Biogeochemical models of solar salterns

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Salterns can be modeled as flow-through pond systems with distinct biogeochemical attributes associated with each salinity. High N and P nutrient loads promote the development of planktonic (suspended) algae and bacteria that increase the turbidity of the ponds, shade the bottom, and inhibit the development of bottom mats in the middle concentrators. Imbalances in the N:P ratio in the brines may lead to slime production by some cyanobacteria. High biological productivity leads to high organic loads both in the sediments and as dissolved organic carbon (DOC) in the brines. Decomposition in the sediments results in the release of nutrients and DOC and may cause the development of anoxic conditions that favor the activity of sulfate-reducing bacteria. These bacteria release sulfide (which is toxic to aerobic organisms), lower the redox potential (which favors trace element reduction and dissolution), and they can cause gypsum to dissolve. DOC can chelate trace elements in concentrator and crystallizer brines, and potentially enhance their levels in salt.

1. INTRODUCTION

It is generally accepted in the solar salt industry that microorganisms and their products can affect the quantity and quality of salt that is eventually produced in the crystallizing ponds. For example, microbial mats help seal concentrator ponds. Brine shrimp graze on planktonic algae and help clarify the concentrating ponds, while the development of microorganisms producing red carotenoids is desirable in the crystallizers because they aid in solar absorption. However, during poorly defined "unbalanced growth" conditions, slime-producing cyanobacteria (blue-green algae) may "bloom" in the middle crystallizers. The slimes pass downstream and have been shown to affect salt crystallization [1, 2].

There has been no integrated biogeochemical model proposed for solar salt works that demonstrates how nutrients, biology, sediments, and brine chemistry may interact in a predictable manner. This paper brings together concepts from studies of lakes and oceans, environmental microbiology, and geochemistry to present a model that can be employed to predict saltern "behavior" and provide a framework for addressing remediation and potential problems in expansion.

2. METHODS

Dissolved ammonia and phosphate, and planktonic protein and chlorophyll *a* were measured [3, 4]. Dissolved carbohydrates were measured by the hydrazine sulfate method [5] using undiluted and diluted filtered brines and glucose standards. Brine turbidity was assayed by measuring absorbency at 400 nm in a 1-cm cell (crude turbidity) and subtracting the absorbency of clarified brine (by filtration or centrifugation) to yield net turbidity. Sediment organic carbon content was determined gravimetrically by combustion at 550°C for 2 h after drying the samples at 110°C. Sediment phosphate was determined by hydrolyzing dry sediment samples in 1 *N* HCl overnight at room temperature, and assaying the phosphate in aliquots of the hydrolysates. Redox potentials of sulfide solutions were measured with a gold-coated Pt electrode.

3. BIOGEOCHEMICAL MODELS

3.1 Nutrients

Nutrients are a major factor affecting productivity in any aquatic or terrestrial ecosystem. The major nutrients that are required, and that are often limiting, are combined nitrogen (ammonia, nitrate, nitrite, and low molecular weight organic nitrogen) and phosphorus (usually measured as reactive phosphate). When combined nitrogen is limiting, N_2-fixing microorganisms that can convert atmospheric nitrogen to ammonia are naturally selected. When dissolved phosphate is limiting, sediment phosphate is mobilized and utilized by microorganisms. Measurements of combined nitrogen and phosphate in the brines will give an indication of the nutrient status of the system. However, they do not indicate any of the dynamic processes carried out by microbes involved in regenerating nutrients.

Figure 1 is an overall model of biological productivity in solar saltern ponds. In general, the higher the concentration of nutrients, the greater the primary productivity (growth of photosynthetic organisms). However, this model also takes into the account that the ponds are shallow flow-through systems and that the sediments play a role in defining modes of growth. In the high-nutrient system (= *eutrophic* or "well nourished"), the high nutrient load allows algae and bacteria to flourish suspended in the plankton where they can freely scavenge the nutrients. Their abundance may be so great that they shade the bottom sediments and prevent the growth of microbial mats in the lower salinity ponds. In the moderate-nutrient system (= *mesotrophic* or "intermediate nourished"), plankton development is less abundant and microbial mats usually form over the soft sediments. In the low-nutrient system (= *oligotrophic* or "little nourished"), plankton development is negligible, but sometimes microbial mats flourish.

