VII. Summary
VII. SUMMARY

Common salt is one of the most plentiful and cheap substances on earth, obtained as rock salt and solar salt. While, the salt deposits under the state of Kansas alone could supply the world’s entire salt need for the next 2,50,000 years, it is to be noted that the oceans, the most prolific source of solar salt, have salt reserves equal to 50 million billion tonnes. Today rock salt and solar salt contribute equally to the world’s salt production of nearly 215 million tonnes. While, we are familiar with its uses only in cooking, and may not be aware that, it is useful in more than 14,000 commercial applications. It has been a cornerstone to many chemical industries, as a precious and portable commodity.

According to the typical standards adapted in the developing countries the purity required is 99.5% for grade I industrial salt, 98.5% for grade II industrial salt, 97% for table salt and 96% for edible common salt. In the developed countries the specifications are more stringent, the minimum purity prescribed for table salt being 99.5%.

At present, in Kanyakumari District, the southern part of India, solar salt cultivation is carried out in ten saltpans covering an area of 338.63 ha. Salt cultivation in this area is a traditional semi agricultural operation and salt quality as low as 78.6% sodium chloride has been reported on wet basis as early as 1950. As high purity is needed for industrial as well as for human consumption, quality rather than quantity consideration becomes more important.
In the present investigation, the first chapter is an introductory one which deals with the history of salt, its importance in various fields, the different sources of salt, the world’s salt production and India’s contribution to the world’s salt production.

The second chapter details the history of the saltpans of Kanyakumari District and also the biology and ecology of *Artemia*, the key organism involved in salt quality and quantity enhancement. The chapter also describes the statistical methods employed to interpret the results obtained in the present investigation.

The third chapter explains the variations observed in the physico-chemical parameters at different stages of salt production process, from the source to the bittern stage, during the study period from May 2005 to April 2006. Since, the solar salt production involves considerable reduction in volume, (100 to 3%) when it reaches the bittern stage, evaporation is carried out in open places covering an extensive area. This makes the solar salt evaporation highly susceptible to weather fluctuations especially the monsoon. The various physico-chemical parameters determined were pH, electrical conductivity, brine density, brine temperature and the concentration of chloride, sulphate, calcium, magnesium, sodium and potassium.

The following are the results.

- The atmospheric temperature was found be the maximum during April and the minimum during December. The annual mean atmospheric temperature recorded in the saltpans ranged between 29.4 ± 1.8 and 30.0 ± 1.9°C.
• The pH increased slightly from the source to the reservoir and then decreased gradually till bittern formation. The mean pH range in the source sample was from $7.2 \pm 0.22$ to $8.15 \pm 0.18$, whereas in the bittern it was from $6.99 \pm 0.03$ to $7.16 \pm 0.09$.

• The electrical conductivity increased steadily from the source to the bittern. In the source water samples, the mean values ranged from $6.3 \pm 0.63$ to $18.5 \pm 2.0$ mhos and in the bittern it ranged from $70.6 \pm 5.0$ to $94.5 \pm 6.8$ mhos.

• The brine temperature increased from the source to the bittern stage. In the source water samples the mean temperature ranged from $27.1 \pm 0.6$ to $29.1 \pm 0.25^\circ$C and in the bittern its range was from $36.1 \pm 1.6$ to $40.4 \pm 1.5^\circ$C.

• From the source to the bittern stage brine density (salinity) increased gradually. The source water samples had a mean salinity range of $1.7 \pm 0.49$ to $6.50 \pm 0.28^\circ$Be and the range observed in the bittern was from $28.0 \pm 1.4$ to $30.8 \pm 1.40^\circ$Be.

• The chloride concentration showed an increasing trend from source to the bittern, though chloride got separated as sodium chloride in the crystallizer stage. This increase in chloride concentration in the bittern was due the presence of highly soluble chlorides of magnesium and potassium in the bittern. The mean chloride concentration in the source samples ranged between $9.8 \pm 4.2$ and $26.2 \pm 0.16$ gL$^{-1}$ and in the bittern the range observed was from $171.9 \pm 10.5$ to $234.9 \pm 11.4$gL$^{-1}$. 174
• Though sulphate ion was eliminated as gypsum in the intermediate salinity range in the condensers, a continuous increase in sulphate concentration was observed from the source to bittern. This increase was due to the greater increase in the concentration of sulphate as magnesium sulphate than its elimination as gypsum. In the source water samples the values ranged from $2.0 \pm 0.24$ to $4.4 \pm 0.34 \text{gL}^{-1}$, whereas in the bittern, it was from $41.8 \pm 1.7$ to $87.2 \pm 5.4 \text{gL}^{-1}$.

