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Research Article

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Studies on the chemical parameters of brine at various stages of different salt-pans of Kanyakumari District, Tamil Nadu, India

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ABSTRACT

Common salt is nothing but sodium chloride and its quality is determined by the sodium and chloride ions present. Besides human requirement of good quality salt, high purity salt is necessary for all kinds of heavy chemical industries which use salt as the basic material. The present study focuses on the chemical parameters of brine at various stages of different salt-pans of Kanyakumari district. The parameters included are percentage of chloride, sulphate, calcium, magnesium, sodium and potassium. The study revealed that the values of these parameters showed a marked variation in the different stages of the various salt-pans. The percentage of chloride, sulphate, magnesium and potassium were found to increase gradually from source to bittern stage but calcium and sodium showed a different trend. Calcium was found to increase from source to reservoir and then gradually gets decreased. Sodium gradually increased in the initial stages and in the final stage gets decreased.

Keywords: Salt-pan, bittern, brine, crystallizer

INTRODUCTION

India is one of the important salt producing countries of the world. Salt is manufactured from sea water, subsoil brine, lake water etc. As the composition of brine varies, the composition of bittern also varies and so the by-products obtained from all the three sources are somewhat different from each other. The brine from different sources has different mineral concentrations [1]. Contrary to the belief of the salt manufacturers, salt which is unfit for human consumption is equally unsuitable for most industrial uses. There are several instances where chemical manufacturers are incurring high cost in the purification of the salt used by them to make it suitable for their manufacturing process. The presence of salts like magnesium chloride, calcium sulphate, sodium sulphate and sodium carbonate is considered undesirable and their traces are at best treated as unavoidable impurities. Magnesium chloride and sulphate being hygroscopic are looked upon as particularly undesirable impurities. The presence of salts like magnesium chloride, calcium sulphate, sodium sulphate and sodium carbonate is considered undesirable and their traces are at best treated as unavoidable impurities. Magnesium chloride and sulphate being hygroscopic are looked upon as particularly undesirable impurities. The left - out mother liquor after the separation of salt called bittern, contains most of the dissolved elements at a more concentrated level. This bittern is used for the manufacture of epsom and magnesium carbonate which are predominantly magnesium compounds [2]. Bittern contains mainly magnesium chloride which is a raw material for the manufacture of magnesium metal. Thus, brines are considered to be a handful source of various chemicals. The present study elaborates the percentage of chemical parameters in the brine of various stages of different salt-pans.

EXPERIMENTAL SECTION

Samples of brine were collected from different salt-pans namely Swamithoppu where backwater brine is used, Puthalam where subsoil brine is used and Kovalam where sea brine is utilized for salt production. The samples were collected from the five different stages of various salt-pans viz. source, reservoir, condenser, crystallizer and

bittern. The percentage of chloride, sulphate, calcium and magnesium in the samples at various stages of the different salt-pans were determined by standard procedures [3]. Sodium and potassium in mg/L were estimated flame photometrically and is presented in percentage.

