EFFECT OF SALT PRECIPITATION ON HISTORICAL AND PROJECTED SALINITIES OF THE SALTON SEA: SUMMARY COMMENTS FROM WORKSHOP AT THE UNIVERSITY OF CALIFORNIA, RIVERSIDE. JANUARY 30-31, 2001.

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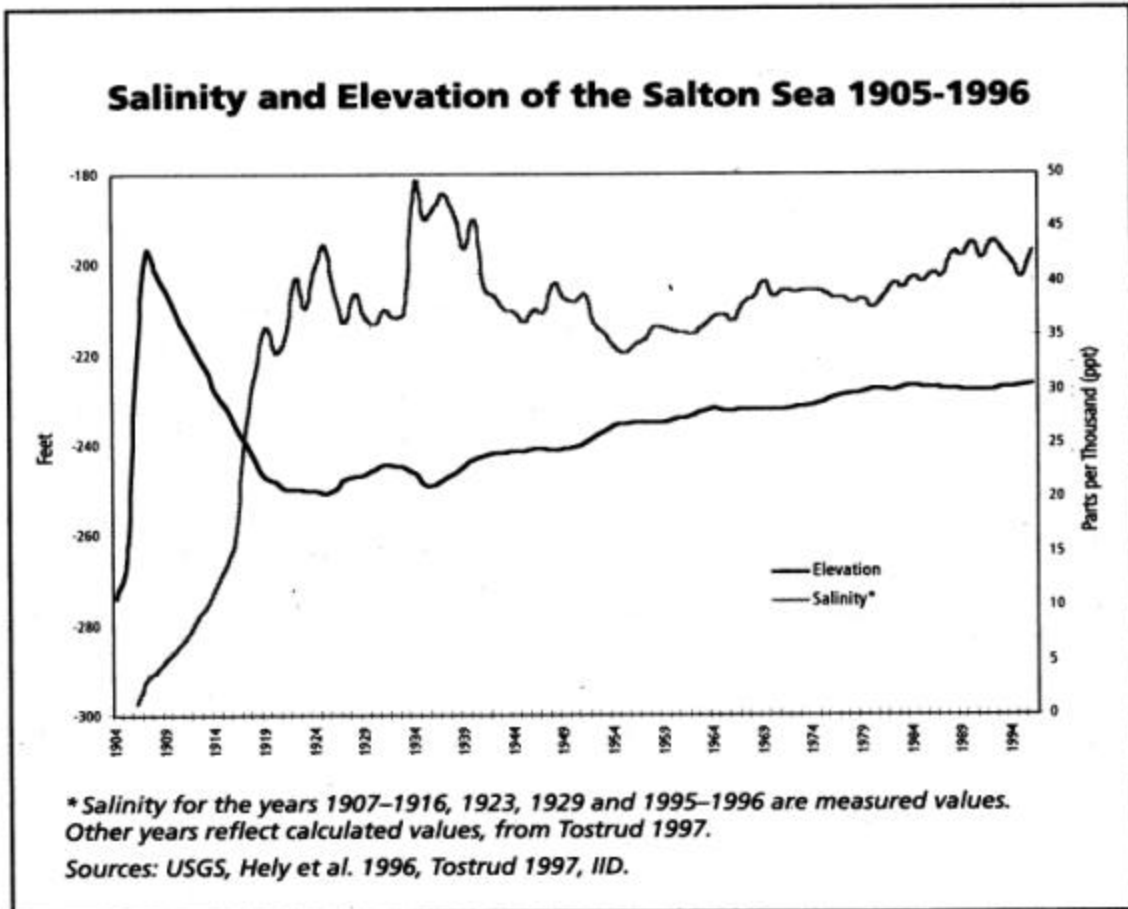
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Figure from Cohen et al., 1999.

Introduction

The Salton Sea Science Office convened a workshop at the University of California, Riverside on January 30-31, 2001, for the purpose of resolving the basic question, "Are dissolved solids precipitating and/or being biologically reduced in the Salton Sea?" The issue of salt precipitation has important economic and environmental implications for the Salton Sea Restoration Project. If salts are precipitating, the lake's rate of increase in salinity will be less rapid and that would provide more time to arrest the increase before salinity levels become toxic to fish. Furthermore, if less salt needs to be removed, the space that must be set aside for restoration (evaporation and disposal of salts) and the engineering cost of remediation are reduced. The issue was addressed through formal presentations from several speakers and by dialogue between the speakers, public, and panel members on the first day of the workshop. The 9 panel members listed at the top of this document then met privately for a day to deliberate on the topic and to produce this "white paper" that contains their conclusions and recommendations. The paper contains 5 sections:

1) a brief discussion of the local hydrologic and geochemical cycles,

2) temporal trends in salinity of the Salton Sea,

3) calculations for the amount of salt precipitating in the Salton Sea,

4) recommendations on future data needs, and

5) the panel's response to questions.

