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The Role of Biological Disturbances in the Production of Solar Salt

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ABSTRACT

The quality and quantity of salt produced in solar fields depend on a number of physical, chemical and biological factors. Salt fields in tropical regions are more likely to experience disturbances to these factors due to the variability of rainfall.

The cyanobacteria *Synechococcus* sp. are shown to have an important bearing on viscosity and chemistry of brines. Salt crystallised from viscous brines had a fragile structure and contained high levels of magnesium and manganese. The causative factors and mechanisms by which biological disturbances develop in the concentrating system are discussed. Minimization of salinity fluctuations and inter-pond transfer of biological material are suggested to be important considerations in the design and management of salt fields in tropical regions.

INTRODUCTION

Cheetham operates nine solar salt fields along the eastern and southern coasts of Australia. Of these, three fields are located in tropical Queensland. Variations in salt yields and salt physical and chemical properties led to the establishment of a brine research program at Bajool in 1985.

This paper presents results from laboratory investigations and field trials from this research program. The major emphasis of the paper is on the causes of increases in brine viscosity, the impact of high viscosity brine on salt quality, and management implications for improving the salt productivity of tropical solar fields.

Viscosity

Ideally sodium chloride has a solid cubic shape that minimizes washing losses and retains little of the brine. Crystals that form in high viscosity brine are hollow, more fragile and retain more of the mother liquor (Fig. 1). High viscosity brines also lead to higher concentrations of non-recoverable drift salt in the crystallisers. Harvesting also becomes a problem because the salt is often too soft for efficient removal and too fine for washing. The impurities can be reduced by increased washing and draining but only at the expense of further losses.

The increased brine viscosity is due largely to the extracellular excretion of mucilage from the blue-green bacteria (cyanobacteria) *Synechococcus* sp. These bacteria have several synonyms in common usage such as *Aphanothece* sp. and *Coccochloris* sp. (Rippka et al., 1979). Since it is likely that more than one species produces mucilage it has been expedient to describe all associated species as *Synechococcus* sp. Several authors argued that some algae produce extracellular mucilage in response to the depletion of either nitrogen or phosphate (Kroen and Rayburn, 1984; Shoshana et al., 1988). Phlips et al.(1989) found that cultures of *Synechococcus* sp. enriched with CO_2 increased their production of extracellular mucilage but the phosphate concentrations were not reported.

Manganese

Field observations suggested a relationship between the concentrations of manganese and magnesium in the harvested salt; the higher the manganese, the higher the magnesium. In the laboratory, addition of manganese to brines resulted in a high level of magnesium in the crystallised salt. At high pH values, where manganese is precipitated in the brine before halite saturation, the magnesium concentration of the salt was reduced to a level comparable to the control (Table 1). Subsequent trials on field brines gave similar results. Salt with a high manganese content is typically opaque and forms hard layers in the crystallisers. These layers can become sufficiently hard to reduce the efficiency of

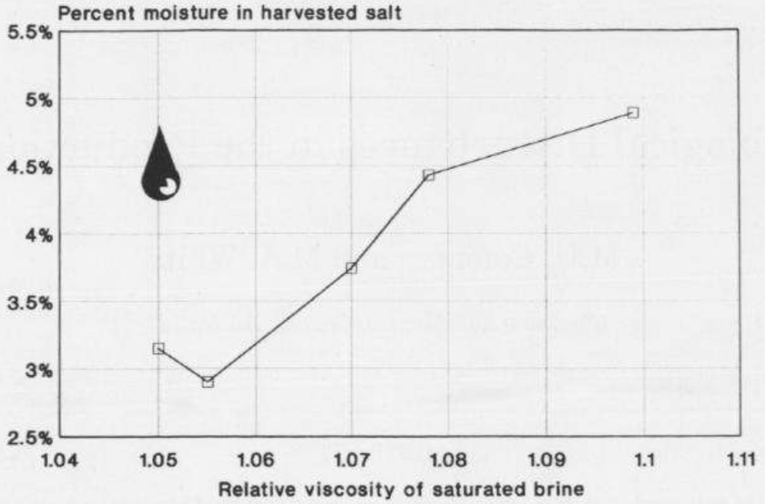

Fig. 1. The effect of brine viscosity on the moisture content of harvested salt.

mechanical harvesting. We believe the manganese, as the chloride form, co-crystallises with sodium chloride causing disruptions in the NaCl crystal lattice thus causing retention of magnesium-rich brine in the crystals.