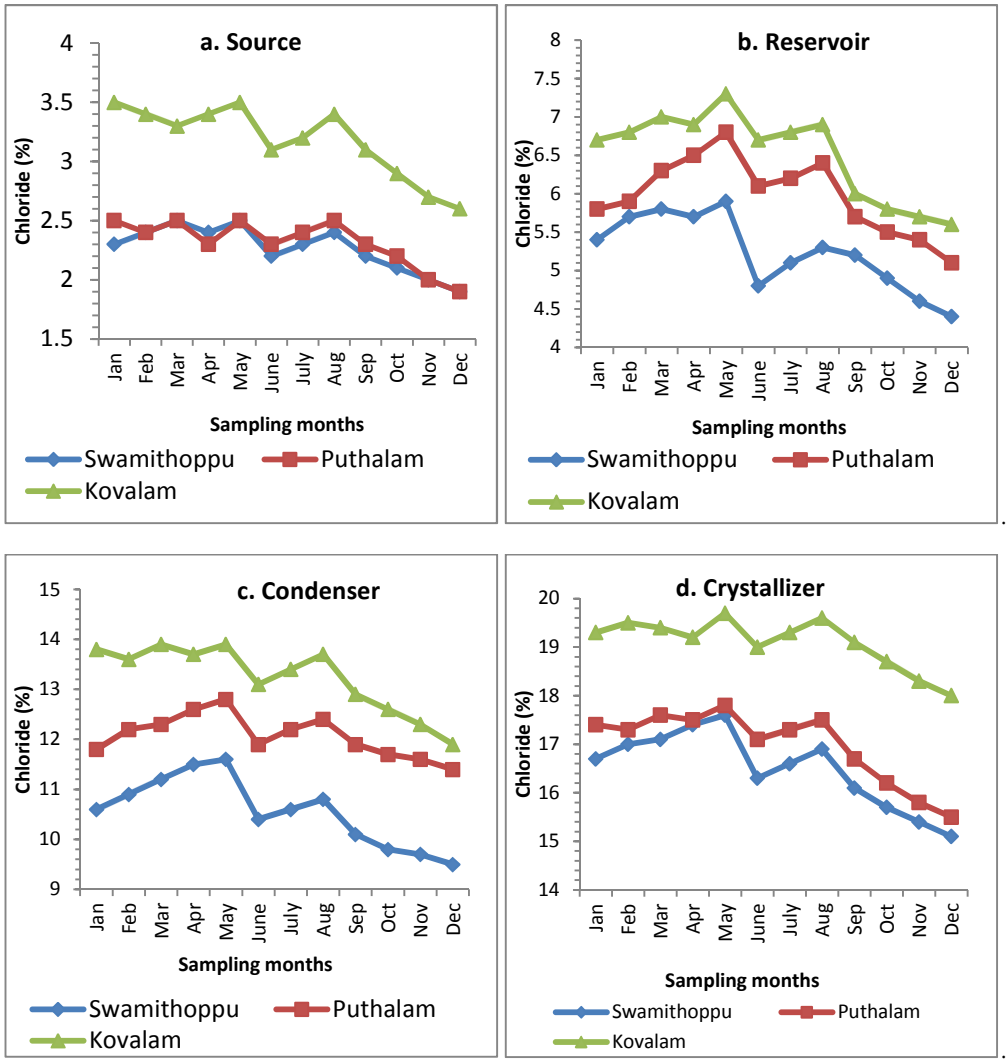
RESULTS AND DISCUSSION

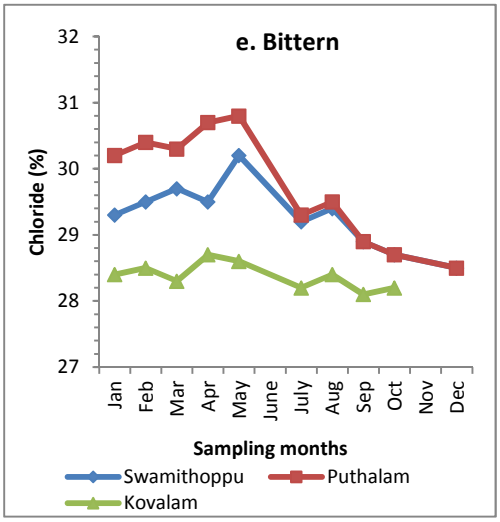
In Kanyakumari District, salt is manufactured by the solar evaporation of various brines viz. back water, subsoil and sea brines. Maximum salinity was observed in sea brine when compared to back water and subsoil brine. Monthly samples were collected for a period of one year from various stages of the different salt-pans and was analyzed for chloride, sulphate, calcium, magnesium, sodium and potassium

(i) Chloride (%)

In the present investigation, chloride ion showed a steady increase in concentration from source to bittern stage. Though the crystallizer discharged chloride as sodium chloride, the concentration continued to increase in the subsequent bittern stage. Earlier reports have confirmed this observation, which was due to factors like the incomplete crystallization of sodium chloride in the crystallizer stage (76%) and also the presence of highly soluble potassium chloride and magnesium chloride in the bittern [4]. Moreover, the volume reduction from 9% in the crystallizer to 3% in the bittern stage contributes much to the above observation.

Fig . 1. Monthly variation of chloride (%) in the sampling stations during the study period 2011





The percentage of chloride at various stages of all the salt-pans was maximum from January to May and also between the monsoon periods. When the northeast monsoon became active, the values went on decreasing [5] i.e., in November and December.

The source at Kovalam had more chloride than the source of the other pans because sea brine is used for salt-making in Kovalam. The maximum average value at Kovalam was 3.18 ± 0.29% and a minimum average value of 2.27 ± 0.18% was observed at Swamithoppu. The average value at reservoir of all the salt-pans ranged between 5.23 ± 0.47% and 6.52 ± 0.55% of which Kovalam had maximum value and Swamithoppu had minimum value.

The condenser of all the salt-pans had the value between 10.56 ± 0.66% and 13.23 ± 0.64%, in which maximum value was observed at Kovalam and minimum value was observed at Swamithoppu. The average value at crystallizer of all the salt-pans ranged between 16.49 ± 0.76% and 19.09 ± 0.50% in which maximum value was at Kovalam and minimum value was at Swamithoppu.

The average value at bittern stage of all the salt-pans ranged between 28.37 ± 0.19% to 29.73 ± 0.81%. The maximum value was recorded in Puthalam and minimum value was observed at Kovalam as more sodium chloride got separated before the bittern level (Fig . 1.a to 1.e).

