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ANALYSIS OF PHYSICO - CHEMICAL PARAMETERS OF SOLAR SALT PAN

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Abstract

In the present study, the physio-chemical parameters of the saltpan water were analyzed. The maximum and minimum pH values recorded during September and May was 7.19 and 6.21, respectively. Electrical conductivity was high in the month of April (84.2 mhos) and it reduced during December (40.1 mhos). The temperature of the crystallizer pond was recorded as 37.8 °C during April and the temperature was lowered during November (31°C). The maximum brine density recorded was 28.1ºBe during September, whereas it was minimal in December with a value of 20.1 ºBe. The chloride content was maximum during April (188.6 g l^{-1}) and it was minimal during June (151.5 g^{-1}). The sulphate content varied between 34.2 g l^{-1} and 39.1g l^{-1}. The calcium content was observed as 0.088g l^{-1} in April and it reduced as 0.21g l^{-1} during November. The maximum and minimum magnesium concentration values recorded during August and November were 12.62 g l^{-1} and 12.1g l^{-1} respectively.The sodium ion concentration ranging from 58.79 g l^{-1} to 58.1 g l^{-1}. The maximum and minimum value of potassium concentration recorded was 3.23 and 2.12 g l^{-1} during June and December respectively.

Key words: Saltpan, Physico-chemical properties, Electrical conductivity, salts

Introduction

Salt pans are unique tide water impounded, enclosed ecosystems adjacent to creek environment, characteristically they are exposed to a wide range of environmental stress and perturbations manifest mainly through salinity changes. As the number of species in each tropic level is low and the ecosystem is simplified. Though solar evaporation salt is produced through salt pans, such system can also be made useful for culturing micro-organisms (Mustafa *et al*., 1999). Evaluating the physico - chemical parameters of the solar saltern give a useful information regarding the sampling environment. The nature of the bacterial environment could be studied which paves way to formulate new medium for the isolation of halophiles which is the top priority in microbiology **(**Oren, 2010).

In solar salt pans, the least soluble calcium carbonate salt separates out first and the highly soluble magnesium salts separate last. The phase chemistry of solar salt production is conveniently divided into four distinct phases. At all these stages the density of the brines differs and it is measured using Baume Hydrometer (^{o}Be) which has a range of 0 – 50 ^{o}Be. The first phase is from 3 to 13 ^{o}Be, where it is characterized by the precipitation of carbonates of calcium, magnesium and iron. The second phase extending from 13 to 25.4 ^{o}Be gypsum starts to precipitate it out. Initially it crystallizes as needle shaped crystals which ranges between 13 to 16.4 ^{o}Be and later form as anhydrous form. Around 85% of gypsum ($CaSO_4$) was precipitated in this phase.

The third phase extends between 25.6 and 30 ^{o}Be where all the major elements present are precipitated and they are at its saturation level**.** At higher saturation, crystallization slows down considerably and this process complete only with the completion of evaporation. The concentration at which sodium chloride starts to crystallize is known as the “salting point” and the mother liquor at this point is called “pickle”. At the end of this phase, where the concentration is 30 ^{o}Be and above, the liquor is called ‘bittern’, because of the characteristic bitter taste (Bowers *et al*., 2011). Table 1 summarized the solubility of major salts of solar saltern.

The fourth phase is related to bittern and its chemistry is complex. A number of salts like sulphates of potassium, magnesium and chloride separate either as single or as double crystals. The volume of water was 19% of the original volume at the end of phase I, 9% at the end of phase II, 3% at the end of phase III, where bittern is formed. Hence, to achieve this, continuous evaporation takes place with lot of other parameters involving **(**Bowers *et al*., 2011**).** In addition, primary mineral salts exhibit rapid response to post depositional modification (including groundwater diagenesis, compaction, lithification, thermal history and oxidation), which can constrain the characteristics of the latest processes to have affected specific localities before liquid water was largely removed from the surface and subsurface (Hardie, 1991; McLennan *et al*., 2005; Smoot and Lowenstein, 1991).