Manganese is known to recycle into the brine from the sediment in concentrating ponds by biological degradation of organic matter and desorption in a reductive environment to form the soluble divalent cation (Malcolm and Stanley, 1982). In alkaline brines manganese readily oxidizes if the brine is well oxygenated. Divalent manganese can also form a carbonate; the availability of carbonate also being pH dependant (Faust and Aly, 1983).

Both brine viscosity and manganese concentration are strongly influenced by biological disturbances. The effect of such disturbances on viscosity and manganese is discussed in the remainder of the paper.

BIOLOGICAL DISTURBANCES

Salinity changes

At Bajool the input brine is estuarine seawater with a usual S.G. of 1.027. The salt field comprises a series of ponds with nine successive increments of S.G. from 1.028 to 1.180. From S.G. 1.180 to 1.216 the brine is held in batching ponds to allow greater control near the halite precipitation point. As the S.G. increases through the system the initial marine-like community changes to halo-tolerant and then halophilic. Overlaying the mosaic of biological and chemical environments are the vagaries of a tropical climate. On average, the Bajool rainfall is 800 mm per year. However, monsoonal rains may precipitate half of this in one to four weeks. Thus, the S.G. of a pond will be strongly influenced by preceding meteorological events and may take several months to return to the original density after heavy rainfall. Other events that have been observed to affect the pond S.G. are the construction of new ponds, breakdown of pumps and changes in the composition of the intake estuarine brine.

TABLE 1

Effect of manganese on chemical quality of crystallised salt

Brine chemistry		Contaminants in the salt		
Mn added (ppm)	pH	Mg (ppm)	Ca (ppm)	Mn (ppm)
0	7.3	128	482	2.00
2	7.3	255	592	3.90
2	7.3	303	510	3.20
2	8.5	130	510	2.26

Brine made from major salts (AR grade) and H_20.

Synechococcus sp.

In the Queensland salt fields, *Synechococcus* sp. characteristically dominates in the ponds that accumulate gypsum. Small changes in the S.G. of a pond have been shown to result in radical changes in the algal dominance. Figure 2 shows, for example, a change in S.G. from approximately 1.115 to 1.095 caused the concentration of the *Synechococcus* sp. to decrease substantially. The dominant species rapidly became *Oscillatoria* sp. Field observations suggest the latter does not have a major effect on the brine viscosity.

The relationship between S.G. and the type of biological community, however, is not simple for two

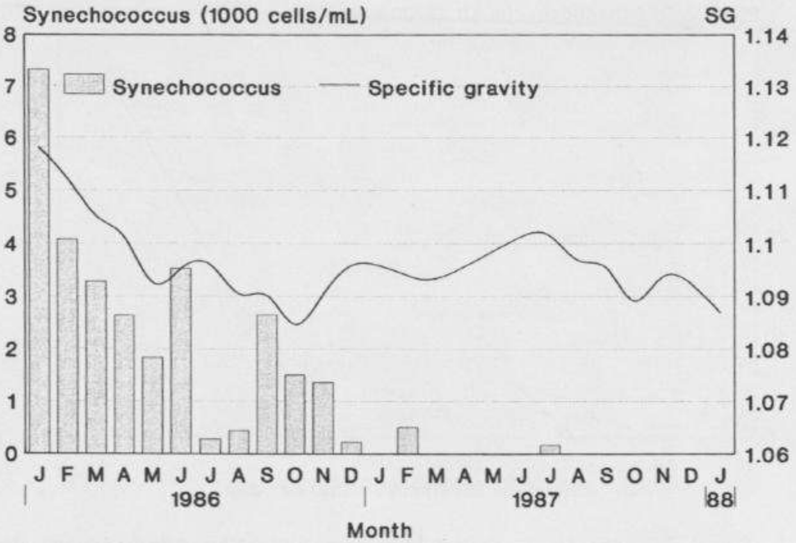

Fig. 2. Relationship between planktonic synechoccoccus and specific gravity of brine.