(ii) Sulphate (%)

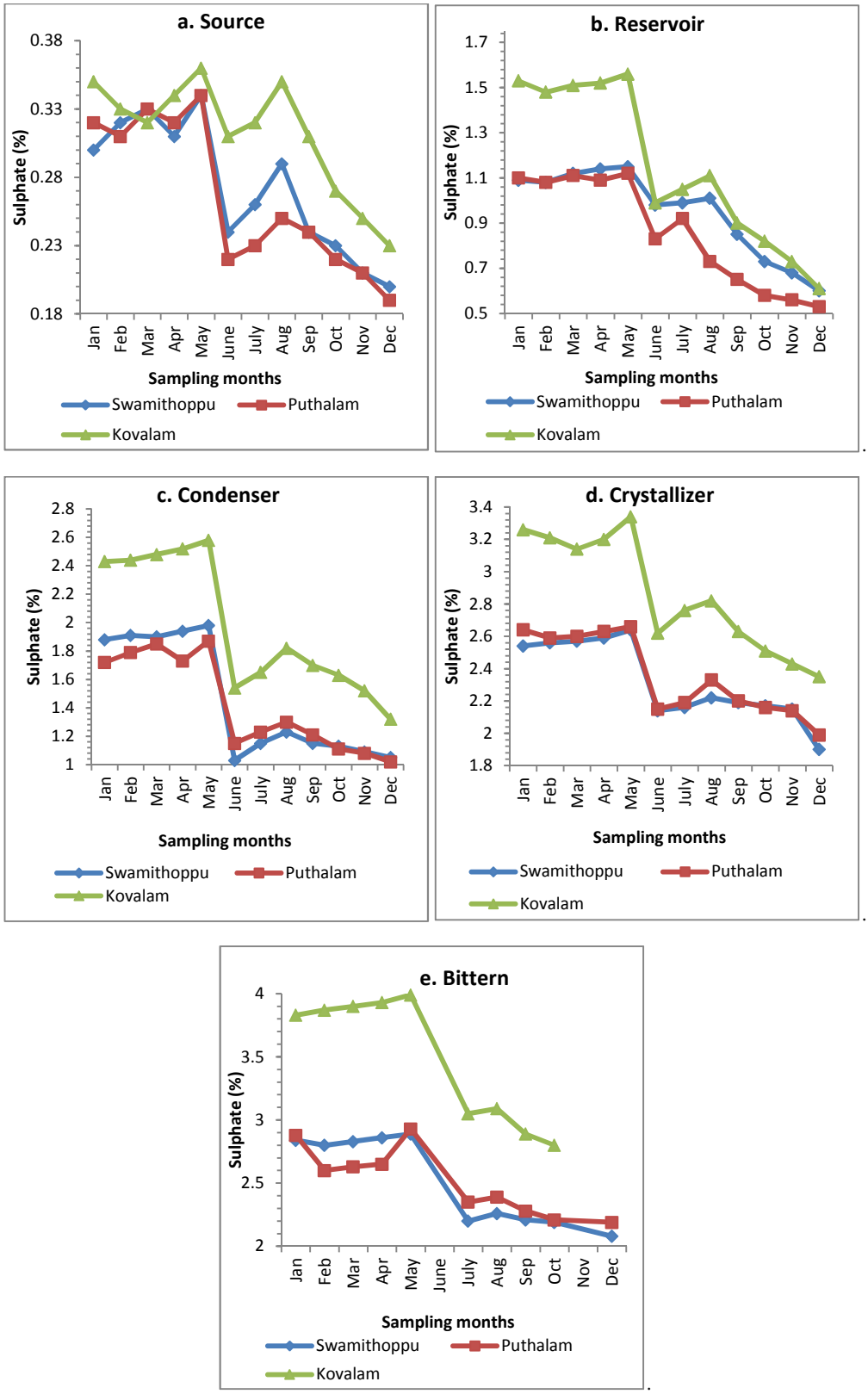
Apart from chloride, brine contains sulphate as the major anion. In the present investigation, the sulphate ion concentration of the brines increased from the source to the bittern stage which is in accordance with earlier works [6]. According to the phase chemistry of solar salt production, sulphate gets eliminated as gypsum, $CaSO_4.2H_2O$ in the condenser stage. The continuing increase in sulphate is due to the remaining gypsum and salts like sulphates of magnesium and potassium which get separated only after 30^{o}Be. The pH was found to decrease from reservoir to bittern and simultaneously the percentage of sulphate increases. This was in accordance with the observation of earlier works [7].

The values were found to be maximum from January to May and also between monsoon periods. But as northeast monsoon became active, the values went on decreasing in November and December which was in accordance with the earlier works [8].

The average value at the source of all salt-pans ranged between 0.27 ± 0.05% and 0.31 ± 0.04%, where Kovalam had maximum value and minimum value was observed in Swamithoppu and Puthalam. The reservoir stage of all the salt-pans had an average ranging from 0.86 ± 0.23% to 1.15 ± 0.34% where Kovalam had maximum and Puthalam had minimum value.