The salt works that use sea water for salt production usually locate closer to the sea. The topography of a salt pan is made in such a position, so as to pump sea brine to the salt pans in a cost-effective manner. The area requirement and the ratio of reservoir, condenser and crystallizer ponds vary from place to place depending on the salinity of brine and the seepage losses. Normally the ratio of reservoir, condenser and crystallizer ponds are 30:60:10. The individual compartments in the condensers are much smaller than those in the reservoir. The brine entering the condensers from the reservoir is about 16^{o}Be and the concentration of it, is to be further raised to 25^{o}Be. This range of concentration is achieved by spreading it in a number of compartments, which prevent mixing of brine of different densities. Concentrating ponds containing brines of widely different densities are not normally located adjacent to each other, because of possible infiltration of the weaker brine into the pond containing the concentrated brine. The crystallizers, where the deposition of salt takes place are the most productive and therefore, they are the most important part of the salt works, they constitute less than 8% of the total work area. The ideal depth of the brine in the salt works is between 15 and 20 cm (Noha *et al*., 2007).

India produces 75% of salt by solar evaporation of sea water, 20% from sub soil brine and inland lakes and the rest from backwater. It is often found the brine wells sunk in the neighbourhood of the seashore often yield much stronger brine than the pure sea water. As evaporation leads to increase in the concentration of brine, changes in the physic - chemical parameters are unavoidable and monitoring physical parameters like pH, electrical conductivity and also changes in the concentration of the various ions present in the brine solution of the salt production process become essential. The changes in brine temperature due to rain and other reasons, the variation in the hydrogen ion concentration (pH) that takes place due to evaporation. The electrical conductivity (EC) of the brine water of crystallizer varies. The most important factor is salinity or brine density, which is the crucial factor in the salt production process. The changes in the ionic content of chloride, sulphate, calcium, magnesium, sodium and potassium ions and their distribution were significantly influenced salt production. EC conductivity is perhaps one of the most complicated physical properties to calculate for the brine compositions (Anderko and Lencka, 1997).

Materials and methods

Sampling

The present study was carried out over a period of one year from September 2018 to August 2019. Water samples were collected monthly from the crystallizer pond of solar salt pan in Kovalam, Kanyakumari District, Tamil Nadu, India (Figure1 & 2).

Figure1: Crystallizer Pond of solar saltpan in Kovalam, Kanyakumari District, Tamil Nadu, India

Figure 2: Sampling location of Kovalam salt pan of Kanyakumari District, Tamil Nadu,India

Analysis of physical and chemical parameters of salt pan water

The following physic-chemical parameters were studied

pH

The pH of all the brine samples was determined using a digital pH meter (Elico model – 21, India).

Electrical conductivity

A digital conductivity bridge (CM82T with dip type conductivity cell) was used to measure the conductivity of the water samples during the study period.

Brine density

The density of the brine samples was measured using a Baume Hydrometer.

Analysis of chemical parameters of salt pan water

The determinations of chemical parameters such as chloride, sulphate and calcium, were carried out by the standard procedures. Estimation of sodium and potassium were carried out using a flame photometer (Marshall, 2002).

Results

The physico-chemical parameters are considered as the most important principles in the identification of the nature, quality and type of water for any aquatic ecosystem. So, the physico-chemical parameters of the solar salt pan water samples in the various ponds of the Puthalam saltworks during the investigation period September 2008 to August 2009 were recorded and described below.

pH

The monthly variation of pH in the crystallizer pond during the study period (September 2008 to August 2009) was shown in Figure 3. The pH values were found to be the maximum of 7.19 and the minimum of 6.21 with the mean pH value of 6.90 ± 0.28 were observed.

Acidic pH was observed in the month of May and alkaline condition was recorded in the month of September.

Electrical Conductivity (EC)

EC is an indirect measure of the salt concentration of the brine at crystallizer of salt production process. It depends upon the concentration of ionized substances present in the brine. The observed EC of water sample varied from 40.1 – 80.1 mhos (Figure 4). The annual mean electrical conductivity of crystallizer sample was 61.12 ± 15.47 mhos.

Brine Temperature

The result of brine temperature at crystallizer pond was presented in Figure 5. The temperature of the brine samples was found to be the highest during the month of September (37.1 °C) and lowest brine temperature was 36.1 °C recorded during October. The annual mean temperature was 35.8°C ± 2.03 °C.