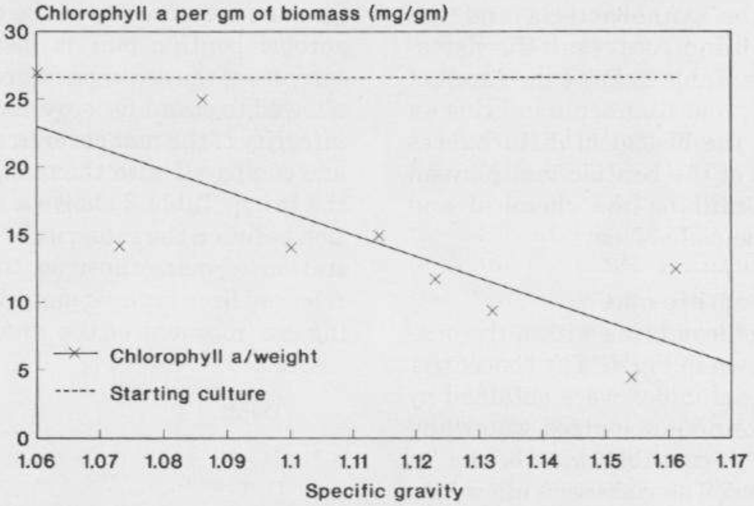

Fig. 3. Growth of benthic synechococcus in cultures of different specific gravity.

main reasons. Firstly, the salinity change does not often last long enough for significant biological recruitment from other sources to occur. Secondly, the chemical composition of rain diluted brine will not match exactly that of evaporated brines of the same S.G.

To test growth preferences, a *Synechococcus* sp. dominated mat was broken into lots (5 g) and cultured in field brines ranging from S.G. 1.06 to 1.16. After two weeks the mat was re-weighed and analysed for Chl-A (chlorophyll a). All samples had an increase in total Chl-A with respect to the inoculum but the increase fell steadily with increasing salinity. This supports the view of Krishnan (pers. commun., 1990) that *Synechococcus* sp. is halo-tolerant but not halophilic. Further, despite a net increase in Chl-A per sample the Chl-A per biomass ratio fell relative to the inoculum (Fig. 3). The most likely explanation for the fall in Chl-A per biomass with increasing S.G. is an increase in extracellular production. If this extracellular production is in the form of mucilage then it follows that brine viscosity should increase. Field observations have shown that growth of benthic *Synechococcus* sp. is rapid when the salinity is reduced by heavy rains. As the rain-diluted brine returns to the normal S.G. the concentration of planktonic *Synechococcus* sp. increases (Fig. 4). This is due to the increased rate of photosynthesis resulting from a combination of high irradiation levels and lower salinity. Photosynthesis at the surface of the benthic mat leads to entrapment of oxygen, gradual fragmentation of the mat, and

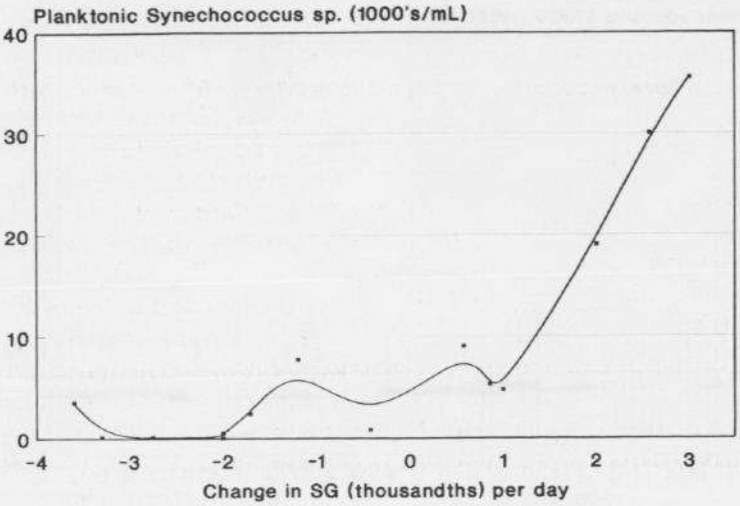

Fig. 4. Synechococcus concentrations in field brine as a function of daily density changes.

eventual release of fragments that float into the brine. This releases the cyanobacteria and the mucilage mixes into the brine. As a result the viscosity of the brine increases. Table 2 shows the result of mild agitation of benthic mat fragments in brine on brine viscosity. Clearly the biological disturbances arising from disruption of the benthic mat play an important role in determining the chemical and physical properties of the pond brine.

