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Oxygen Production and Use in Benthic Mats of Solar Salt Ponds

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ABSTRACT

The benthic mat in the ponds of solar salt producers is important because as a beneficial effect, the mat reduces loss of brine from the field, but it unfortunately also supports species which can have a serious detrimental effect on the halite crystallisation process. Anaerobic and aerobic activity of the mat which is thought to be a significant factor in the management of the salt field is not quantified by traditional monitoring methods. A method of measuring the generation of oxygen from benthic algal mats, tested in the north west of Western Australia at three solar salt fields has been developed to estimate the benthic primary production in solar salt fields. Net oxygen production peaks at approximately 1 g m^{-2} over a 24 hour period for saltfields in the north-west of Western Australia. There was a significant linear relationship between production and salinity with production decreasing with increasing salinity. Maximum production was 100 mmol O_2 m^{-2} day^{-1} and the minimum was -11 mmol O_2 m^{-2} day^{-1}. The average oxygen production in ponds with a normal salinity within the range of 115-250 g l^{-1} was 13 mmol O_2 m^{-2} day^{-1}. The relationship between dissolved oxygen demand at night versus salinity was not significant.

INTRODUCTION

A solar salt field in Australia is typically made up of a series of large ponded areas up to 5000 ha in size, and totalling between nine and twelve thousand hectares. Seawater is pumped into the initial pond and the brine evaporates as it flows or is pumped into successive ponds. The process is carefully controlled so that the pond salinities are kept as constant as possible given meteorological conditions. Salinity at a particular point in a pond is normally controlled to within ± 5 g l^{-1}. As a result, the series of ponds is a constant flow system with ponds maintaining a stable hypersaline environment. At roughly five times sea water, gypsum starts to precipitate. At about ten times seawater concentration, sodium chloride (halite) begins to precipitate and the brine is then passed to specialized ponds that have been levelled and engineered to facilitate mechanical harvesting of the salt. The former ponds are normally called concentrators or condensers and the latter crystallizers. At times this stable system is impacted by episodic events such as cyclones and monsoon rainfall which may reduce the salinity by 100 g l^{-1}.

Biological features in the series of ponds change as water is evaporated from the brine. Different plants and animals predominate according to salinity, temperature and nutritional variation (Figure 1). The most important biological factor in a salt field is the potential for the cyanobacterium *Synechococcus* (*Aphanothece*) to produce mucilage in large enough quantities to degrade the salt. It has been noted that the mucilage is produced at times of environmental disturbance. This mucilage changes the viscosity of the brine interfering with the formation of salt crystals, resulting in fragile crystals and also causing fine salt crystals to form on the surface of the brine (Coleman & White 1993; Roux 1996). These fine and fragile crystals are difficult and costly to harvest, and retain impurities in the final product. Biological attributes also benefit the production of salt by removing soluble metals, nutrients and total suspended solids from the brine and depositing them into the sediments. A saltfield with the biology in equilibrium will produce good-sized solid crystals with low impurities, exploiting evaporation to its greatest potential.

Benthic algae are very important in the stabilization of the pond sediments and in reducing seepage; however they also provide the greatest biomass of the detrimental cyanobacterium *Synechococcus* which is normally found in large numbers in the immediate pre- and post-gypsum ponds. The interaction between the benthic algal mat and overlying brine is difficult to study *in situ*, and more particularly to monitor on a regular repeatable basis. Salt field technologists have traditionally focused on the planktonic biology as it has been difficult to monitor the large biological biomass within the mat. One method of understanding the mat activity is to study the use and production of oxygen as a measure of its productivity. During sunlight hours the cyanobacteria use sunlight as an energy source to produce carbohydrates by which CO_2 is consumed and O_2 is produced. These same organisms use O_2 in their metabolism but the production in the day time far exceeds their use of O_2 (Figure 2).