• The calcium concentration increased slightly from the source to the reservoir and then decreased gradually due to the deposition of gypsum in the condenser ponds. The mean calcium concentration in the source water samples ranged from $0.16 \pm 0.00$ to $0.44 \pm 0.01 \text{gL}^{-1}$. In the bittern stage its concentration was very low ($< 0.1 \text{gL}^{-1}$).

• The mean magnesium concentration in the source water samples ranged from $0.36 \pm 0.00$ to $1.82 \pm 0.02 \text{gL}^{-1}$, whereas in the bittern, its concentration was from $16.8 \pm 1.3$ to $49.6 \pm 4.6 \text{gL}^{-1}$. A steady increase in magnesium concentration was noticed, as magnesium was not eliminated during the course of the salt production process.

• The sodium ion concentration increased from the source to the crystallizer stage and then decreased due to the crystallization of sodium chloride. It's mean concentration in the source, crystallizer and in the bittern ranged from $2.9 \pm 0.65$ to $7.7 \pm 0.28 \text{gL}^{-1}$, $34.1 \pm 0.69$ to $54.1 \pm 2.6 \text{gL}^{-1}$ and $19.6 \pm 0.44$ to $24.2 \pm 0.9 \text{gL}^{-1}$ respectively.

• The potassium ion concentration also increased gradually from the source to the bittern. No potassium salt got separated during the course of the salt production process as potassium salts are highly soluble. The range of potassium in the source water samples was from $0.21 \pm 0.00$ to
0.32 ± 0.01 gL⁻¹, whereas in the bittern it was from 3.53 ± 0.15 to 5.77 ± 0.11 gL⁻¹.

The results on the various physico-chemical parameters determined for the different seasons showed that all the parameters become the minimum during season III in all the saltpans. The decrease in values was due to the dilution of brine by the heavy northeast monsoon during the same season. Highest values for most of the parameters in almost all the saltpans were recorded during season IV.

The fourth chapter elaborates on the quality of salt obtained from the ten saltpans during the study period. As salt quality is specified on the basis of moisture content, insoluble impurities, calcium sulphate, magnesium sulphate, magnesium chloride and sodium chloride content, these parameters were estimated. Salt samples were not available during season III of the study period due to the heavy northeast monsoon.

The results of the analysis on the different salt quality parameters of the various saltpans are given below.

- The mean moisture content of the salt samples ranged from 8.0 ± 1.3 to 13.3 ± 1.3%. The maximum value was recorded at the SP10 salt samples and the minimum value was registered at SP1 salt samples.
- The mean insoluble impurities ranged from 0.64 ± 0.03 to 2.0 ± 0.46%. The minimum mean value (0.64 ± 0.03%) was recorded at the SP4 salt samples, and the maximum value (2.0 ± 0.46%) was recorded at SP8 salt samples.
The mean calcium sulphate content in the salt samples of the various saltpans was within the range, 0.24 ± 0.03 and 0.62± 0.08%. While the lowest value (0.24 ± 0.03%) was recorded at the SP6 salt samples, the highest value (0.62 ± 0.08%) was monitored at the SP10 salt samples.

The mean magnesium sulphate and magnesium chloride contents varied from 0.76 ± 0.05 to 2.6 ± 0.24% and from 1.1 ± 0.12 to 2.4 ± 0.2% respectively. The salt samples from SP9 witnessed the maximum mean value of both the impurities and the salt samples from SP4 recorded the minimum values.

The mean sodium chloride content of the salt samples of the various saltpans ranged from 78.8 ± 0.93 to 87.3 ± 0.75%. SP1, which used sea water as source, harvested salt with the maximum mean sodium chloride content (87.3 ± 0.75%) and SP6 with estuary water along underground water as source, harvested salt with 86.4 ± 0.70% sodium chloride content. SP9 which used estuarine water for salt production harvested salt crop of the minimum mean sodium chloride content (78.8 ± 0.93%).