Manganese and the benthic mat

A typical daytime profile of brine within the benthic mat and mud is shown in Fig. 5. The concentration of phosphates and sulphides were obtained by locating open vials containing deionized water and covered with a semi-permeable membrane at various depths in the mud. The vials were allowed to equilibrate with the interstitial brine for four weeks before analysis. The upper 20 mm represents that portion of the sediment occupied by the benthic mat (dominated by cyanobacteria). The low pH of the brine in the pond mud (pH 5.5) reflects the original mangrove mud base of the field and the anaerobic decomposition of the organic debris transported from earlier ponds over thirty years of operation.

TABLE 2

Effect of agitation of benthic mat on brine viscosity

S.G.	Relative viscosity	
	Prior*	Post*
1.109	1.073	1.87
1.117	1.100	1.62

*Brine viscosity before and after agitation.

Laboratory studies have shown that the manganese concentration in the brine is higher when the aerobic benthic mat is disturbed (Table 3). Core samples of the sediment were covered with brine and allowed to stand for several days. The continuity or integrity of the mat cover in each sample was ranked and compared with the manganese concentration in the brine. Table 3 shows a strong negative correlation between the integrity of the mat and the concentration of manganese in the brine. Manganese is released from organic material in the strongly reducing environment of the mud. Following the distur-

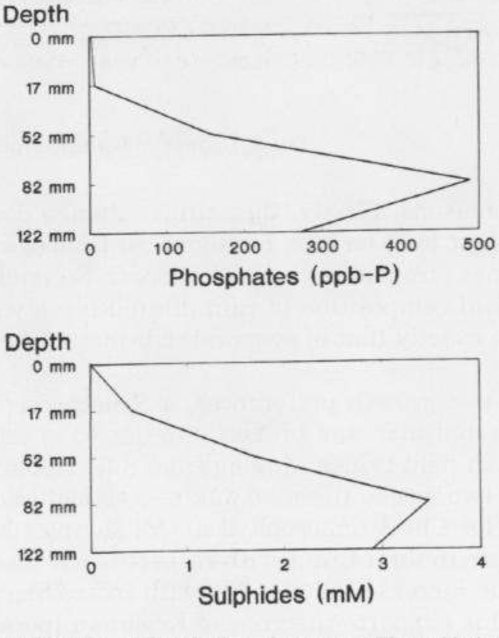

Fig. 5. Sulphide, pH and phosphorus profiles of brines (S.G. 1.130) within the benthic mat. (Note: Depth measured from top of mat layer.)

TABLE 3

Effect of mat integrity on release of manganese into the overlying brine

Mat integrity*	Mn in brine (ppm)
1 (undisturbed)	0.02
2	0.24
3	0.30
4	0.06
5	0.55
6	0.37
7 (highly fragmented)	1.73

*Mat integrity: Ranked as 1 (undisturbed) to 7 (highly fragmented).
Spearman Rank Correlation 0.893 (significant at 0.01).

bance of the algal layer, the manganese moves from the mud into the brine, either as the sulphide or the free ion. The low pH in the mat (due to the sulphate reducing bacteria) means that little carbonate is available to react with the manganese. Photosynthesis in the surface layers of the mat would maintain an aerobic environment at the brine/mat interface. In the absence of such activity there would be a greater release of manganese from the sediment into the overlying brine.

Phosphate and the benthic mat

Figure 5 shows that the concentration of reactive phosphate in the mud and mat brine is 40–50 times higher than the concentration in the pond brine (5–15 ppb PO_4–P). In the pond sediment, anaerobic and sulphate reducing bacteria decompose the organic debris to produce phosphorus and nitrogen compounds. These nutrients, like manganese, would move into the brine when the mat is disturbed or when they become available for assimilation by algae and bacteria during day–night fluctuations. The mat normally partitions these nutrients off from the brine. An influx of nutrients from the sediment would extend the biological disturbance in the ponds.