Microbial mats dominated by cyanobacteria are often present on the concentrator floors at salinities of ca. 5% to gypsum saturation. Feeding and sediment disruption by fish and invertebrates prevent cyanobacterial mats at lower salinities. Microbial mats depend upon nutrients regenerated by decomposition in the soft sediments immediately

Figure 1. Development of planktonic and sediment communities in saltern ecosystems.

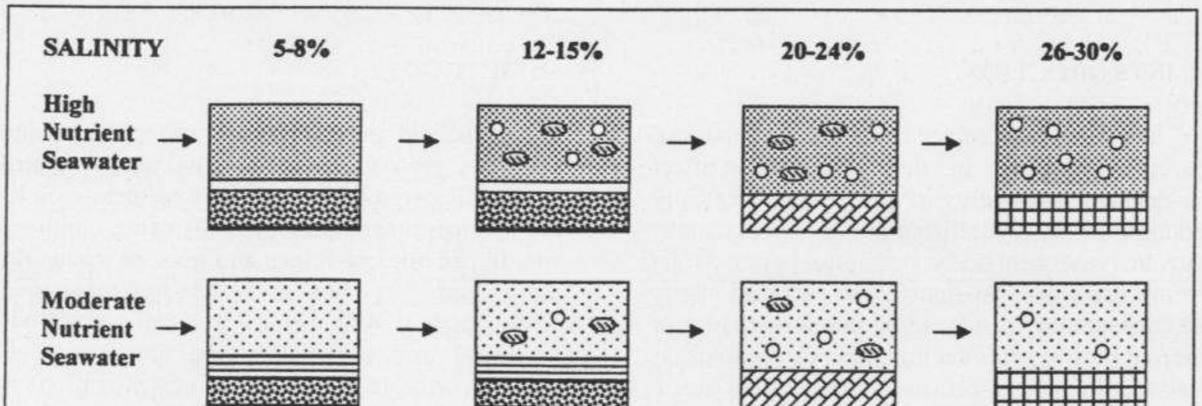

Table 1
Typical concentration ranges of biological factors in oligotrophic and eutrophic saltern ponds

	OLIGOTROPHIC			EUTROPHIC		
	Pre-gypsum ponds	Gypsum ponds	Crystallizer ponds	Pre-gypsum ponds	Gypsum ponds	Crystallizer ponds
Salinity, °Bé	3-15	15-25	26-30	3-15	15-25	26-30
Ammonia, µM	0-7	0-7	0-7	1-50	1-50	5-50
Phosphate, µM	0	0	0-2	0.3-20	1-10	2-60
Carbohydrates, mg/L	<10	10-20	10-40	0-20	25-60	≥100
Turbidity, O.D. 400 nm	≤0.050	≤0.020	≤0.030	0.010- >0.400	0.140- 0.250	0.200- 0.400
Particulate protein, mg/L	<0.4	<0.4	<0.4	<1-7	4-15	20-35
Chlorophyll *a*, mg/L	0-30	0	0	2-100	2-70	15-90
Sediment P, µg/g	≤500	---	---	150->1000	---	---
Sediment % organic C	3-5% no mat 10-15% mat	---	---	2-16%	---	---

From B. Javor (unpublished data) and references [2-4]. Net turbidity measurements exclude intake brines.

below the mats. Hence, even if dissolved N and P nutrients appear to be low in the overlying brines, they may be in sufficient concentrations near the sediment-water interface to sustain the microbial mats. Under very oligotrophic conditions, microbial mats are poorly developed or absent.

