Biological and chemical features associated with salt production in solar saltfields at Dry Creek, South Australia

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Thesis submitted in fulfilment of the requirements
for the degree of Doctor of Philosophy.

May, 1997

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ABSTRACT

Sodium chloride is important in the manufacture of chlorine, caustic soda and soda ash. It is obtained from several sources, an important one being solar saltfields. One third of the world's sodium chloride is from solar salt fields. Solar salt fields at Dry Creek are the major site of salt production in South Australia. They comprise a series of interconnected evaporating and crystallising ponds where seawater is evaporated and the concentration of sodium chloride increases. Finally, water terminates in crystallisers where evaporation continues and sodium chloride precipitates and is then harvested. The aims of this research are to evaluate the biological and physico-chemical parameters and their interactions with the production of salt.

Salt production is strongly dependent upon biological, physical and chemical factors. These were investigated in eight ponds at Dry Creek solar saltfields. Nutrient and other chemical and physical parameters, including salinity, alkalinity, pH, dissolved oxygen, temperature, wind and rainfall, which control the composition of the biota and salt production in the solar saltfields, were measured. Salinity ranged from 46 to 243.5 g/L. The systems were alkaline and low in oxygen concentrations (0.4 - 9.5 mg/L). Ranges of nutrients were 7-22 and 4-19 μg/L for reactive phosphate and nitrate-nitrogen concentrations in the study ponds, respectively.

There are two sources of seawater intake, Middle Beach (low nutrient) and Chapman Creek (high nutrient). Seawater from Middle Beach with low salinity (38 g/L) and nutrients (SRP, 40 μg/L; total P, 52 μg/L; NO_3-N, 4.5 μg/L) is different from seawater from Chapman Creek with high salinity (47 g/L) and high nutrients (SRP, 250 μg/L; total P, 290 μg/L; NO_3-N, 133 μg/L). This excessive amount of nutrients that enter the ponds with intake seawater caused high biological productivity in several ponds. The major source of these nutrients is from the outfall of the nearby Bolivar sewage works.

Standard methods of analysis of plant nutrients (NO_3-N and PO_4-P) may lead to significant errors when applied to saline water. For this reason, analytical methods for the estimation of both NO_3-N and PO_4-P in saline water were re-examined. It was established that the ascorbic acid with antimony (III) phospho-molybdenum blue method is the most useful method for phosphate determination in saline water and shows minimal salinity interferences. For nitrate estimation it was shown that there are substantial salt errors when using the Cd column technique followed by colorimetric procedures. Methods involving dilution, standard addition or the application of a salt error correction are essential for accurate nitrate determination in saline waters.

The biota and biological communities in the solar saltfields at Dry Creek are similar to those found in other solar salt fields. Forty - two species of algae dominated by diatoms, and Cyanobacteria, and 10 species of zooplankton dominated by crustaceans, were identified. Marine brackish fauna and saline forms are the dominant groups of organisms in early stage ponds. As salinity increases through the series of ponds, species diversity falls and finally only halobiont species remain. In early ponds the fauna includes fishes, gastropods, isopods, amphipods and copepods (calanoids, cyclopoids and harpacticoids),

ostracods and insects (Trichoptera and Diptera). The fish, *Atherinosoma microstoma and Pseudogobious olorum*, have been recorded from study ponds with salinity 46-110 g/L. Two isopods, (*Exosphaeroma bicolor* and *Synischis* sp.), the amphipod, (*Parhyalella kunkel*), one gastropod (*Hydrododdus tasmanicus*) and *Palaemon serenus*, a large swimming prawn in pond XD1 at a salinity of 55 g/L, represent tolerant macrospecies. They may prevent the growth of benthic mats in this pond. *Acartia* is the main copepod and tolerates a salinity up to 110 g/L. As salinity increases through the series of ponds, species diversity falls and finally only halotolerant species remain. *Daicypris dictyote* and *Reticypris herbsti* were present at a salinity 55.5-137.5 g/L. They did not occur at a higher salinity probably not only due to high salinity but also due to deficiency of some ions, such as carbonates (see Chapter 2). The occurrence of *Symphitoneuria wheeleri* was notable because this insect is rare in saline water and does not belong to the Philanisidae, the family containing the only known marine Trichoptera. Two species of chironomids (*Cladotanytarsus* sp. and *Tanytarsus barbitarsis*) and one species of Ephydridae (?*Ephydra riparia*), occurred in most ponds. The planktonic community of these highly saline evaporating ponds consists mainly of *Artemia franciscana* and *Parartemia zietziana*. Seasonal variation in zooplankton populations reflects seasonal changes in temperature, light, nutrients and algal abundance. Thus, the presence of zooplankton is governed primarily by its salinity tolerance and its abundance by trophic conditions. At salinities above 180 g/L, brine shrimp (*Artemia franciscana* and *Parartemia zietziana*), hypersaline algae (*Dunaliella salina*), and a hypersaline Cyanobacterium (*Synechococcus*) are abundant.