The results obtained for the seasonal variation in the salt quality parameters revealed that the moisture content was the maximum during season I and the sodium chloride content was the maximum during season IV. Though the highest percentage of sodium chloride was witnessed by the salt samples of SP1, the only saltpan to use sea water, SP6 which used underground water along with estuary water, harvested salt samples of similar sodium chloride content. In SP9, the sodium chloride content of salt was as low as 78.8%, because of high contamination of the salt with magnesium and
hence associated with higher percentage of moisture content. The low quality salt is often harvested from salt pans which fail to eliminate bittern.

Chapter V details the heavy metal analysis in the source water and in the salt samples harvested from the salt pans under investigation. It is true that, except for the insoluble matter, the origin of all the other impurities in the salt was, due to the source water (sea water, estuarine water and underground water) used for salt production. Heavy metals in water sources are of natural origin as well as from anthropogenic activities. Hence an estimation of heavy metals in the source water samples used for solar salt manufacture and those in the harvested salt became essential. The different heavy metals analyzed were chromium, lead, nickel, iron, cobalt, copper, zinc and manganese.

The concentration of heavy metals in the source water and the heavy metals in the salt samples are given as follows.

- The chromium concentration in the source water ranged from 3.5 ± 0.16 to 9.2 ± 0.30 ppb, the lead concentration from 1.7 ± 0.05 to 7.8 ± 0.03 ppb, and the nickel concentration from 0.49 ± 0.03 to 1.4 ± 0.03 ppb. The highest concentration of these metals was observed in the sea water source of SP 1.

- The mean concentration of iron and cobalt in the source water samples ranged from 141 ± 5.1 to 1257 ± 20.1 ppb and 1.2 ± 0.02 to 3.9 ± 0.35 ppb respectively. The underground water samples of SP10 and SP2 witnessed the highest concentration of these metals respectively.

- The maximum mean concentration of copper (6.4 ± 0.5 ppb) in SP6, zinc (16.1 ± 0.60 ppb) in SP8 and manganese (7.3 ± 0.2 ppb) in SP5 was recorded for estuarine water and their concentration ranged from
1.3 ± 0.08 to 6.4 ± 0.5; 3.8 ± 0.02 to 16.1 ± 0.60 and 1.5 ± 0.01 to 7.3 ± 0.2 ppb respectively.

The maximum accumulation of chromium (2.9 ± 0.01 ppm) and lead (1.3 ± 0.01 ppm) was observed in the salt samples of SP1. Likewise, the maximum amount of nickel (0.15 ± 0.02 ppm), manganese (0.24 ± 0.03 ppm) and iron (48.3 ± 3.5 ppb) in SP10, and cobalt (1.7 ± 0.05 ppm) in SP2 was observed in the salt samples harvested from underground brine. Estuarine salt samples from SP6 and SP5 witnessed the maximum copper (0.075 ± 0.02 ppm) and zinc (0.17 ± 0.05 ppm) respectively.

Chapter VI elaborates on the inoculation of brine shrimp *Artemia* in the solar salt pans. As proper biological management using brine shrimp *Artemia* enhances the quality and the quantity to design capacity, *Artemia* was inoculated in three salt pans that use sea water, underground water and estuarine water exclusively for salt production. The study includes the determination of the evaporation rate, the estimation of the amount of salt harvested, estimation of the salt quality parameters in the salt samples and finally the heavy metal analysis in both the control and the experimental salt samples.

The results of the analysis revealed that the maximum percentage increase in evaporation from the control to the experimental crystallizers recorded at SP1 was 19.8 ± 1.3 % with an increase in sodium chloride production (quantity) of 15.1 ± 0.68 %. In SP7, the maximum increase in evaporation observed was 21.2 ± 0.90 % and the corresponding increase in the percentage of salt observed was 14.9 ± 1.6%. In SP8, the maximum increase in evaporation observed was 20 ± 0.66 % and the corresponding increase in the percentage of sodium chloride produced was 15.5 ± 0.88%.
The results of the analysis of the salt quality parameters revealed that moisture content, insoluble impurities, calcium sulphate, magnesium sulphate and magnesium chloride content decreased from the control to the experimental ponds and the sodium chloride content increased at all seasons in all the three saltpans.