Brine Density

The results of brine density at crystallizer were presented in Figure 6. In the crystallizer pond, the brine density was 28.1 ^{o}Be during the month of September and it varied significantly throughout the study period. The brine density range varied from 20.4 – 28.1 ^{o}Be. And the annual mean brine density was 24.31 ^{o}Be ± 2.32.

Magnesium

The Magnesium ion concentration of brine samples was tabulated in Figure 7. During the month of September, the Magnesium content was 12.5 g l^{-1} and increased as 12.9 g l^{-1} in the month of October. The annual mean value of magnesium concentration was 12.42 ± 0.26 gl^{-1}.

Sulphate

The data shows the monthly variation of sulphate concentration of brine samples at crystallize stage (Figure 8). During the month of September, the sulphate was 38.5 g l^{-1} and increased as 39.1 g l^{-1} during October. The sulphate concentration varied from 34.2 g l^{-1} - 38.5 g l^{-1}). The annual mean value of sulphate ion concentration was 36.3 ± 1.29 gl^{-1}.

Potassium

The potassium concentration of brine sample at crystallizer pond varied significantly. During the month of September, the Potassium ion concentration was 2.64 gl^{-1} and further increased as 3.02 gl^{-1} in the month of October (Figure 9). The potassium ion concentration varied from 2.12 – 3.31 gl^{-1}**.** The annual mean value of potassium concentration was 2.92 ± 0.35gl^{-1}.

Chloride

The results of chloride ion concentration in the crystallizer were presented in Figure 5. In the crystallizer pond, during the month of September the chloride was 170.1 g l^{-1} and it decreased as 165.7 g l^{-1} in the month of December. The Chloride ion concentration varied from 160.8 – 188.6 g l^{-1} and an annual mean value was 171.24 ± 11.06 gl^{-1}.

Sodium

The data on monthly fluctuation in Sodium concentration of brine sample at crystallizer was represented in Figure 11. During the month of September, the Sodium content was 58.79 g l^{-1} and it was 58.54 g l^{-1} in the month of May. The (58.54 – 58.88g l^{-1}) during the study period. The annual mean value of sodium concentration was) 58.63 ± 0.2 gl^{-1}).

Calcium

The data on monthly fluctuation in calcium ion concentration of brine samples were listed in Figure 10. During the month of September, the calcium was high (170.1g l^{-1}) and low calcium content (161.2 g l^{-1}) was reported in the month of August. The calcium ion varied from 160.8 – 188.6 g l^{-1}. The annual mean value of calcium concentration was 0.12 ± 0.17 gl^{-1}.

Above discussed details are represented in Figure 3-12 and in Table 1 &2.

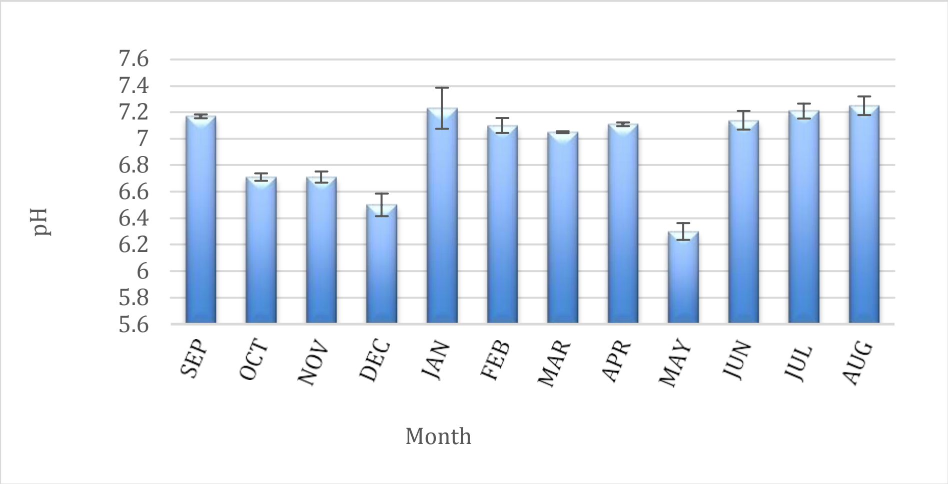

Figure 3: The monthly variation of pH in experimental salt works in crystallizer pond.

