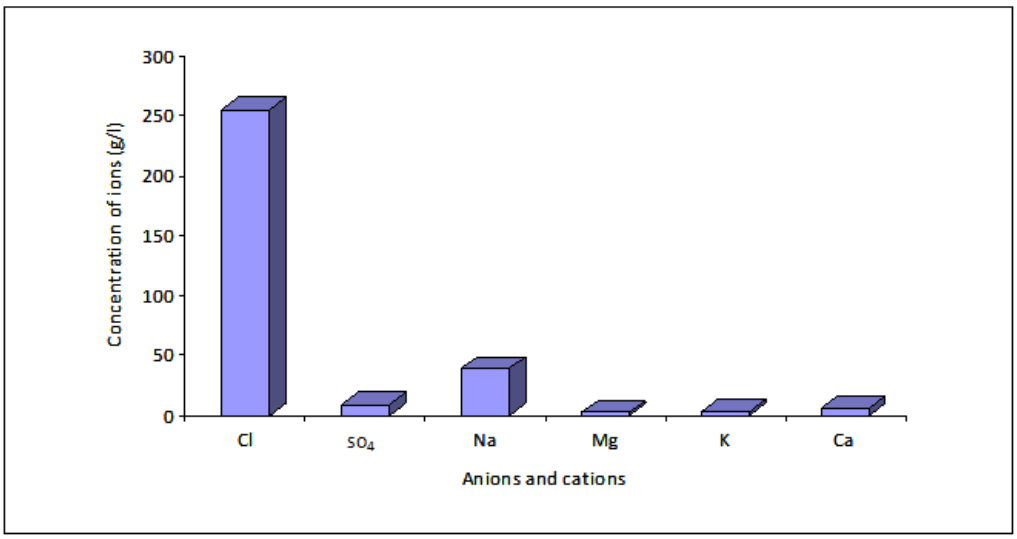

Fig. 18 Amount of anions and cations in the salt

In the case of salt, chloride and sodium ions were available to a maximum level than other ions. From the brine solution and salt sufficient amount of ions got settled into the pan soil, and hence the amount of ions increased in the pan soil.

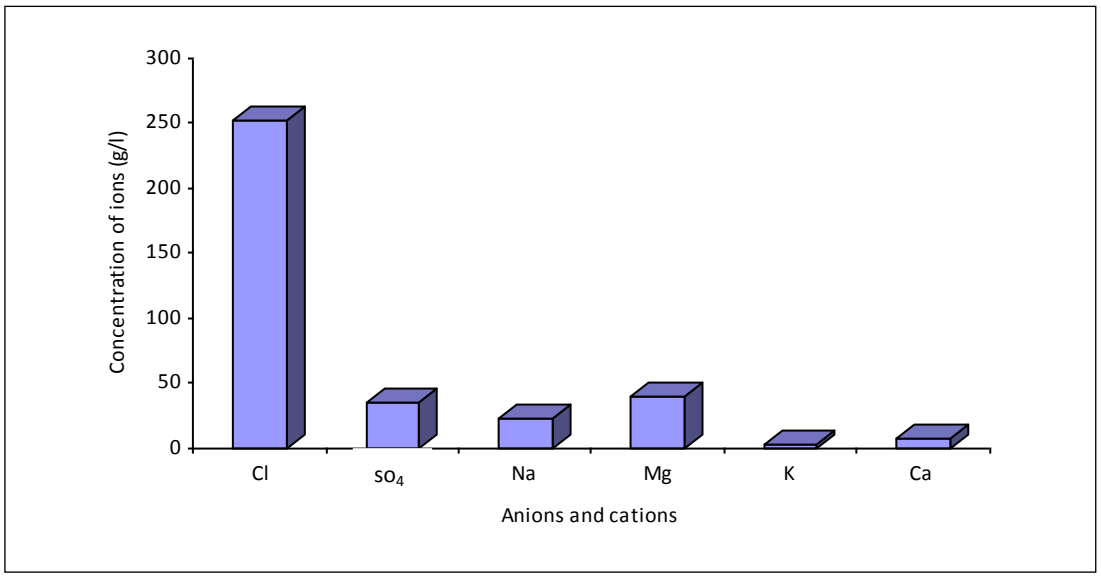

Fig. 19 Amount of anions and cations in the pan soil

IV. Conclusion

Fluctuations of fluoride concentration in the saline water, salt and pansoil samples have been reported from various salt pans of our study area. Among the nine salt pans, sea water is used as a main source for most of the salt pans. In Marakkanam, bore well water happens to be the main source. In some salt pans in order to increase the concentration of saline water, both sea water and bore well water are used. In these regions, the probable source of fluoride in ground water is due to weathering and circulation of water in rocks and soils. Fluoride gets leached out, and dissolves in ground water. The mandatory standard GB 5461 – 2000 "Table salt" specifies that the content of fluorine shall not exceed 5.0 mg/kg [36]. As found here, the fluoride content of saline water in all the nine salt pans was slightly higher on the fifth day. The concentration of fluoride in the salt pans ranged between 0.6 and 1.7 mg/l. A decrease in the concentration of fluoride could be mainly due to considerable accumulation of fluoride into the pan soil. It was also found that in all the brine solutions and salt samples, fluoride concentration was within the permissible limit. A relatively high fluoride accumulation into the pan soil was noted in Veppalodai. In this salt pan the fluoride concentration was 1.7 mg/l on the fifth day. But in the salt it was estimated as 1.0 mg/l. Chloride concentrations was very high (283.62 g/l) in Veppalodai (Station 4) salt pan. Similarly ions such as sulphate, sodium, magnesium, potassium and calcium concentrations were also fairly high on the fifth day samples. But during the salt formation, considerable amount of these ions get settled into the pan soil. It is construed from of the study that the salt from all the nine salt pans in the study area are safer for domestic purpose.

Acknowledgements

The authors are thankful to Mr. Ramamoorthi, Mr. Muthuraj and Mr. K. Rajendran, Secretary, Punavasal PACB in the collection of brine samples. The authors also thank the officials of Sahayamatha Salt Terns and Southern Salts for their great support.

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