At the condenser stage, the average value ranged between 1.42 ± 0.32% and 1.97 ± 0.46%, of which the maximum value was observed at Kovalam and minimum value was observed at Puthalam. The crystallizer stage of all the salt-pans had an average ranging between 2.32 ± 0.23% and 2.86 ± 0.34%, where again Kovalam had the maximum value and Swamithoppu had minimum value. The available bittern sample of all the salt-pans had an average ranging from 2.51 ± 0.25% to 3.48 ± 0.48%. The maximum value was observed at Kovalam and minimum value was observed at Swamithoppu and Puthalam (Fig.2.a to 2.e).

Fig. 2 Monthly variation of sulphate (%) in the sampling stations during the study period 2011



(iii) Calcium (%)

During the process of solar salt manufacture, calcium followed a unique pathway. In the present study, the concentration of calcium in the source samples was comparatively lower than the other ions. The percentage of calcium increased from source to reservoir and as maximum calcium sulphate got separated before the condenser stage, the values went on decreasing from reservoir to bittern through condenser and crystallizer. As all the calcium

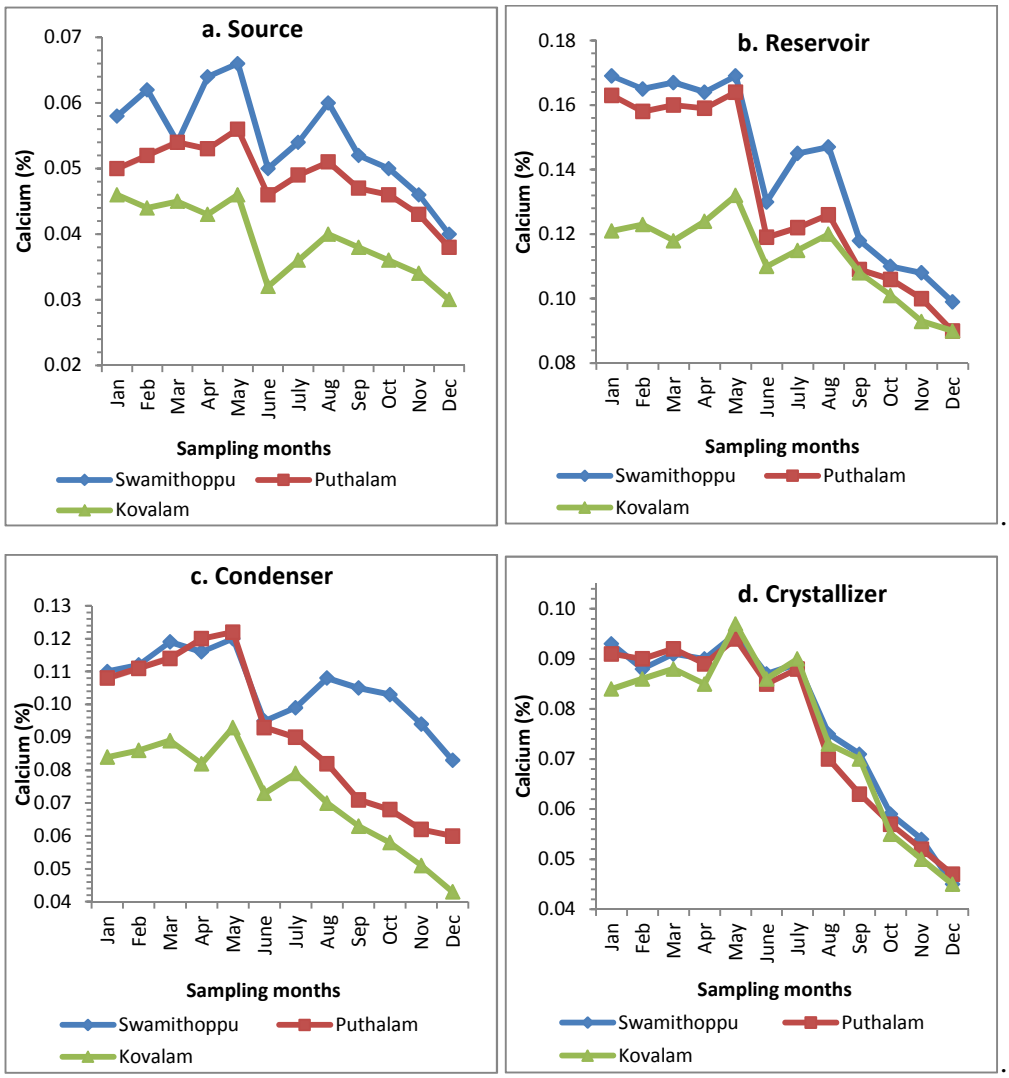
sulphate cannot be collected and in due course it forms a distinct crust on the bottom of the salt-pans, which makes the surface very hard [9].Trace amount of calcium in the crystallizer and bittern stages may be attributed to the excessive organic matters complexed with calcium in high saline concentrating ponds that lead to deposition of this mineral.