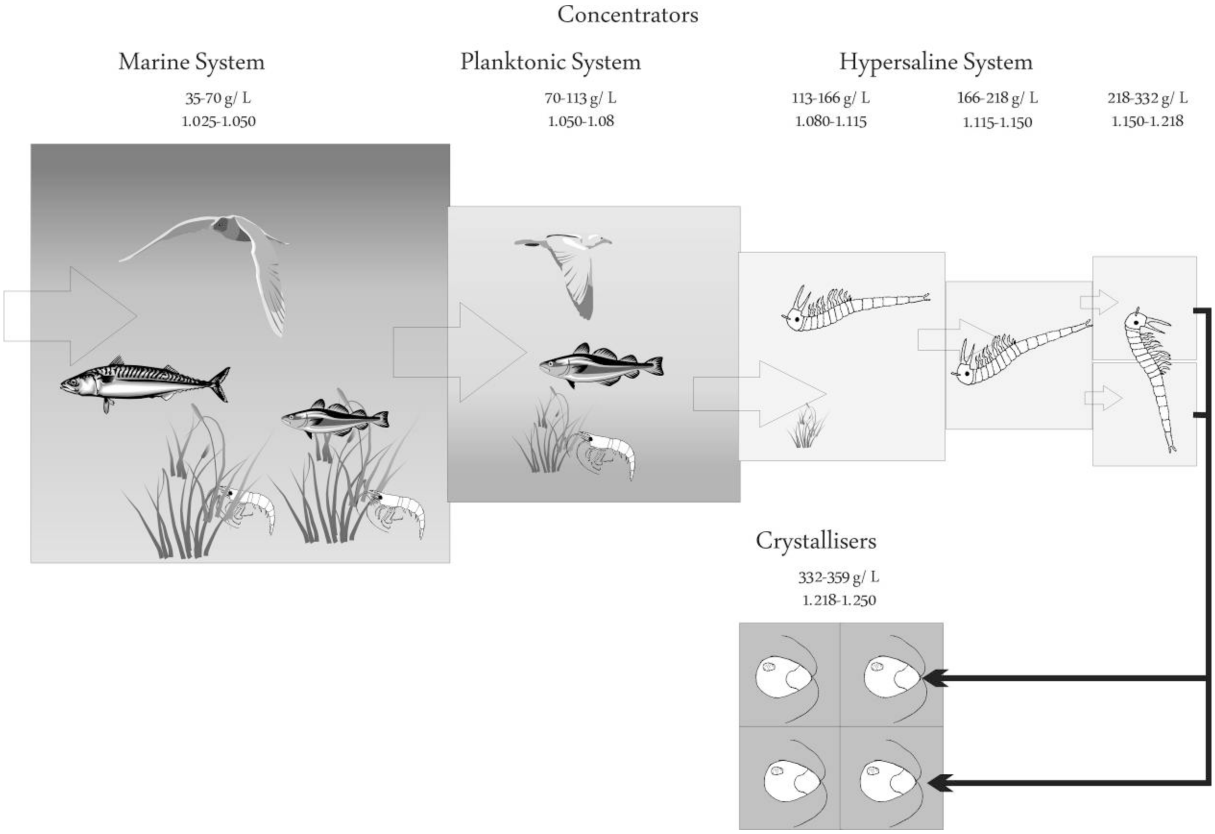

Figure 1–Biology of a salt field.

A matrix of possible changes has been compiled and presented in Table 1. These are not meant to be definitive and all dissolved oxygen (DO_2) production and use scenarios must be interpreted within the context of local events. It does give an understanding of what might be expected if all other factors were constant. The aim of the current work is to understand what changes can be measured in the field, and if those changes are real, and what conditions are likely to impact on the production of salt.

METHODS

Introduction

A technique was devised to study dissolved oxygen changes in situ. In situ studies provide more accurate estimates of changes in the field for management of a commercial field. For this purpose a technique was devised to isolate algal mats in the ponds of commercial saltfields. This technique is similar to that used by Segal et al. (2006) and others. The equipment used was a Perspex dome pressed into the benthic mat, with automatic physical chemistry probes measuring conductivity, DO_2, temperature, pH and light intensity in the brine above the benthic mat enclosed by the dome. This technique isolates a portion of benthic mat and its composite biology under the mat's 'normal' conditions of light, temperature and salinity.

The DO_2 method has the additional advantage of estimating carbon sequestration in the ponds which is becoming of great interest as the concept of 'Carbon Credits' is introduced into Australia. In all but exceptional circumstances carbon would be sequestered on a mol by mol ratio with O_2 produced.