Hydrology and the Salt Cycle

When catastrophic flooding of the Colorado River discharged to the Salton Sink in 1905-07, the fresh water rapidly dissolved salts that had accumulated on the dry lakebed and led quickly to the formation of a brackish lake. With the continuing discharge of wastewater from agriculture and municipal wastewater from towns in the Salton Basin, salts have continued to accumulate in the terminal lake, which is now about 20% more saline than the ocean. Soluble salts, like sodium chloride, continue to accumulate in the water column; while less soluble salts, like calcite and gypsum, will accumulate in the water column until their concentrations reach saturation, after which the excess precipitates and accumulates within the bottom sediment. The extent to which the precipitation of these minerals is taking place will affect the rate at which the salinity of the Salton Sea is increasing.   Just as the first few years of flooding dissolved accumulated salts from the dry lakebed, it seems likely that irrigation initially must have leached some salts from the newly farmed soils. It takes an average of 5 years for irrigation water applied to the area's fields to percolate through the soil until it is discharged by subsurface drains (Michel and Schroeder, 1994). Therefore, over the years the soils have been leached multiple times by the application of about 6 ft of irrigation water annually. As a result, the local geochemical cycle is now sufficiently close to steady state that the salt load carried by the Colorado River diverted at the Imperial Dam yields a fairly accurate estimate for the annual load of salt carried in rivers and surface drains that discharge to the Salton Sea. Average salt concentrations for the waters in the basin are presented in Table 1.

Table 1 shows that although the dissolved salt concentration in subsurface drainwater from the Imperial Valley is increased through evapotranspiration by about an order of magnitude compared to irrigation water, the relative proportion of the most abundant anions, chloride and sulfate, remains virtually unchanged during the waters transit through the soil. Although sulfate reduction occurs at depth in Imperial Valley soils (Schroeder and others, 1991), and even in some shallow depths as evidenced by the presence of H_2S in a few drainwater sumps close to the Salton Sea, the effect on drainwater composition derived from the entire valley is minimal. Based on the cation composition of the drainwater and irrigation water, it appears that there may be a small increase in Na, and a loss of Ca, due to cation exchange processes and calcite precipitation in the soil.

Insofar as Colorado River water is itself oversaturated with respect to calcite (Figure 1), precipitation of calcite ($CaCO_3$) within the soil during the high evaporative concentration that occurs in this arid environment might be anticipated, and is illustrated by the following reaction.

$$Ca^{++} + 2HCO_3^- \rightarrow CaCO_3 + CO_2 + H_2O \qquad \text{Eq. 1}$$
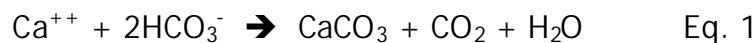
It is possible to estimate the amount of calcite that that is currently precipitating in the soil using the Ca, Cl, and alkalinity (HCO_3) concentrations in the irrigation water and drainwater. Based on these ion ratios, we calculate that approximately two-thirds of the dissolved Ca^{2+} and HCO_3^- precipitate within the soil during the lengthy travel time from soil surface to drain. Although not all of the applied water infiltrates the soil (possibly as much as 30% goes to tailwater runoff), the precipitation of calcite within

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the soil constitutes the first major loss of dissolved ions from the water. Based on the data in Table 1, we estimate that approximately 400,000 tons of $CaCO_3$ precipitate in the soils every year, or about 10% of the total salt load to the basin.

The subsurface drainage water is diluted by the addition of tailwater runoff (surface water at the end of the fields) and municipal wastewater. These combined flows contribute to the "River water" (Table 1), which is a time-averaged and flow-weighted composition of the New, Alamo, and Whitewater Rivers. These data suggest that the average river is approximately two-thirds tailwater and one-third drainwater. The municipal flows are similar in chemical composition to the tailwater. The salt load of this average river constitutes the major inflow to the Salton Sea.