The percentage decrease in moisture content from the control to the experimental samples varied between 11.8 ± 0.68 and 22.6 ± 0.41 %, insoluble impurities from 3.8 ± 0.18 to 16.4 ± 1.2%, calcium sulphate from 3.2 ± 0.18 to 5.5 ± 0.52%, magnesium sulphate from 13.3 ± 1.4 to 28.3 ± 2.3% and magnesium chloride from 8.1 ± 0.6 to 20.0 ± 1.2% at different seasons in the saltpan that used sea water (SP1).

In the saltpan that used underground water (SP7), the percentage decrease in moisture content from the control to the experimental samples varied between 16.2 ± 1.2 and 22.5 ± 2.2 %, insoluble impurities from 2.8 ± 0.23 to 22.2 ± 1.3%, calcium sulphate from 3.3 ± 0.29 to 10.6 ± 0.78 %, magnesium sulphate from 17.9 ± 0.98 to 39.2 ± 2.6% and magnesium chloride from 7.7 ± 0.39 to 28.5 ± 1.52% during different seasons.

In SP8, the saltpan that used estuary water, the percentage decrease in moisture content varied between 19.8 ± 1.0 and 23.5 ± 0.94%, insoluble impurities from 8.2 ± 1.4 to 24.1 ± 1.6%, calcium sulphate from 12.7 ± 0.9 to 25.8 ± 2.7 %, magnesium sulphate from 12.5 ± 1.1 to 27.1 ± 1.3% and magnesium chloride from 16.5 ± 1.3 to 20.7 ± 1.2% during different seasons.

The percentage increase in sodium chloride content from the control to the experimental samples at different seasons ranged between 3.0 ± 0.12 and 3.6 ± 0.19 % at SP1 (sea water), 3.3 ± 0.32 to 3.7 ± 0.40 % at SP7
(underground water) and 4.2 ± 0.30 to 4.5 ± 0.40% at SP8 (estuary water). The increase in sodium chloride was more in estuarine sample than in the other two.

Heavy metal analysis of both the control and the experimental salt samples revealed the following.

- All the heavy metals in the salt samples from the three salt works (SP1, SP7 and SP8) were found to decrease from the control to the experimental salt samples except nickel in SP1 sample and lead and manganese in the samples of SP7. These three elements remained the same in both the control and the experimental samples of the respective saltpans. The maximum decrease in percentage accumulation observed in the experimental salt sample with respect to the control sample was chromium (18.7 ± 1.6%), zinc (20.5 ± 1.4) and manganese (10.2 ± 0.51%) in SP1, lead (5.8 ± 0.30%) and copper (23.0 ± 1.8%) in SP8, nickel (9.09 ± 1.0 %), iron (47.3 ± 2.8%), and cobalt (24.5 ± 1.3%) in SP7.

Though biological processes are involved, the operation of solar salt works is based mainly on chemistry, but this fact is little realized by the chemists. Even, those who manage the salt works have no knowledge about the science involved in salt production. They do it more as a semi agricultural operation than as a scientific process.

The work thus concluded that sodium chloride which is an edible commodity needed by the living realm of the biosphere is not available in the required quality. At present large amount of money has to be spent to enhance the quality of the edible salt as well as that used in chemical industries. It has
been proved in the present study that proper biological management of the saltpans using brine shrimp *Artemia* at a large scale can be of greater effect both qualitatively and economically. Moreover salt farming can be coupled with *Artemia* cultivation, which may be a source of additional income to the salt farmers via *Artemia* biomass and cyst production, since it is readily used in the aquaculture industries, especially as live feed for larval stages of marine cultivable organisms. In the saltpans used for this research, most of the heavy metals have been found within permissible limits and many of these are vital in trace amounts for the health of human beings. Heavy metals beyond permissible limit can lead to dangerous consequences. Research can be extended to the saltpans in other parts of the country, so that the heavy metals can be kept within the required limits. Thus, besides opening further avenues for research, the present study also becomes socially significant.