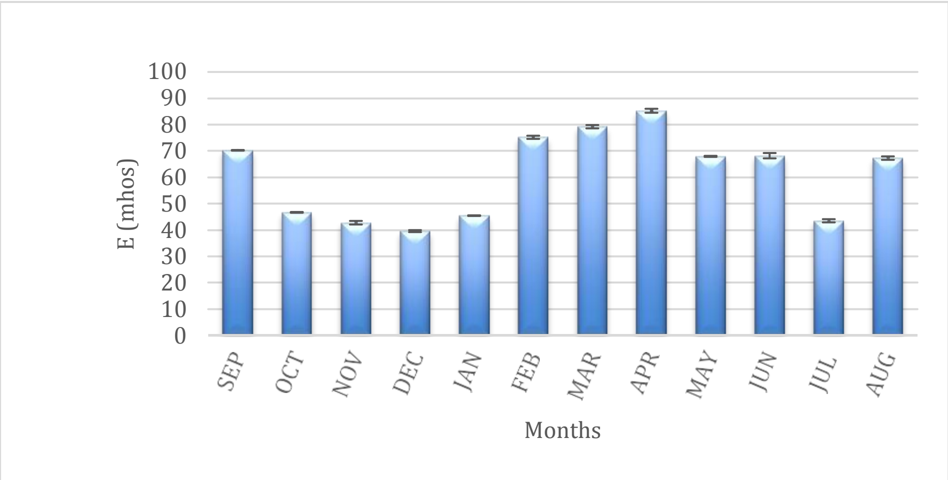

Figure 4: The monthly variation of Electrical Conductivity (mhos) in the crystallizer pond