Phytoplankton blooms

The phytoplankton concentrations of *Synechococcus* sp. in three sequential ponds were measured weekly at Bajool for over a year. Blooms of phytoplankton with densities as high as 20 g/m^3 were frequently recorded. Field observations suggested some relationship between the blooms in consecutive ponds. The large variation in phytoplankton densities between and within ponds makes it difficult to visualize the periodic nature of the blooms. Figure 6, which expresses the phytoplankton density as a percentage of the largest bloom measured in the study shows that the different pond biomass densities sometimes peak during the same month. Examples of this are ponds 2 and 3 in November and ponds 3 and 4 in March. This suggests a change in an external factor such as weather. When the biomass densities did not peak during the same month (e.g. pond 4 in November) or where the peaks were sequential (e.g. ponds 3 and 4 for June and July) a mechanism by which conditions that encourage blooms must be transported from pond to pond.

The transport of biomass between ponds is an obvious reason for the movement of biological disturbances through the system; that is, movement of phytoplankton between ponds increases the concen-

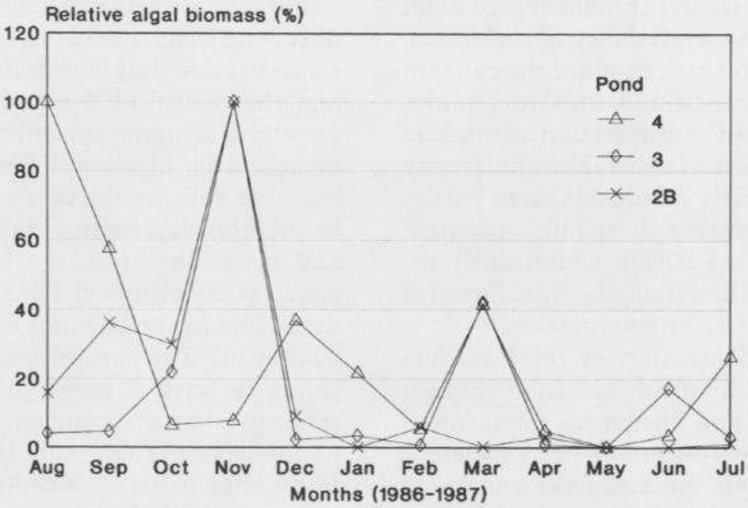

Fig. 6. Relative cyanobacteria biomass in sequential ponds. (Relative biomass calculated as percentage of maximum biomass for each pond).

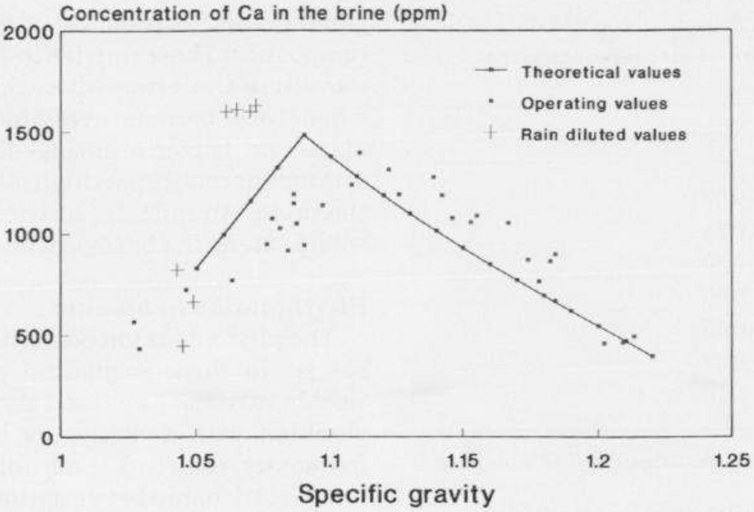

Fig. 7. Relationship between calcium and brine density (theoretical values from Bassegio, 1974.)

tration in the next pond in the series. If the algae die then the nutrients released from their decomposition become available for primary production in the new pond.