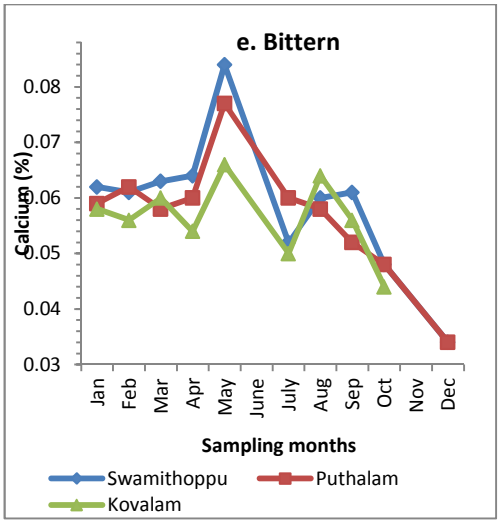
The values were maximum from January to May and also between monsoons. But due to active northeast monsoon, the values went on decreasing in November and December which was in accordance with earlier works [10].

The average value at the source of various salt-pans ranged from 0.04 ± 0.01% to 0.05 ± 0.01%, of which maximum value was at Swamithoppu and Puthalam and minimum value was at Kovalam. The minimum value at Kovalam indicated that sea brine had lesser proportion of calcium.

The average value at reservoir ranged from 0.11 ± 0.01% to 0.14 ± 0.03%, in which maximum value was at Swamithoppu and minimum value was at Kovalam. The condenser stage of all the pans had an average ranging from 0.07 ± 0.02% to 0.11 ± 0.01%, where maximum value was at Swamithoppu and minimum value was at Kovalam.

Fig. 3. Monthly variation of calcium (%) in the sampling stations during the study period 2011





The crystallizer had an average value of 0.07 ± 0.02% in all the salt-pans. The bittern stage had an average ranging from 0.058 ± 0.01% to 0.06 ± 0.01%. The maximum value was at Swamithoopu and minimum value was at Puthalam and Kovalam. Sea brine had lower concentration of calcium initially than subsoil brine, but once calcium sulphate got separated, the average value of calcium was almost similar for the remaining stages (Fig.3.a to 3.e).

(iv) Magnesium (%)

In the present study, the magnesium ion concentration was found to increase gradually from source to bittern. No magnesium salt gets eliminated during the process of solar evaporation. Instead magnesium salts like magnesium chloride, magnesium sulphate etc. remain in the solution on account of their greater solubility and can be crystallized only after 30^{o} Be[11].

The values were found to be maximum from January to May. But when the northeast monsoon became active, the values went on decreasing in November and December. This was in accordance with the earlier works. [12]

The average value of magnesium at source in all the salt-pans ranged from 0.21 ± 0.02% to 0.27 ± 0.05%. The maximum value was observed at Puthalam and minimum value was at Kovalam. The reservoir stage of all the salt-pans had an average ranging between 0.48 ± 0.09% and 0.74 ± 0.19% of which the maximum value was at Puthalam and minimum value was at Kovalam. The condenser had an average ranging from 0.95 ± 0.33% to 1.71 ± 0.22%, in which maximum was at Puthalam and minimum was at Kovalam.