Temporal Salinity Trend

Salinity of the Salton Sea has been measured over the years by a number of different laboratories at varying frequencies. It is beyond the scope of this paper to cite or review these data other than to note additional comment on this topic in the section on Future Data Needs. Temporal changes in historical salinity of the Salton Sea are discerned from these individual measurements and long-term annual trends are computed by averaging the change in salinity over a number of years. Annual changes in salinity of the Salton Sea also have been computed from flow and chemical data on the Colorado River water that is diverted for use in the Salton Basin, together with lake volume as monitored by lake level.

Inter-annual changes computed in this manner cannot be confirmed from analyses of the Salton Sea because the uncertainty in the Sea's salinity, obtained either

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by summing individual ion concentrations or by weighing the residue following evaporation at high temperature (160°C), is subject to a one-sigma precision of no better than 5% (based on historical information from the USGS National Water Quality Laboratory in Denver). This corresponds to an uncertainty of ~2,000 mg/L in measurements of salinity, and is equivalent to about 5 times the salt load delivered annually to the Sea (annual salt load is ~4 million metric tons and total dissolved salt contained in the Salton Sea is ~400 million metric tons). As a result, any concordance between measured salinity change in the Sea and salt discharge on an annual basis is merely fortuitous. However, by carrying the inventory forward over a period of many years, a decrease in the Sea's measured salinity (and the concentration of individual ions as well) from the trend line established by adding the annual salt loads to the volume of water in the Salton Sea can be used to infer removal of salts by precipitation. Panel member Weghorst used an accounting approach similar to this to infer inception of gypsum precipitation in the Salton Sea around the mid-1980's. He also estimated an annual salt precipitation in the Salton Sea of 1.4 million metric tons, which equals about one-third the annual salt discharge to the Sea.

Tostrud (1997) estimated the annual salt precipitation at 1.5 million tons. This calculation was based on long-term trends in the chemical constituents being discharged into the sea and the actual composition of the sea. Differences between salt load to the sea and salt content of the sea were attributed to the precipitation of Ca, HCO_3, and SO_4. Apparent increases in Na, Cl, and Mg were attributed to mineral dissolution from the sea floor.

Salt Precipitation

Thermodynamic potential for minerals (salts) to precipitate from solution is often expressed in terms of a saturation index (SI) defined as

$$SI = Log (IAP/K_{sp}),$$

where IAP is the measured ion activity product and K_{sp} is the "solubility product" for the same ions in a saturated solution. Positive values of SI indicate a solution that is supersaturated so if the kinetics is favorable, the mineral will precipitate. Negative values indicate that dissolution of the mineral can occur. The Salton Sea, Alamo and New Rivers, and irrigation water are all oversaturated with respect to calcite. Panel member Schroeder reported measuring calcium carbonate contents close to one-third (dry weight basis) in bottom sediment from an area near the center of the Salton Sea. Anderson and Amrhein (2002) reported sediment $CaCO_3$ contents averaged 24% $\pm$11% dry weight basis on 90 samples collected throughout the sea. A maximum of 75% $CaCO_3$ was found in one sample. Given its saturation in Colorado River water, it is likely that calcium carbonate has been precipitating throughout the history of the Salton Sea.

Surface water sources of discharge to the Salton Sea are clearly undersaturated with respect to gypsum (Figure 1) so it is not surprising that some considerable time had to elapse before calcium and sulfate ions concentrations became high enough for gypsum to possibly precipitate in the Salton Sea. Hely and others (1966) suggested the Sea was saturated with respect to gypsum as early as the 1960s. There is some evidence that gypsum may be precipitating, including geochemical calculations, measurement of sulfur in the sediments, and direct observations of gypsum crystals

from the sea sediments. Some of the panel members suggested the gypsum is remnant from earlier periods of drying in the Salton Sink. Laboratory studies by panel member Weghorst, have shown that an additional 20% concentration is needed before gypsum will precipitate from Salton Sea water.   However, this may be due to the slow precipitation rate of gypsum at the level of oversaturation that currently exists in the sea.