Phytoplankton, calcium and phosphate

Algal blooms are also believed to have an impact on the calcium content of the brine. Figure 7 shows the brine calcium from different ponds as a function of S.G. Our field results show that significant variations from the expected values (Baseggio, 1974) do occur. One source of variation is the precipitation of aragonite (calcium carbonate). Brine at an S.G. of 1.06 is saturated with respect to aragonite (Baseggio, 1974). The availability of carbonate to effect saturation depends on the pH of the brine, which in turn is affected by the biological activity in the ponds. That is, an increase in pH following an algal bloom would increase the availability of carbonate, precipitate aragonite, and hence reduce the calcium concentration. Phosphate would also precipitate similarly although it could be argued that adsorption to newly formed aragonite is more relevant. In any case the biological activity would stabilize in the disturbed pond as the reactive phosphate concentration is reduced. The brine with a significantly reduced calcium concentration would be transferred to the next pond.

The maximum concentration of total soluble phosphate in brine can be estimated from calcium phosphate equilibrium and phosphate dissociation constants (Fig. 8). These estimates are consistent with measured values in the sediment and brine (Fig. 5) and are used here to demonstrate the effect of the daily light–dark cycle on brine chemistry and on biological activity in the upper layers of the benthic mat. Figure 9 shows that relative to the daytime the brine pH falls and sulphide concentration increases as photosynthesis stops during the dark period. These changes reflect the anaerobic activity in the mud and evidence the chemical exchange between the mud and overlying brine. It follows then that this exchange is a continuous process and includes the nutrients from organic degradation and trace metals such as manganese. It has already been shown that there is an exchange of ions between the sediment and brine when there is a break in the mat (Table 3). Hence when the calcium concentration falls, more phosphate will become available for phytoplankton (Fig. 8). The turbid brine from high phytoplankton concentrations will shade the algal mat thereby encouraging anaerobic activity further into the brine column.

Movement of the calcium depleted brine to the next pond would lead to an increase in the phosphate concentration (but depending on the pH of the brine and the biological demand for carbon). Increased growth of *Synechococcus* sp. in these ponds due to biological disturbances in earlier ponds has the same effect as salinity fluctuations described earlier, ie. the benthic mat fragments and releases phosphates and manganese into the brine. The lack of light penetration means that there is less oxygen produced and the brine tends to be more anaerobic with a lower pH. The natural tendency of the more saline ponds to have a lower pH and dissolved oxygen concentration accentuates the problem (Coleman, unpublished). The result is high viscosity maiden brine with a high concentration of reduced manganese. Salt made from such brine is of a very poor quality with a high magnesium concentration and a high proportion of drift salt.