Figure 5: The monthly variation of Temperature in the crystallizer pond

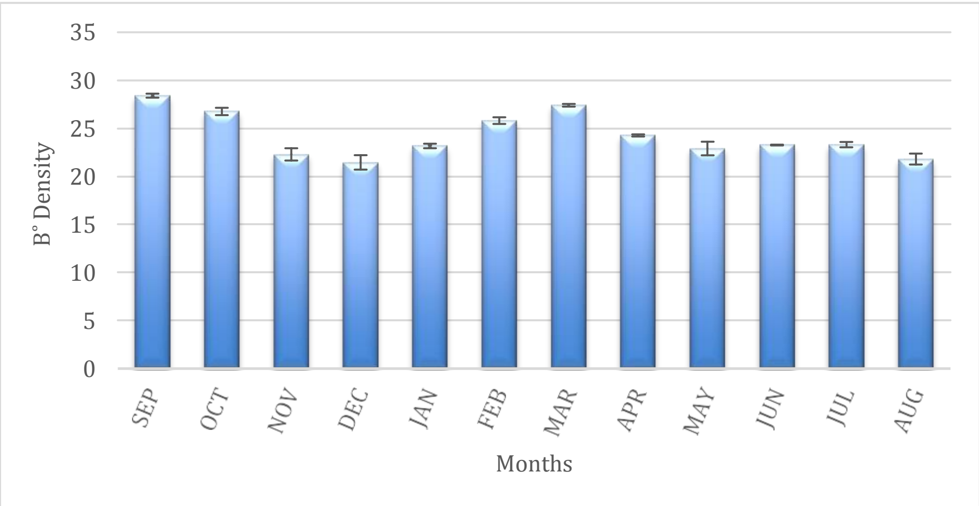

Figure 6: The monthly variation of Brine density (B^o) in the crystallizer pond

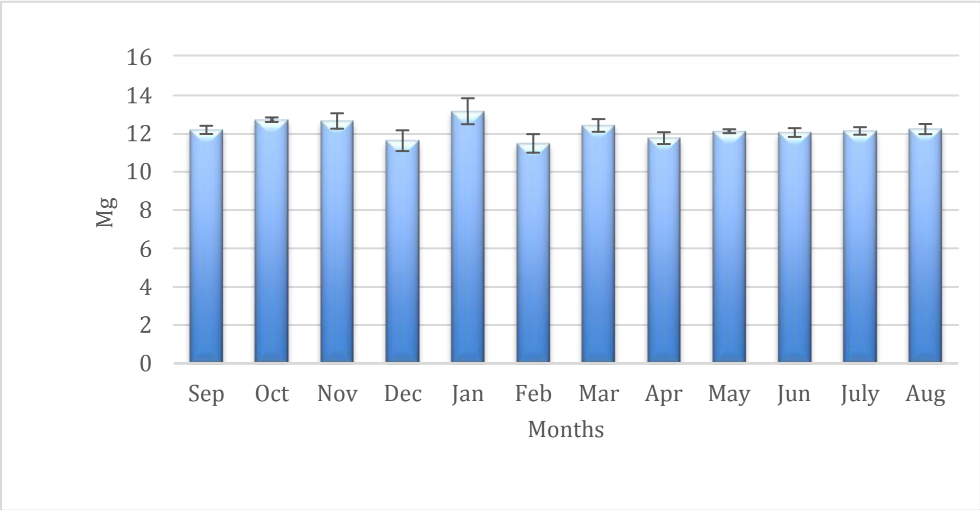

Figure 7: The monthly variation of magnesium (g l^{-1}) in the crystallizer pond

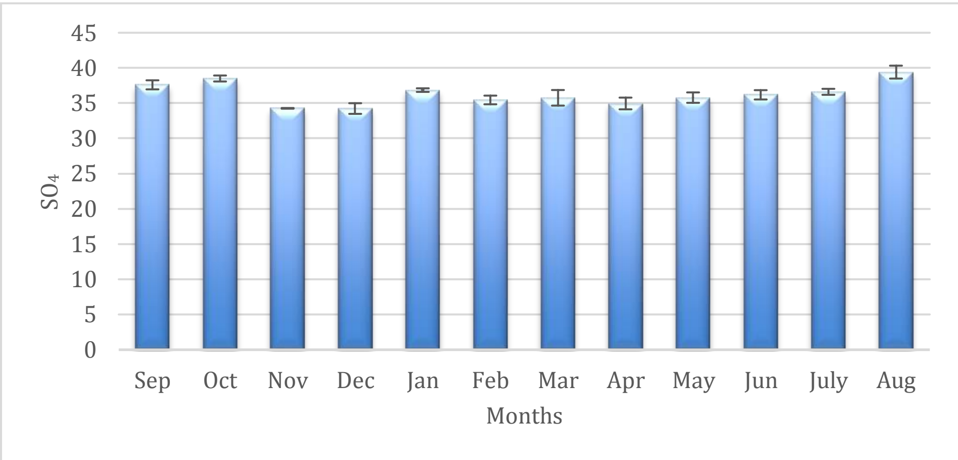

Figure 8: The monthly variation of sulphate content (g l^{-1}) in the crystallizer pond