Once a stable gypsum crust has formed in the pickle ponds, microbial mats cannot thrive because there can be no regeneration of nutrients from subsurface sediments. From this point downstream to the crystallizers, N and P nutrients are concentrated by evaporation and recycled by microbial activity solely in the brine.

The model in Figure 1 also shows that brine shrimp can only thrive where there are sufficient algal and cyanobacterial cells in the plankton. The common unicellular brine algae, *Dunaliella viridis* and *D. salina*, are only present in mesotrophic and eutrophic salterns. Crystallizer coloration in more oligotrophic systems is due to halobacteria that obtain their carbon nutrients from the accumulation of dissolved organic carbon (DOC) released by organisms upstream. Halophilic bacteria also thrive in eutrophic crystallizers.

Table 1 presents typical ranges of concentrations of dissolved nutrients in oligotrophic and eutrophic salterns. Dissolved carbohydrates (which are relatively easy to measure) and estimates of total standing crop in the plankton (turbidity, cell protein, and chlorophyll *a*) are also indicated. These values may change throughout the year, especially in the mid-latitudes where pronounced summer and winter conditions promote nutrient utilization and regeneration, respectively. The table also indicates typical concentrations of organic carbon and phosphate in sediments from these two different systems. This suite of measurements provides a picture of the "health" of a saltern that may be of predictive value for management.

3.2. Balanced growth and slime production

Most aquatic microorganisms have a cellular C:N:P ratio of 106:16:1, called the Redfield ratio [6]. When concentrations of N and P are in a ratio of 16:1, and there are sufficient carbon sources and trace elements, organisms will demonstrate "balanced" growth. When N or P is limiting, "unbalanced" growth occurs in which an organism shuttles cell carbon to alternate products.

Aphanothece halophytica (called *Coccochloris elabens* by some researchers) is a good model for showing balanced and unbalanced growth. This cyanobacterium is usually found in the middle density concentrators both in the plankton (eutrophic ponds) and in microbial mats (meso- and oligotrophic ponds). Under certain conditions that have not been clearly defined (but likely involve a suboptimal N:P ratio in the brines), it can form large clumps of slime that lift from the pond floors and flow into downstream ponds. The slime is largely composed of complex carbohydrates.

During daylight, cyanobacteria cannot "turn off" photosynthesis. When there is insufficient N (e.g.,

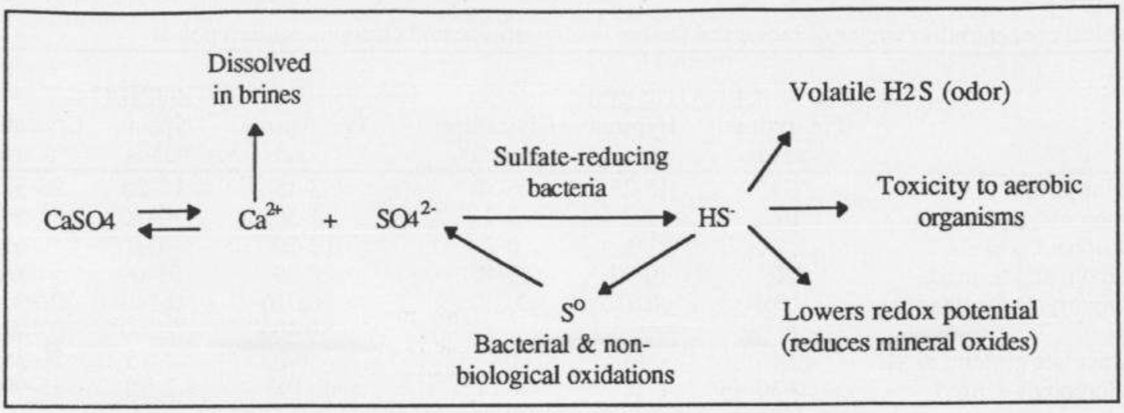

Figure 2. Effect of sulfate-reducing bacteria in organic-rich gypsum ponds, 15°-18° Bé.

when the N:P ratio falls below 6:1), the cells must excrete much of the photosynthetically fixed carbon because they cannot use it for growth. For example, early in the summer *A. halophytica* may experience balanced growth, but later on one nutrient may become limiting and cause the cells to secrete slime. Under low nutrient conditions, there are few cells producing small amounts of slime. Under eutrophic conditions, the slime formation may become a nuisance for the saltern.