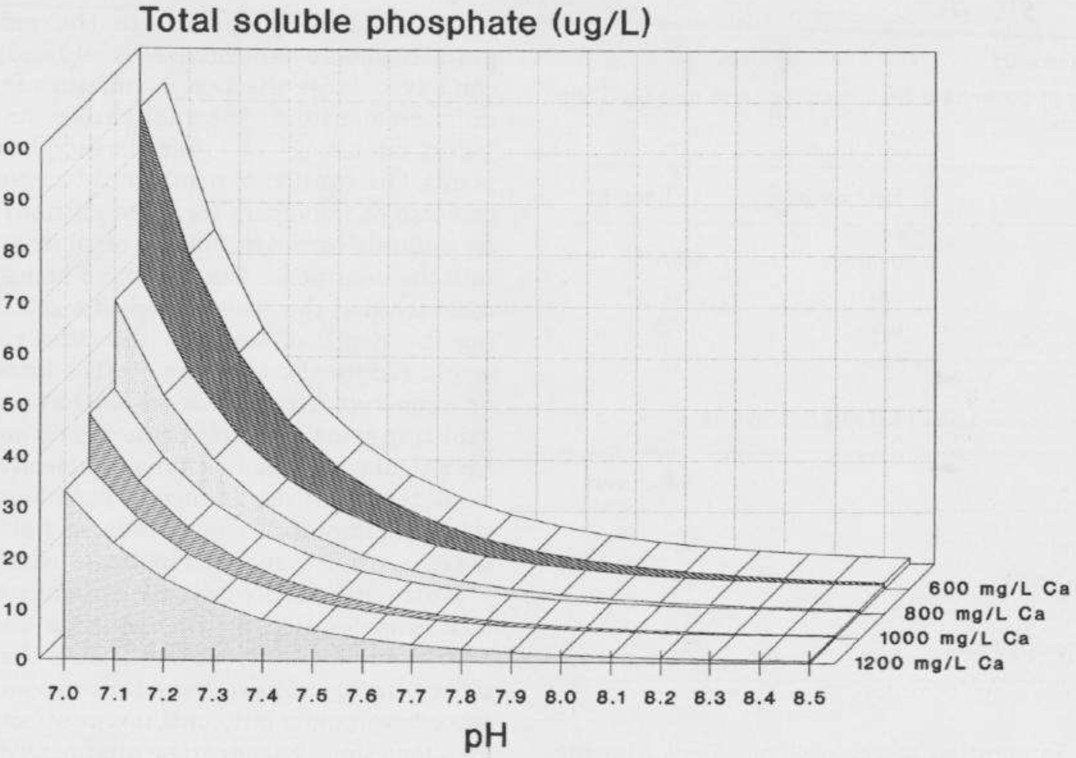

Fig. 8. Maximum theoretical phosphate concentration versus calcium and brine pH. (Calculated from dissociation and apatite solubility products.)

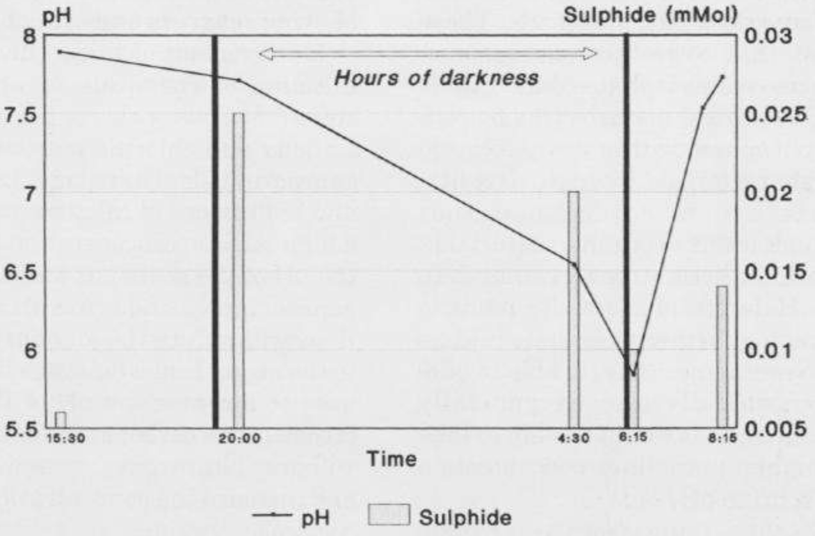

Fig. 9. Diurnal changes in pH and sulfide concentration. (Pond S.G. 1.18.)

Phosphate selection of *synechococcus* sp.

Experiments with the *Synechococcus* sp. dominated mat have shown that the cyanobacterial mucilage has high concentrations of acid soluble phosphate associated with it (Table 4). In the laboratory, portioned samples of an algal mat were washed in water or dilute HCl. The reactive phosphate concentration from the acid wash was much higher than the water wash. (Care was taken to avoid release of phosphate from ruptured cells by gentle washing for five seconds.) Also shown in Table 4 are the results from a second experiment where viscous field brines were treated, dosed with phosphate and then analysed for reactive phosphate. The phosphate that

TABLE 4

Phosphate recovery

A. Recovery of phosphate from cyanobacteria mat (μg P/gm cyanobacteria)

Sample	H_2O wash	HCl wash
1	0.00	33.0
2	0.00	16.0
3	0.36	10.5

B. Recovery of spiked phosphate from field brines

Treatment	% Recovery
Control brine	50
Reduced Ca brine	65
Filtered brine	94
Reduced viscosity brine	92

remained in solution after post treatment filtering (0.45 μm) was defined as reactive phosphate. The treatments which gave nearly 100% recovery of reactive phosphate were pre-filtering (0.45 μm) and where the suspended mucilage (measured as viscosity) was reduced before adding the phosphate. These observations suggest that *Synechococcus* sp. may take advantage of increased phosphates during diurnal fluctuations and biological disturbances by concentrating reactive phosphate within the associated mucilage. In fields characterized by high viscosity, halophilic bacteria are more common that *Dunaliella* sp. The high levels of organic material in the brine would encourage heterotrophic rather than autotrophic growth. Heterotrophic activity tends to lower the pH encouraging further phosphate release from the sediment. *Synechococcus* sp. is able to photosynthesize anoxygenically and oxygenically (Padan and Cohen, 1982), so it would be able to take advantage of the higher phosphate concentration during periods of low brine pH.