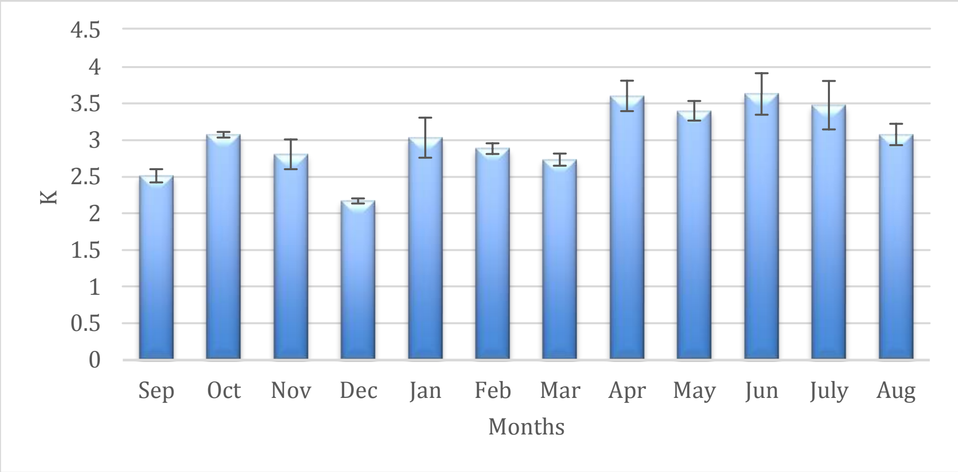

Figure 9: The monthly variation of potassium (gl^{-1}) in the crystallizer pond

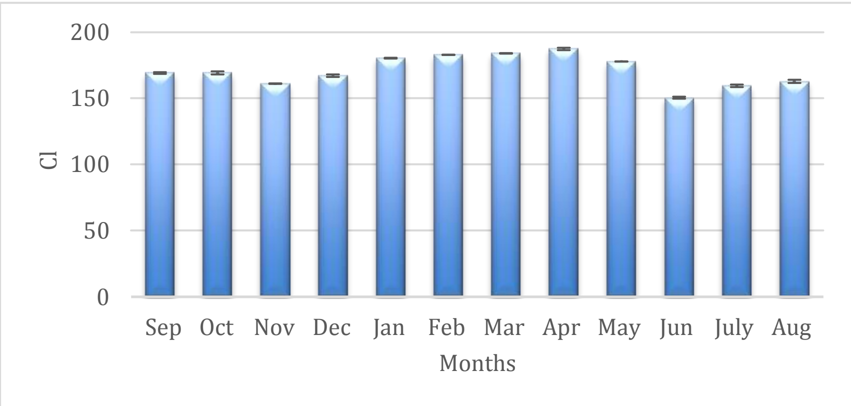

Figure 10: The monthly variation of chlorine content ($g\ l^{-1}$) in the crystallizer pond

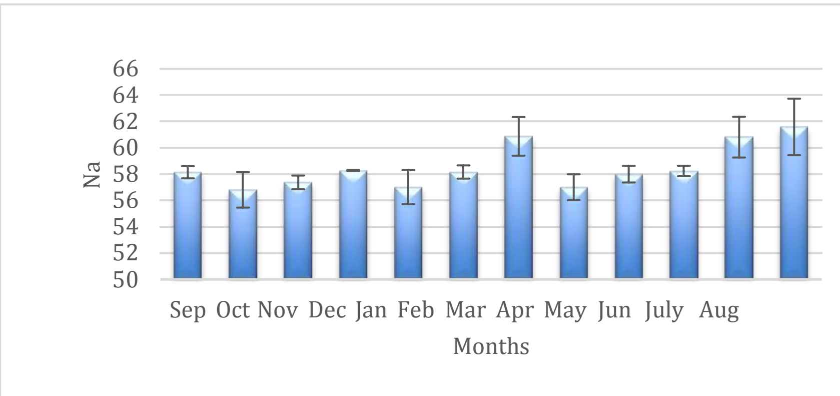

Figure11. The monthly variation of sodium (gl^{-1}) in the crystallizer pond

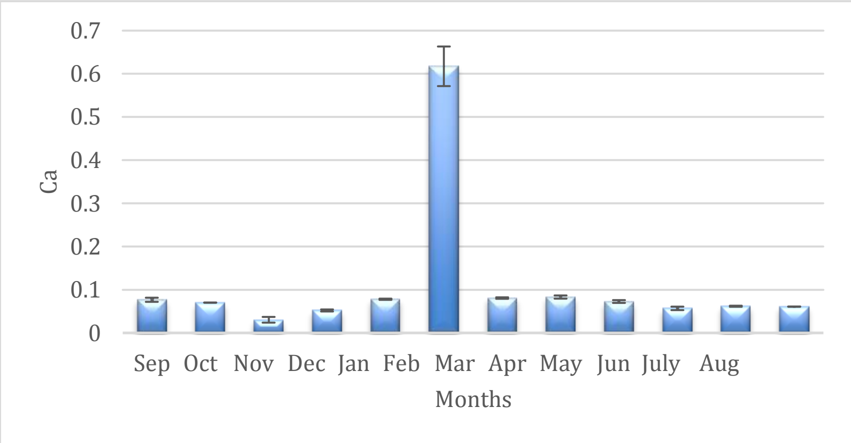

Figure12: The monthly variation of calcium (gl^{-1}) content in the crystallizer pond

Table1: The variation of physical parameters in the crystallizer pond during the study period (September 2008 - August 2009).

	pH	EC mhos	T (°C)	Density(°Be)
Sep	7.17±0.014	70.23±0.120	37.36±0.183	28.4±0.212
Oct	6.71±0.028	46.63±0.162	36.6±0.353	26.76±0.381
Nov	6.65±0.042	42.73±0.685	32.46±0.466	22.3±0.636
Dec	6.5±0.084	39.56±0.381	31.8±0.212	21.46±0.749
Jan	7.23±0.155	45.4±0.141	35.76±0.254	23.16±0.240
Feb	7.1±0.056	75.16±0.608	35.46±0.240	25.8±0.353
March	7.05±0.007	79.23±0.615	35.9±0.212	27.4±0.141
April	7.11±0.014	85.26±0749	37.4±0.282	24.26±0.113
May	6.3±0.063	67.9±0212	37.06±0.098	22.9±0.707
June	7.14±0.070	68.16±1.018	37.06±0.028	23.26±0.042
Jul	7.21±0.056	43.46±0.608	37±0.141	23.2±0.282
Aug	7.25±0.070	67.3±0.636	36.8±0.565	21.8±0.565