The dome technique (as with most sampling) is limited because:

1. Small areas are used to extrapolate over the entire pond.
2. It assumes the mat to be homogenous over the entire pond and sampling locations.
3. Isolation of an area is critical to monitoring changes but that in itself introduces changes.

LOCATION

The surveys were completed at three tropical solar salt fields in north-west Australia (Figure 3). The salt fields have an operational concentrator area of approximately 100 km^2. The sampling sites were located in ponds which were normally within the operational salinity range of 115 to 215 g l^{-1}. Rainfall had sometimes temporarily reduced the salinity at the time of survey. Port Hedland and Onslow have three ponds within the above range while Dampier has four such ponds.

Table 1–Matrix of changes to varying oxygen production scenarios.

	O_2 production increased	O_2 production static	O_2 production decreased
O_2 use increased	Unsure if only cyanobacteria increased but likely all biological activity greater	Anaerobic activity greater	Anaerobic activity greater with reduced cyanobacteria activity
O_2 use static	Likely that cyanobacteria biomass greater	No change	Cyanobacteria biomass reduced
O_2 use reduced	Cyanobacteria biomass greater	Reduced biological activity	Reduced biological activity generally

Dome Construction

The Perspex domes were 700 mm in diameter with an approximate rise of 200 mm to the top of the dome. Each dome had a 100 mm PVC skirt that dropped from the rim of the dome. The dome also had several ports: a large port at the apex of the dome to allow air to be removed, a large port at roughly 45° to insert the probe and two small ports lower on the dome profile for recirculating brine within the dome, by a small pump. All ports could be sealed for water tightness. The Perspex dome was then placed in a stainless steel base that protected it and enabled the dome to be fixed to the substrate with iron stakes through four channels welded to the base. The assembled dome can be seen in Figure 4. The area of the dome was 0.385 m^2, and its volume was 0.0725 m^3.

The loggers for the domes were Tyco CS304 loggers with multiple probes for temperature, pH, DO_2 and conductivity. An Odyssey PAR light meter was attached to each dome. The light meters and loggers were calibrated by Murdoch University Marine and Fresh Water Research Laboratory. Care was taken when assembling and placing the domes that the light meters and domes were not shaded by infrastructure or sediment disturbed on installation of the domes. A 12V pump was used to circulate the brine within the dome.

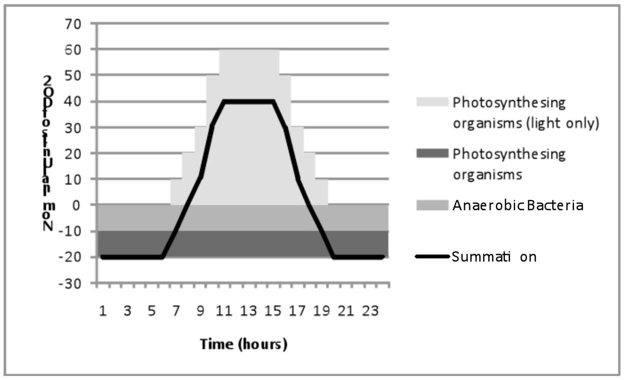

Figure 2–Hypothetical production and use of oxygen in the mat structure.

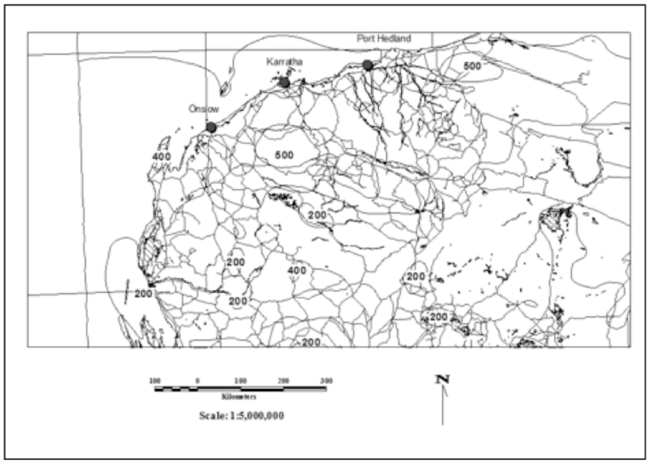

Figure 3–North-west Australia showing field locations (contours of annual rainfall mm isohyets).