Based on total sulfur analysis of 98 sediment samples from the Sea, Amrhein calculated the average gypsum content of 6.9% $\pm$6.1% (one standard deviation) dry weight sediment (unpublished data). These values were corrected for organic sulfur, pyrite, and entrained sea water sulfate in the sediment samples. The high variability of the measured gypsum content suggests that gypsum is not precipitating evenly throughout the sea. In fact, pore water samples from the deep water, organic-rich parts of the sea have been found to be undersaturated with respect to gypsum due to the lower sulfate concentration that results from sulfate reduction (Amrhein, unpublished data and chemical speciation using PHRQPITZ). Thus, gypsum is not forming in sediments that are strongly reducing, which leads to the sporadic recovery of gypsum in sediment samples. This indicates that areas of intense sulfate reduction can actually be dissolving gypsum.

Geochemical Modeling

Panel member Parkhurst used the geochemical model PHREEQC to simulate the evolution of water quality in the Salton Sea and calculate the amount of calcite and gypsum that might precipitate. Total volume of the Salton Sea is assumed to be 7.6 X

10^6 acre-ft and composition used in the simulation is given in Table 1. A volume of water equal to 1.36 X 10^6 acre-ft with composition given by the "average river water" column in Table 1 was added each year to the Sea and then evaporated to maintain constant volume. Results after 1 year and after 50 years of simulation are given in the two columns on the left side of Table 2. In the simulation we assumed that the current level of oversaturation was maintained ($SI_{calcite}$ = 1.15 and SI_{gypsum} = 0.18) and the Sea has an average pCO_2 = -3.01. The assumption of constant SI values for calcite and gypsum was made because of uncertainties in the actual equilibrium values for these minerals in the Salton Sea. We assumed that the rates of mineral formation are at steady state and slow at these SI values, and thus any increase in Ca, HCO_3, or SO_4 concentration due to inflow and evaporative concentration will result in precipitation that returns the sea to these steady-state SI values.

In the first year, 0.35 mmol/L of calcite and 0.69 mmol/L of gypsum precipitate, and 0.39 mmol/L of CO_2 is evolved due to the precipitation of calcite (Eq. 1). This equates to the precipitation of 330,000 metric tons of calcite and 880,000 metric tons of gypsum, and a summed total of 1.2 million metric tons of salt during year 1. If the process is repeated, during the 50th year 360,000 metric tons of calcite and 540,000 metric tons of gypsum precipitate—a gradual decrease in the amount of gypsum precipitating and a total of 0.9 million metric tons in the 50th year.

[The masses of salt reported here are the amounts that would be measured using the standard method of evaporation to dryness at 160°C. Under these conditions gypsum, $CaSO_4?2H_2O$, is dehydrated to $CaSO_4$. The mass of "gypsum" reported is

given as anhydrous $CaSO_4$. This is also the amount of dissolved ions that will be removed from solution, not the actual mass of gypsum that will potentially accumulate in the bottom of the sea. To convert to the tons of gypsum, as the dihydrate solid, multiply the tons of $CaSO_4$ by 1.26.

The mass of calcite reported is the amount that would potentially precipitate as a solid and the amount that would be measured during an evaporation test. It is not an accurate measure of the mass of dissolved ions removed from the water. The precipitation of calcite occurs via Equation 1, which shows that 2 bicarbonate ions are lost from solution for each Ca ion precipitated. The total mass of ions removed from solution is greater than the tons of calcite precipitated because CO_2 is evolved. To convert the tons of calcite precipitated to tons of calcium and bicarbonate removed from solution, multiply the tons of calcite by 1.62.]

Additional calculations were done using PHREEQC and selecting different values for pH and pCO_2. Biological degradation of organic matter in the sediments would likely lower the pH and raise the CO_2 in the sediment porewater. (This has been confirmed by pore water analysis done by panel member Amrhein.) Dropping the pH to 7.5, and raising the CO_2 about 5 fold to $pCO_2 = -2.29$ by maintaining the same initial alkalinity as in the previous simulation, yields little change in total accumulation of calcite and gypsum, provided the new steady state (SI = 0.63 for calcite and 0.18 for gypsum) is maintained. Results are given in the two columns on the right side of Table 2.

Panel member Pyles, who has experience with ocean water evaporation and desert dry lake brines, was skeptical that gypsum precipitation was taking place to any

great extent in the Salton Sea. Gypsum is found in the sea but there is uncertainty

whether the crystals found in the sediments are prehistoric or modern. Some of the

crystals found in the Sea are single, isolated lenticular crystals found near the sediment

surface, and others are masses of aggregate crystals near the bottom of the sediments.