Table 2: The variation of chemical parameters (g l^{-1}) in the crystallizer during the study period (September 2008 - August 2009).

	SO_4	Mg	K	Cl	Na	Ca
Sep	37.6±0.636	12.2±0.212	2.5±0.089	169.14±0.674	58.14±0.459	0.076±0.004
Oct	38.5±0.424	12.73±0.117	3.07±0.037	169.2±1.150	56.80±1.348	0.07±0
Nov	34.2±0.047	12.6±0.400	2.8±0.202	161.08±0.200	57.3±0.518	0.030±0.006
Dec	34.2±0.754	11.6±0.542	2.17±0.035	167.06±0.964	58.27±0.042	0.0516±0.002
Jan	37.2±0.259	13.17±0.678	3.03±0.273	180.38±0.296	57.01±1.291	0.078±0.001
Feb	35.4±0.612	11.4±0.485	2.8±0.073	182.9±0.094	58.15±0.504	0.617±0.045
March	35.7±1.107	12.4±0.329	2.7±0.082	184.03±0.164	60.8±1.466	0.080±0.001
April	34.9±0.824	11.7±0.306	3.6±0.207	187.3±0.872	56.9±0.985	0.082±0.003
May	35.7±0.730	12.12±0.098	3.4±0.134	177.7±0.082	57.9±0.626	0.072±0.003
June	36.1±0.659	12.06±0.226	3.63±0.282	150.4±0.754	58.23±0.395	0.056±0.004
Jul	36.6±0.424	12.13±0.193	3.4±0.329	159.41±0.982	60.8±1.546	0.061±0.001
Aug	39.4±0.919	12.24±0.268	3.07±0.146	162.8±1.178	61.58±2.149	0.060±0.0002

Discussion

The physio - chemical characters prevailing in a solar salt work play an important role in the salt production strategy. A biological system maintained at a desired condition allows continuous production of high-quality salt at design capacity On the other hand, physiochemical disturbances can affect the quality and quantity of salt (Coleman and White, 1993). The physiochemical parameters such as pH, EC, brine density, temperature, calcium, magnesium, chloride, sodium and potassium concentration were studied in the saltpan of Puthalam for a period of one year.

pH is a measure of the intensity of acidity or alkalinity and it has no adverse effect on health. In the present study the observed pH values varied from 6.21 to 7.19. The decrease in pH during monsoon may be attributed to the reduction of photosynthesis and maximum during summer can be the result of the increased photosynthesis. Moreover, monsoon decrease in the pH may be attributed to heavy rain fall (Murugan *et al.*, 1987). pH values of the water samples of Oollapalam salt pan of Karnataka State, India were alkaline and the pH value ranges from 7.56 to 9.91 (Lithakumari *et al.*, 2001).

In Chila Lake, Orissa, India, the pH varied from 7.13 ±0.25 to 8.41± 0.62 (Patra *et al.,* 2010). In Thondi Palk Bay, the pH varied from 7.4 to 8.4 and the pH ranges from 7.5 to 8.0 in Dharma estuary, Bhubaneswarm, India (Parasanna and Rajan, 2010). The lowest pH was observed in Thane Salt pan (Mustafa *et al.*, 1999). In salt pans the values below 4.0 generally produce sour taste and values above 8.5 show alkaline taste (Karunakaran, 2008).