ANALYSIS OF DATA COLLECTED

The procedure for the analysis of data collected from the field is as follows. The data were downloaded from the logger and analysed at the close of each trial. Percent saturation was converted to DO_2 concentration using the following equation, derived by the author in previous unpublished work:

$$DO_2 \text{ at saturation (ppm)} = 10.79 - 0.113 \times \text{Temperature (ºC)} - 0.032 \times \text{Salinity (g l}^{-1}\text{)}$$

Ambient light was calibrated and expressed as accumulative incident light (PAR). Finally daytime *in situ* DO_2 versus the ambient accumulative light relationship was calculated and the slope of the linear regression determined. The slope of the curve gave the rate of DO_2 change per unit of light, an indication of the photosynthetic activity of the algae.

The DO_2 demand of the benthos at night was expressed as change of DO_2 per unit time. There was a slight discrepancy due to plankton activity in the entrapped brine within the dome, but as the majority of the biomass is within the benthic mat in these ponds it has been ignored as trivial. Excess oxygen during the day time was collected in an air trap at the top of the dome. This was measured and compared with the calculated production/respiration rates, but was not used other than as a check. The statistical analysis was completed using Mintab 14.

Figure 4–Assembled dome and probe/logger ready for use.

RESULTS

The production of DO_2 in the daytime and its use in the dark (night) for all sites at the three locations is shown in Figure 5 and Figure 6 respectively. The net use of oxygen per day is presented in Figure 7. The results are an accumulation of surveys over three years at a frequency of twice a year for each site. The results have been filtered to remove data sets used to evaluate unusual benthic locations in the ponds such as localized exposed sulfide mud and spring holes.

The highest production of oxygen for all sites in a 24 hour period peaked at approximately 1 g of O_2 m^{-2} day^{-1}. The average was much lower at approximately 0.2 g m^{-2} day^{-1}. The maximum production was 100 mmol O_2 m^{-2} day^{-1} recorded at a salinity of 125 g l^{-1} and the minimum was -11 mmol O_2 m^{-2} day^{-1} recorded at a salinity of 68 g l^{-1} in a pond that was normally at a salinity of 115 g l^{-1}. The average production in ponds with a normal operating salinity, each at a point in the range of 115-250 g l^{-1}, was 13 mmol O_2 m^{-2} day^{-1}.

DISCUSSION

There have been a number of papers (Canfield et al. 2004; Wieland et al. 2004; Wieland & Kühl 2005) on the productivity of benthic mats in saltfields in the salinity range between 100-200 g l^{-1}. Many found that with increasing salinity benthic primary productivity decreased while respiration remained relatively constant. Levels of DO_2 production found in this study are comparable to those found by Canfield et al. (2004).

It has also been suggested (Coleman & White 1993; Canfield et al. 2004) that cyanobacteria habituated to a constant salinity within this range will increase productivity if the salinity is decreased. It is thought that most species within this range are halotolerant and not truly halophilic and organisms typically have an optimum salinity less than found in the in a salt field.

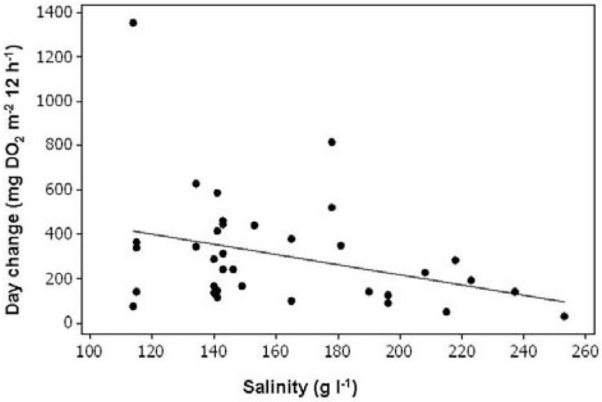

Figure 5–Dark period DO_2 flux.