3.3. Role of sulfate-reducing bacteria in brine chemistry

Aerobic conditions prevail under oligotrophic conditions and low organic loads in aquatic sediments. Under more eutrophic conditions and higher organic loads, O_2-respiring organisms deplete the O_2 levels faster than photosynthetic organisms and wind mixing can restore aerobic conditions. Oxygen depletion in brines and associated sediments can be especially important during summer months when biological productivity is high and during the nighttime when O_2 is not replenished by photosynthesis.

Under anaerobic conditions, sulfate-reducing bacteria are dominant agents of organic decomposition, especially in the top cm of the sediments [7]. The major effect of their metabolism is the reduction of sulfate (SO_4^{2-}) to sulfide (H_2S gas and HS^- ions at pH 7-8). However, there are a number of other environmental effects in saltern ponds that should be considered.

At salinities of ca. 15°-18° Bé, where gypsum normally precipitates over the soft sediments, sulfate depletion by bacterial activity can be so intense that it drives the chemical equilibrium towards dissolving gypsum. Figure 2 shows the overall reactions and some of the associated effects of intensive sulfate reduction.

The effects of sulfate reduction can be easily visualized in sediment cores. In aerobic, low-organic, brown or grey sediments, relatively large gypsum grains can be found in 15°-18° Bé density ponds that typically show a transition zone between soft sediments and a firm gypsum crust. In eutrophic ponds, black slimy muds may have few small gypsum grains or none at all at these same brine densities. Where moderate levels of organic matter are found, there is a gradation of smaller gypsum grains at the surface to larger grains below. A gypsum crust may be totally absent near the surface on the leeward side of such ponds where rafts of organic matter accumulate.

High organic loads in the sediments and the activity of sulfate-reducing bacteria can potentially cause the following interrelated phenomena and problems in saltern ponds:

• Increase in Ca^{2+} content of brines by gypsum dissolution.

• Mortality to aerobic plants, algae, and animals. Anaerobic conditions and toxic sulfide concentrations can cause algal mats to die, lift from the bottom, and either raft on the surface (which retards brine evaporation) or drift to the leeward edges of the ponds.

• Lower redox potential in sediments, which reduces some mineral oxides and enhances their solubility [8].

• Odor problems.

3.4. Do microbial activities affect minor cations in saltern crystallizers?

The activities of sulfate-reducing bacteria in sediments promotes the solution of some minerals in marine sediments. These processes appear to have played a signficant role in the co-precipitation of certain secondary minerals in ancient bedded salts [9]. DOC in the brines may potentially enhance this process. These phenomena have *not* been documented in the published literature for solar saltern systems in which the sources of sulfide and much of the DOC are separated in space and time from the crystallizing ponds. This aspect of the biogeochemical model remains speculative for saltern systems. The general model that shows how concentrations of minor cations may be increased by microbial processes in brines and how these cations can potentially enter salt crystals is shown in Figure 3.

The sulfide found in sediments can lower the redox potential of the porewaters, which should promote the dissolution of some mineral oxides and trace elements trapped in organic particles. A 50 μM sulfide solution in pH 8 buffered seawater has a redox potential of –89 mV, and a 500 μM sulfide solution lowers the Eh to –159 mV (B. Javor, unpubl. data). Organic decomposition in sediments also results in the accumulation of DOC. Various classes of DOC chelate trace cations and prevent their precipitation. Organic chelation enhances the stability of low concentrations of certain trace cations, and chelation is believed to play a significant role in raising the concentrations of some trace elements in natural waters [8]. This phenomenon is known as a factor affecting Ca^{2+} behavior and supersaturation with respect to $CaCO_3$ in seawater [2]. It was suggested as a mechanism that promotes the precipitation of celestite ($SrSO_4$) in the halite phase rather than the gypsum phase in solar saltern ponds [3].