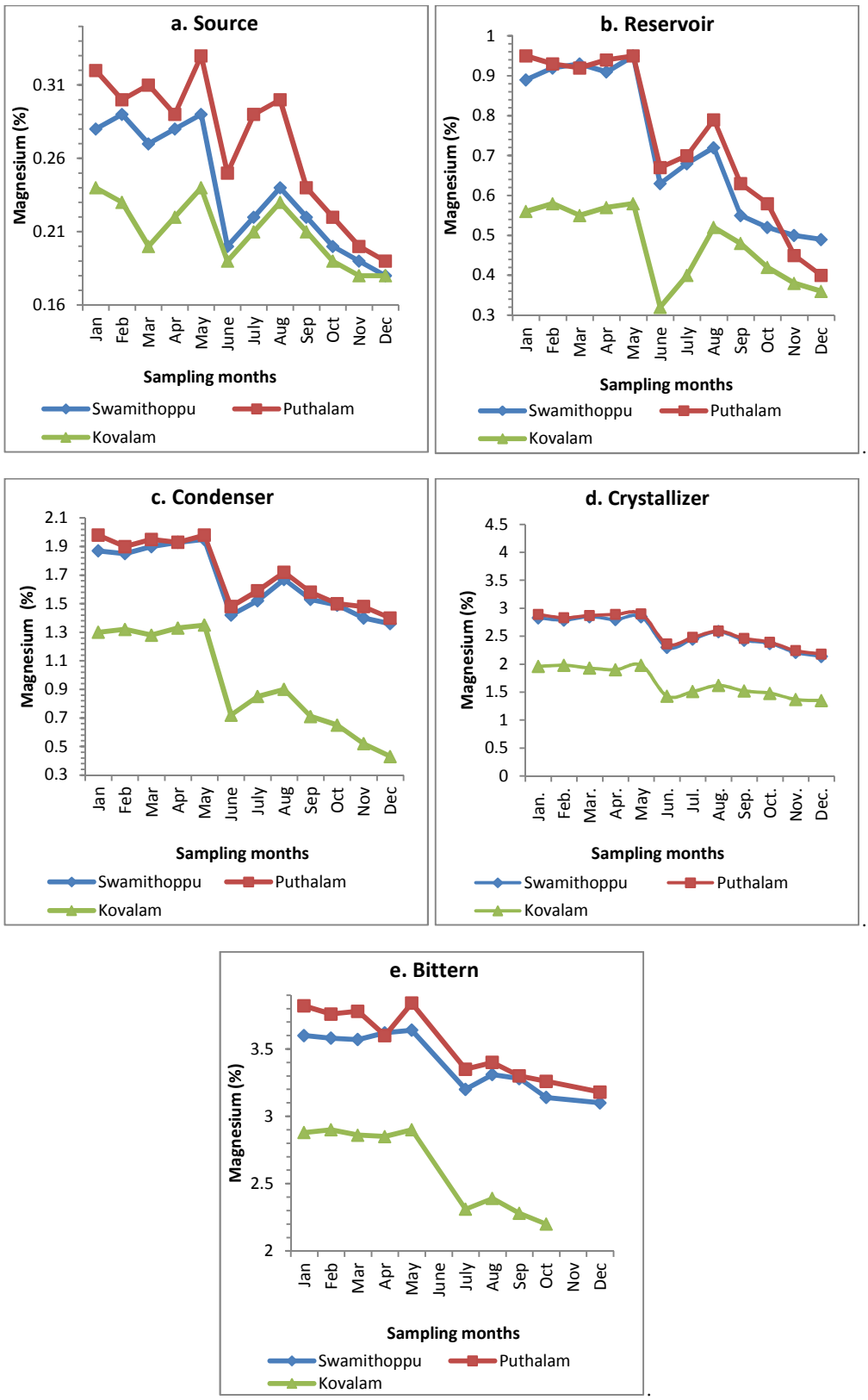
The average value of magnesium in all the salt-pans at crystallizer ranged from 1.67 ± 0.25% to 2.59 ± 0.26%, the maximum at Puthalam and minimum at Kovalam. The bittern sample of all the salt-pans had an average ranging from 2.62 ± 0.29% to 3.53 ± 0.24%, where maximum was at Puthalam and minimum was at Kovalam. The minimum values of magnesium at Kovalam indicated that sea brine had lower amount of magnesium chloride than subsoil brine and back water. (Fig. 4.a to 4.e).

(v) Sodium (%)

The concentration of sodium ion increased from source to crystallizer through reservoir and condenser. Once maximum sodium chloride gets separated before 29.5^{o}Be, the value was found to be minimum at bittern stage. The presence of sodium at bittern stage indicates that not all sodium gets separated as sodium chloride. The percentage of sodium was found to be maximum from January to May and also between monsoons. During monsoon periods, the values were minimum due to the dilution of brine by rain.