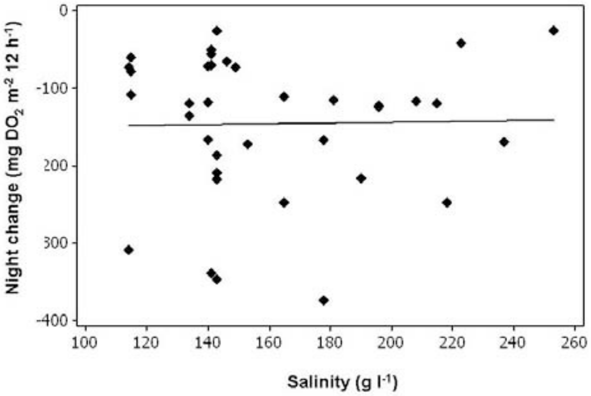

Figure 6–Light period DO_2 flux.

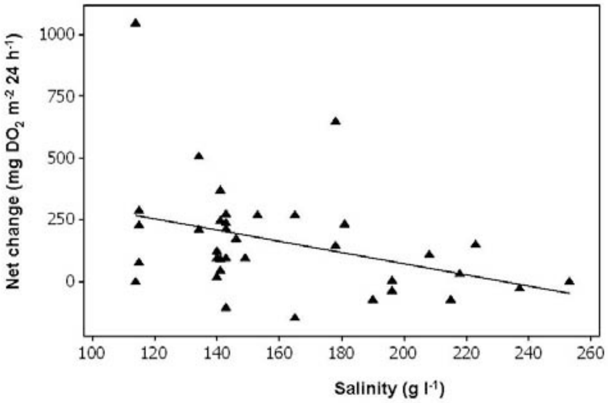

Figure 7–Net daily DO_2 flux.

Regression analysis of daytime production versus salinity showed that there was a significant linear relationship between production and salinity (P = 0.045) with production decreasing with increasing salinity (Figure 5). However the R^2 value was small (0.12), indicating that salinity is not a major factor in production. The relationship between DO_2 demand at night versus salinity as shown in Figure 6 was not significant at a probability of 0.91. Net production over a 24 hour period versus salinity analysis (Figure 7) showed that net production decreased with salinity at a significance of P = 0.026 but a relatively low R^2 of 0.14. This is consistent with the literature cited above.

The data were sorted under individual ponds normally maintained at targeted salinities. At times salinity of the brine in the pond was reduced due to large rain events. The purpose of this analysis was to determine if benthic mats that are normally maintained at a constant salinity would increase production of oxygen at times of radical salinity decrease. When the relationship between salinity and production/use was tested for individual ponds, the probability was much lower with most (five out the eight sites) having no significant relationship between oxygen production and salinity (see Table 3). This indicates that although there were significant relationships between DO_2 production and static salinity the relationship between DO_2 production and temporary reductions in salinity was much weaker.

Table 2–Probability (ANOVA) of a relationship between changing DO_2 and salinity.

Pond	Light	Dark	Net
D Pond 1A	NS	NS	NS
D Pond 1B	0.026		NS
D Pond 2	NS	NS	NS
O Pond 2	NS	NS	NS
O Pond 3	0.028	NS	0.036
P Pond 4	NS	NS	NS
P Pond 5	NS	NS	0.017
P Pond 6	0.019	NS	NS

D=Dampier; O=Onslow; P=Port Hedland; NS=not significant

This was somewhat surprising as it did not fit the observed bloom of algae in the ponds after rain. One possible explanation is that there is often a significant time lag between rain events and sampling. Ideally the mat should be sampled immediately before a rain event and immediately after an event but access to the ponds immediately after rain is restricted for safety reasons. The current program may have delays of up to three months after rain before the ponds are surveyed so the mats may have acclimatised to the new salinity regime.

Most of the sites were net DO_2 producers. Under normal circumstances the generation of one mol of O_2 would signify that one mol of C was fixed. This has important implications for the commercial fields under the new ‘carbon credit’ scenario proposed by the Australian Government as most ponds were net producers of O_2. Anecdotal evidence points to significant amounts of organic matter being deposited in the ponds over time.

In terms of biological management of salt fields the methodology is still being developed, and at this stage, still needs to demonstrate its use as a monitoring tool. The difficulty is that a biological disturbance is not a common occurrence and until one has been recorded it is difficult to know if this methodology will accurately predict such an event by the changes to the benthic activity. It is possible to state that if a biological event is heralded by a change in benthic mat activity over a period of months then this method would adequately quantify those changes. The method is adequate for quantifying the oxygen cycle of the benthic mat and a measure of carbon sequestration for the ponds.

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