At high salinity, *Synechococcus* excreted large amounts of extracellular material and this caused an additional increase in brine viscosity with effects on salt production. The effects of the extracellular material produced by *Synechococcus* were tested in a field experiment which used microcosms to investigate how *Synechococcus* affected the quantity and quality of salt produced. Five tanks were filled with brine from salt ponds and inoculated with different amounts of *Synechococcus*. The tanks were monitored for 12 weeks in two stages. In stage I, *Synechococcus* was present in evaporating tanks until the brine concentration increased to the point of sodium chloride crystallisation. Regular measurements were made of salinity and viscosity in different treatments. In stage II, *Synechococcus* was excluded and salt was allowed to crystallise in the tanks; deposited salt was harvested at the end of the experimental period. The values of pH in the brine ranged 7.3 to 9. The value for salinity ranged 210 to 326.5 g/L and correspondingly, for specific gravity, from 1.1495 to 1.2278 during the period of experiment. The relative viscosity increased throughout stage I; it ranged from 1.103 to 1.290, 1.301, 1.336, 1.346 and 1.353 in tanks 1, 2, 3, 4 and 5, respectively. The highest value occurred in tank #5 which contained the highest amounts of *Synechococcus*. The salt quality harvested from each treatments was evaluated by the dry sieve technique using a Scanning Electron Microscope (SEM) and Energy Dispersion X-Ray Analyser (EDX) was used to determine crystal form, size and elemental composition, thus to determine impurities in the harvested salt. The results showed that the size and shape of salt crystals harvested are affected by liberated organic material (ECP) produced by *Synechococcus*, and that more brine is retained in these salt crystals which affects the composition of the salt and leads to a decreased in the quality of salt crystals. Data on size distribution of salt crystals showed that it was unimodal for all tanks and ranged from 0.125 to 4 mm. Overall, the largest crystals were

from the control tanks (tank #1), and the smallest from the high *Synechococcus* tank (tank # 5). Moreover, the quantity of harvested salt decreased with increasing amounts of *Synechococcus* due to the decreasing percentage of evaporating water.

The effects of high salinity and high light intensity on the production of extracellular material were tested by an experiment using aquaria as microcosms. Twelve aquaria with the same amounts of *Synechococcus* standing crop were filled with low and high salinity brine from ponds PA7 (190.5g/L) and FA1 (285 g/L) and kept under covered and uncovered conditions. Viscosity values were 1.51340 and 1.5790 centistokes in ponds PA7 and FA1, respectively. Regular measurements were made of salinity and viscosity in different treatments. The highest value of viscosity occurred in high salinity-uncovered sample in week four with viscosity of 1.94342 centistokes and the lowest value was in low salinity-covered aquarium and in week one. The salinity was almost constant throughout the experiment. Samples from the aquaria were taken to assessthe amount of extracellular material and to investigate its structure. The results of ash free dry weight (AFDW) of the *Synechococcus* standing crop showed that more organic material was produced under high salinity and high light intensity than at low salinity and low intensity of light. Part of this organic material produced by *Synechococcus* was released to the media and increased the viscosity of the brine. Thus, relative viscosity was higher in conditions of high salinity and high light intensity due to the ECP produced by *Synechococcus*. The chemical composition of extracellular material was investigated by solid state resolution 13C Nuclear Magnetic Resonance (NMR) with Cross Polarisation and Magnetic Angle Spinning technique. These technique indicated that the samples were mixture of glycoproteins and glycolipids.

The information collected from the physico-chemical, biological and experimental investigation is used to make appropriate recommendations about solar salt pond management. Proper management of biological systems is essential for production of high quality salt.