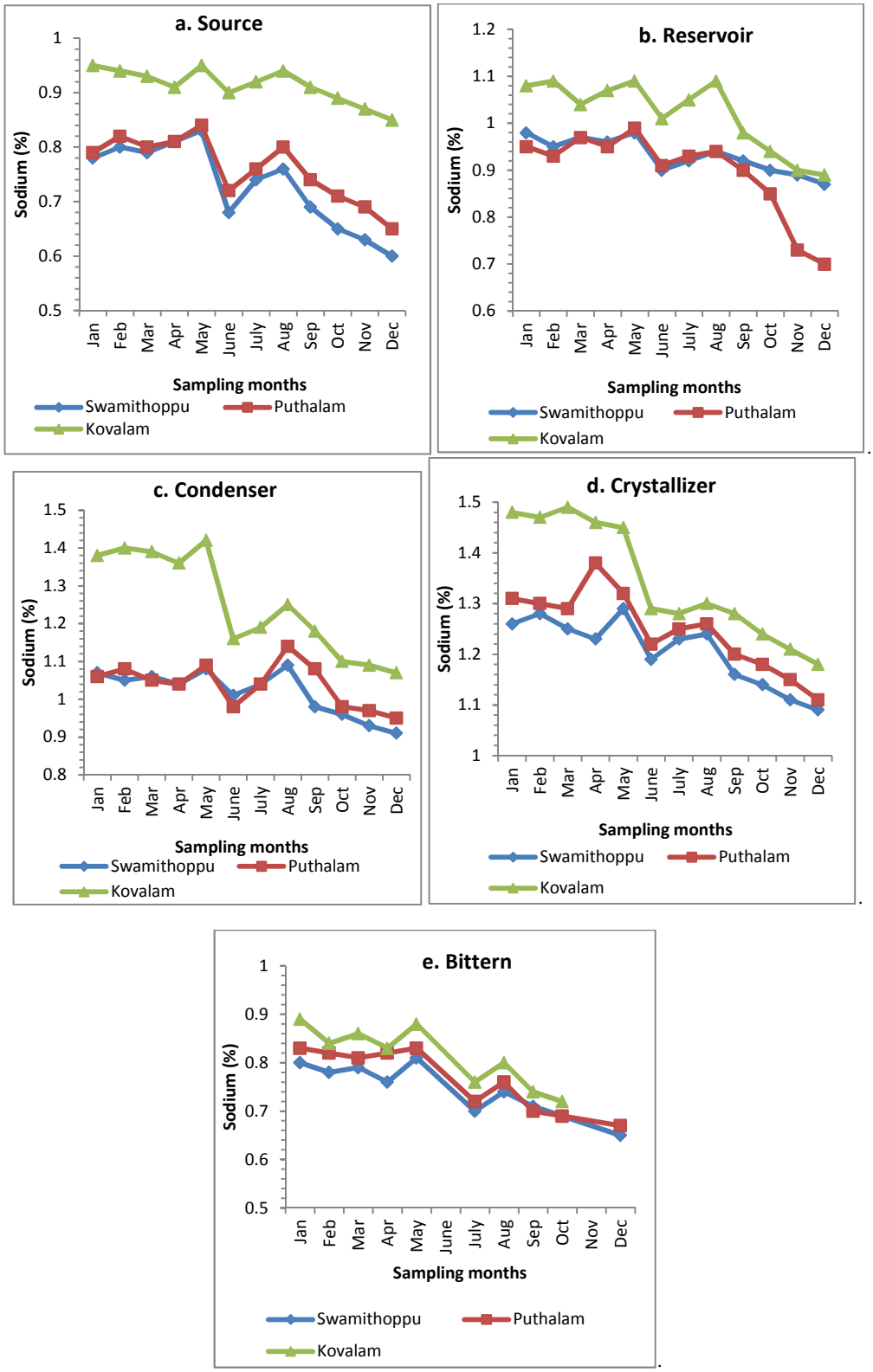
The average value of sodium at the source of various salt-pans had an average ranging from 0.73 ± 0.07% to 0.91 ± 0.03%. The maximum value was at Kovalam and minimum value was at Swamithoppu. It was clear that sea brine had more sodium as expected than other brines. At reservoir, the average ranged from 0.9 ± 0.09% to 1.02 ± 0.07%, of which the maximum was at Kovalam and minimum was at Puthalam.

Fig . 4 Monthly variation of magnesium (%) in the sampling stations during the study period 2011



At condenser, the average ranged from 1.02 ± 0.06% to 1.25 ± 0.13%, where maximum was at Kovalam and minimum was at Swamithoppu. The average value at crystallizer ranged between 1.21 ± 0.06% and 1.34 ± 0.11%. The maximum value was at Kovalam and minimum was at Swamithoppu.

Fig.5 Monthly variation of sodium (%) in the sampling stations during the study period 2011



From the available samples of bittern, the average percentage of sodium in all the salt-pans ranged from 0.74 ± 0.05% to 0.81 ± 0.06%. Since maximum sodium chloride was separated before reaching 30°Be, the value was minimum at bittern stage. It was observed that the percentage of sodium was maximum in Kovalam when compared to other pans because sea brine has more amount of sodium as sodium chloride.(Fig. 5.a to 5.e).