The EC is an index to represent the concentration of soluble salt in water. It was observed that water with high EC value was rich in sodium and chloride ion and further it was noticed that the EC was higher during summer session**.** In the present study, the maximum of 84.2 mhos was recorded in Kovalam salt pan in the month of April. It was in accordance with the earlier works that higher salinity is associated with higher electrical conductance. It was observed that water with high EC values were predominal in sodium and chloride ions (Lithakumari *et al.,* 2001). These were in accordance the observations made with the earlier reports that higher salinity is accordance the observations made with the salt pan of Prakasam district, Andra Pradesh (Lithakumari *et al.,* 2001). Moreover, the EC depends upon the concentration of ionized substances present in the brine (Tripathi and Singh, 1996). In the surface water of Dharma estuary, the EC was recorded as 3.97-46.03 mhos/cm (Parasanna and Rajan, 2010). In the great Vedaranyam swamp in South East Coast of India, the EC was recorded as 34.4-88.8 mho/cm **(**Manikandan *et al.,* 2011).

In the solar salt pan, the brine density normally lies in the range of 3.0 to 6.5 °Be. The Baume degree gradually increases due to evaporation, and is between 10 to 16 °Be in the reservoir stage. The brine with the density from 16.5 to 25 °Be represents the condenser and from 26 to 29.5 °Be represents the crystallizer state. As 70% sodium chloride gets separated out at 29.5 °Be in the crystallizer stage (Radhika *et al*., 2011). Once sodium chloride crystallizes out, the resulting mother liquor called bittern has the density of 30°Be.

The temperature is one of the important physical factors which affect the chemical and biological reactions in water. It regulates the rate of photosynthesis in aquatic ecosystem (Pandian *et al.,* 2009). In the present study the brine temperature varied from 31.8 ^{o}C to 37.8 °C. This result was in accordance with the earlier results Basically, the temperature of the water reflected the air temperature or the atmospheric temperature (Puthiya *et al*., 2009). In the great Vedaranyam swamp in South East coast of India, the salt water temperature was ranged from 20.6 to 34^{o}C (Manikandan *et al*., 2011). In the present study, during the summer season, maximum temperature was observed. These results were in accordance the observations made by (Radhika *et al*.,2011).

In the present study the maximum calcium concentration observed was 0.088 g l^{-1} and minimum calcium concentration was 0.021 g l^{-1}. The Oollapalam salt pan of Karnataka, showed varying concentration of Ca^{2+} ion from 0.042 to 0.050 g l^{-1} and 0.032 to 0.040 g l^{-1}(Lithakumari *et al.,* 2001). The calcium and magnesium hardness were caused by far greatest portion of hardness occurring in natural waters (Foppen, 2002). In the present study the maximum sulphate concentration of 39.1 g l^{-1} was recorded and minimum was 34.2 g l^{-1}. Hutchinson *et al*. (1988) reported 22.56-22.163 mg l^{-1} sulphate ion in Oollpalam salt pan and this sulphate concentration was because of the evaporation of $MgSO_4$ and K_2SO_4.

The occurance of chloride concentration was maximum (188.6 g l^{-1}) during the month of April while the lowest of 151.5 g l^{-1} was recorded during December. The water samples of Oollapalam salt pan showed a maximum of 524.83 mg $l^{-1}$and minimum value was 389.87 mg l^{-1}(Lithakumari *et al.,* 2001). In Ooguru salt pan, the chloride concentration varied from 67.07 - 49.18 mg l^{-1} (Lithakumari *et al.,* 2001).

In the present investigation, the maximum sodium concentration observed was 58.79 g l^{-1} and minimum concentration was recorded as 58.1 g l^{-1}. The presence of sodium at the bittern stage indicates that not all sodium gets separated as sodium chloride (Minif *et al.,* 2001). According to the observation made in Oollpalam salt pan, the maximum sodium concentration was 22.8 mg $l^{-1}$and minimum concentration was 22.5 mg l^{-1} (Lithakumari *et al.,* 2001). Maximum sodium chloride got separated in the crystallizer stage and so the value is low at bittern stage. In the present study maximum potassium concentration was 3.42 g l^{-1} in the month of January and minimum of 2.12 g l^{-1} was recorded in December. In Oollapalam salt pan the potassium ion concentration was reported as 0.083.8 – 0.010.6 g l^{-1} (Lithakumari *et al.*, 2001)

Conclusion

The present study conducted on September 2008 - August 2009 to evaluate different physical and chemical parameters of slat pan water sample to identified suitable conditions for the halophiles growth. The following details are concluded based on the observation and literature collection.pH-7, Temperture 40̊ C, Density 25% and all essential elemental concentration above 40%.

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