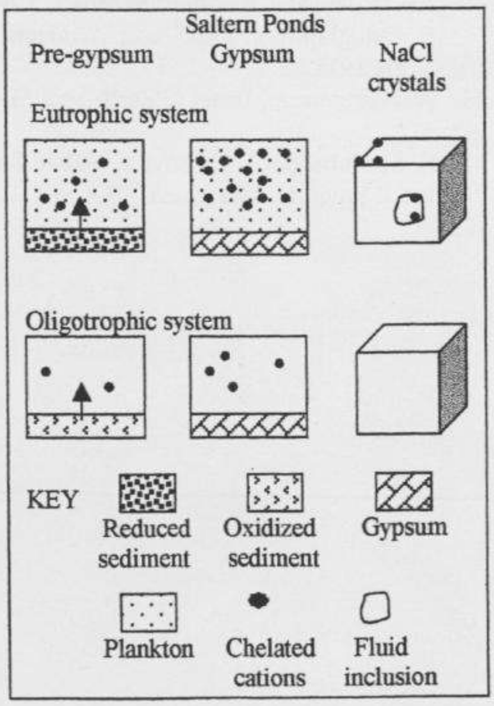

Figure 3. Model of the potential effects of sulfide and DOC on trace cation concentrations in salt.

Table 2 shows the concentrations of some trace divalent cations in average seawater and their theoretical values in 20X concentrated seawater. A major challenge for future work will be the development of analytical techniques for measuring trace elements which overcome salt interference that may result in anomalously high values. For example, the original estimates of the concentrations of some dissolved trace cations in Dead Sea brines gave values of hundreds to thousands of micrograms per liter [11], while revised methods yielded typical values of a only a few micrograms per liter or no detection at all of those trace elements [12].

These data can be incorporated into a saltern model for trace cation accumulation (Figure 3), but empirical data for saltern brines are needed to prove that biogeochemical processes may increase the concentrations of dissolved trace cations above those predicted by simple evaporation (Table 2).

Table 2. Concentrations of some trace cations in seawater [8, 10].

	Average seawater composition	Theoretical 20X concentrated seawater
Salinity, %	3.5	NaCl-sat'd
DOC, mg/L	0.5-1.2	10-24
Fe, μg/L	2	40
Mn, μg/L	0.2	4
Cu, μg/L	0.5	10
Co, μg/L	0.05	1
Zn, μg/L	4.9	98
Ni, μg/L	1.7	34

This model shows that in eutrophic salterns, decomposition in the highly organic upstream sediments causes the release of relatively high concentrations of reduced trace elements. These cations are likely chelated by both the organic matter released from the sediment and DOC produced by plankton. Once these brines flow downstream to the gypsum ponds and crystallizers, evaporation increases the concentration of chelated cations in solution. The trace cations may co-precipitate with NaCl crystals through ionic interactions with growing crystal faces or by incorporation into brine inclusions. In oligotrophic salterns with less DOC and less sulfate reduction, there should be fewer trace elements in solution and less tendency to form mushy halite with abundant brine inclusions.

4. CONCLUSIONS

The overall biogeochemical model for salt production in solar salterns is a complex web of interactions that involve such diverse factors as: 1) inorganic nutrient concentrations that enter the system, 2) dissolved and particulate organic matter produced in the saltern, 3) microbial processes in sediments of the pre-gypsum concentrators, and 4) climatic conditions that influence biological activity. These factors are usually not considered when appropriate sites for saltern construction and expansion are evaluated. In order to truly understand why each solar saltern has its own unique profile of attributes and to propose corrective measures for production problems, the biological, geological, and chemical factors within the system that make it unique should be evaluated.

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