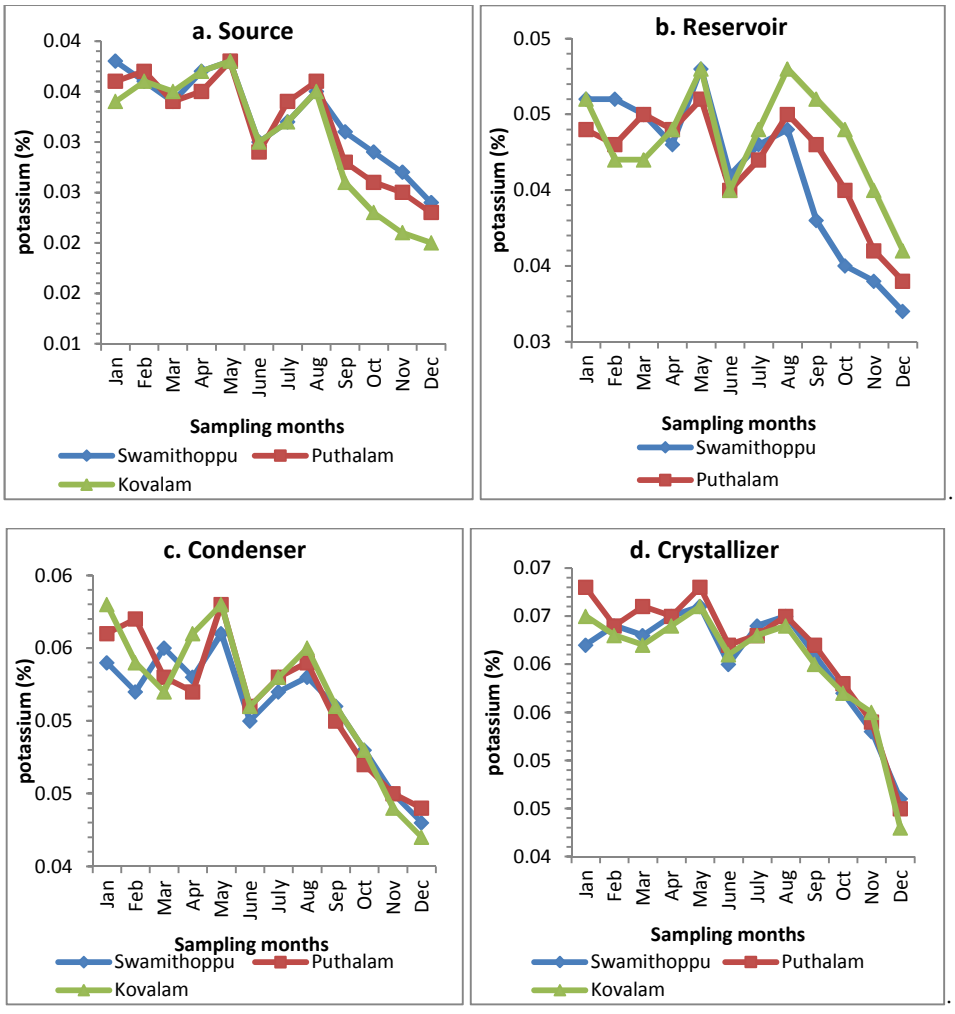
(vi) Potassium (%)

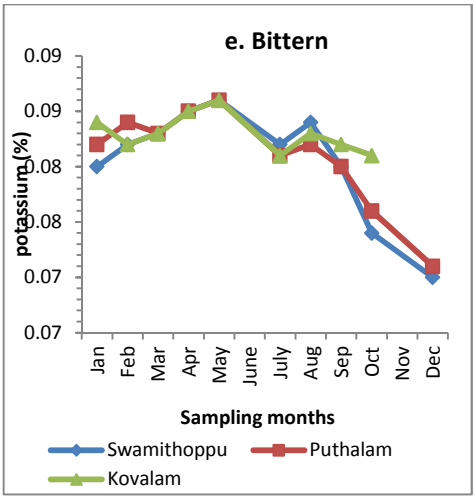
Potassium ion is generally found to be minimum at all the stages of salt production because potassium salts are highly soluble and also no potassium salt is found to be crystallized before the bittern stage which is in accordance with earlier findings [13]. The concentration of potassium was found to increase from the source to bittern through the reservoir, condenser and crystallizer, though the increase was not significant.

The percentage of potassium was found to be maximum from January to May and in between monsoons, which was in agreement with earlier works [14]. As northeast monsoon became active, the values went on decreasing in November and December due to heavy rainfall.

The average value of potassium at the source of various salt-pans had a similar value of 0.033 ± 0.004%. The average value at reservoir was also found to be almost similar i.e., 0.043 ± 0.0035%.The average values were found to be almost similar at the condenser, crystallizer and bittern. From the above values, it was clear that despite the brine used for salt making differed, the average potassium present at various stages of the different salt-pans were found to be almost similar (Fig. 6.a to 6.e).

Fig.6. Monthly variation of potassium (%) in the sampling stations during the study period 2011





CONCLUSION

The present study on the variation of chemical parameters suggest that the percentage of chloride increased from source to bittern stage and was maximum in Kovalam salt-pan which uses sea brine for salt production. The percentage of sulphate was also found to increase gradually from source to bittern stage. There was a continuous increase in sulphate content due to the presence of salts like magnesium and potassium sulphates and the maximum value was observed in Kovalam. Regarding the percentage of calcium, the value increased from source to reservoir and then decreased till bittern stage and this was due to the separation of calcium as calcium sulphate before the condenser stage. The percentage of magnesium increased gradually from source to bittern stage as the salts of magnesium remain in solution due to high solubility and crystallize only after reaching bittern stage. The percentage of magnesium was found to be maximum in Puthalam which uses subsoil brine for salt production.The percentage of sodium gradually increased from source to crystallizer and was minimum in bittern due to separation of sodium chloride. The percentage of sodium was maximum in Kovalam as it uses sea brine for salt production. Regarding the percentage of potassium, it increased from source to bittern but the increase was not very significant. The average values of potassium was found to be almost similar for all the three pans.

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