The environment that favours *Synechococcus* sp. growth would also favour increased manganese concentration because low levels of dissolved oxygen decrease the oxidation rate of manganese in the brine.

MANAGEMENT IMPLICATIONS

Environmental disturbances have important implications for the quality and quantity of salt produced at a solar field.

In general, variations to the pond salinity gradient should be minimized. Field and pond design can have a large effect on the mixing of the brines of different densities. Internal banks can reduce the "short circuiting" of lower density brine between ponds. Orientation of ponds to the prevailing winds can also be important for more efficient mixing and for minimizing the transfer of algal mats and blooms into the next pond. Clearly, pond biology should be considered at the design stage of a salt field. Reducing the depth of brine in the final concentrators would reduce the tendency for the brine to become anaerobic at night. This would have the effect of oxidizing some of the manganese and encouraging a firm algal mat, which is a major objective no matter what the algal dominance. Magnesium oxide and selected aluminium compounds may also be used to lower nutrient levels and increase oxidation.

Nutrients, particularly phosphate, are an important consideration in the operation of a solar salt field. A sudden nutrient injection in the system can induce biological responses that not only influence successive ponds but continue to affect the system for a long time. These can be minimized by removing the source of nutrient injection (run-off) or damping the system by selective harvesting of biomass. Examples of the latter would be the use of aquaculture systems to prevent plankton increases and removal of dying seagrass and cyanobacteria mats.

Management of brine chemistry either by direct injection of chemicals or appropriate selection of stone for banks is also important. For example, caustic soda and chlorine may be used to oxidize manganese and algal mucilage. Limes such as the oxides and hydroxides of calcium may be used to maintain a high calcium concentration in the brine, to increase the pH of the sediment and assist oxidation of manganese. Increasing brine pH and calcium concentrations will reduce the amount of phosphate available to the algae. Limestone as a banking material can be used to increase the pH of the sediment whilst increasing the carbonate alkalinity of the brine. This will precipitate manganese as manganous carbonate and increase the concentration of free CO_2 in brines. *Synechococcus* sp., as a bicarbonate user, has an ecological advantage in low free CO_2 brines (Krishnan, pers. commun., 1990). There is very little aragonite available for phosphate absorption in the *Synechococcus* sp. dominated ponds because as gypsum precipitates, the calcium is no longer saturated with respect to aragonite. Addition of limestone to these ponds would have the advantage of absorbing free phosphate in the brine.

At Bajool, limestone and lime have been shown to provide the most cost effective method of controlling the quality of brine for salt production. Moderate additions of Ca into the concentrators had little effect on the Ca purity of the salt because dissolved sulphate ultimately controls gypsum precipitation in the crystallisers.

There seems to be a connection between the acidity of the original sediment that the field was built on and the magnitude of the salt quality problem. The Queensland fields are all built on mangrove mud (pH 5.5). The salt grown on this substrate is opaque and high in manganese and magnesium. Cheetham fields built on more alkaline soils in southern Australia have fewer problems with manganese contamination and *Synechococcus* sp. infestations because alkaline soils inhibit the release of reduced manganese and nutrients into the brine.

CONCLUSIONS

The laboratory and field results described in this paper have been useful in developing management strategies for optimizing salt quality and output from Cheetham's Queensland fields. The basic philosophy of field management has changed from one of treatment of evaporation ponds as discrete entities to one of management of the system as a continuum from sea water intake to crystalliser brine. Disruptions to one pond are now recognized as having the capability of cascading through to subsequent ponds. The overall guiding strategy is to operate with a stable ecosystem and with low nutrient inputs.

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