Panel member Pyles commented that gypsum formed from brine precipitations typically

is seen in large agglomerations of fine crystals.   One of the outside reviewers of this

document commented that his or her observations have been that agglomerations of

fine crystals of gypsum are formed in beakers of seawater, but not in solar ponds. The

outside reviewer commented that in solar ponds, "gypsum occurs as single, lenticular

crystals at and near the surface of the sediments." Gypsum of this description has been

recovered from the sediments, although not all sediment samples have gypsum.

Because disagreement as to the extent of gypsum precipitation within the sea, we did

another series of calculations in which precipitation of gypsum was blocked.

Allowing the SI of gypsum to increase, so that no precipitation of this mineral

occurs, has almost no effect on the amount of calcite precipitated. This is because

calcite precipitation is limited by insufficient bicarbonate alkalinity. Repeating the first

simulation without gypsum precipitation yields 360,000 metric tons of calcite during the

1st year and 370,000 metric tons during the 50th year, while SI for gypsum increases

from an initial value 0.18, to 0.52 at the end of 50 years. This increase in SI

corresponds to a more than a doubling of the ion activity product at the end of 50

years. This means that if gypsum precipitation is blocked, the Ca concentration in the

sea will continue to increase over the whole time period. This is contrary to the

evidence that the Ca concentration in the sea is not increasing, and may even be decreasing (Tostrud, 1997). Thus, either there is extensive gypsum precipitation (880,000 tons/year) or there is another source of bicarbonate alkalinity that allows more calcite to precipitate than the model predicts. An important mechanism of alkalinity generation is sulfate reduction. This is discussed below in further detail.

It is well known that the PHREEQC chemical speciation model was not designed for high salinities. The calculations are thought to be reasonable, but to be sure, panel member Holdren repeated these calculations given above using PHRQPITZ, a computer program designed to calculate ion activities and saturation indexes at very high salinities. Holdren's simulation using PHRQPITZ yields a salt deposition of 343,000 metric tons/yr for calcite and 403,000 metric tons/yr for gypsum. The calcite value is close to the PHREEQC estimate (330,000 tons), but the gypsum value is less than half (compare 403,000 with 880,000) suggesting much less precipitation of gypsum.

Holdren also repeated the simulation while blocking the precipitation of gypsum but allowing calcite precipitation. This simulation using PHRQPITZ yielded 356,000 metric tons/yr of calcite and compares very closely with the PHREEQC calculation of 360,000 tons. In both models, the amount of calcite formed appears to be controlled by the alkalinity of the sea. The largest difference between the two models is for gypsum precipitation. In this case, the estimate by PHRQPITZ of 403,000 metric tons/yr for gypsum is thought to be more reliable because the chemical speciation was designed for elevated salinities.

Based on these calculations and the fact that well-formed isolated crystals of gypsum are found in some sediment samples, gypsum precipitation appears to be occurring in some parts of the sea, although the annual amount is not known.

Other Reactions Affecting Mineral Precipitation

The biological activity, which includes carbon fixation by algae and oxidation-reduction reactions by bacteria within the sediments, almost certainly has a major effect on salt precipitation in the Salton Sea. However, the information necessary to quantify this effect is not known.

Because of the high nutrient loading to the sea and high temperatures, algal growth is intense. Dead algal cells fall to the sediments where they are oxidized by bacteria. Oxidation will occur with oxygen (O_2), nitrate (NO_3^-), Fe(III), and sulfate as terminal electron acceptors. Aerobic oxidation of organic matter will increase the CO_2 concentration in the sea and porewater. Nitrate and Fe(III) reduction are occurring in the sea, but are believed to be small due to their low concentrations relative to sulfate. Organic matter oxidation via sulfate reduction appears to be an important oxidation reaction in the sea based on pore water analysis for sulfate and sulfide (Anderson and Amrhein, 2002). The idealized reaction showing the oxidation of organic matter (CH_2O) with sulfate at the terminal electron acceptor is as follows:

$$SO_4^{2-} + 2CH_2O \rightarrow 2HCO_3^- + H_2S \qquad \text{Eq. 2}$$
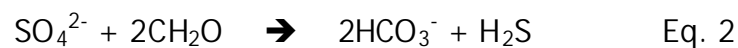
This reaction, which occurs in the absence of oxygen in the sediments of the Salton Sea, generates both bicarbonate alkalinity and hydrogen sulfide gas. The panel members hypothesized that this reaction is occurring, and shifting the relative

proportions of calcite and gypsum precipitating. The generation of additional alkalinity allows for more calcite to form than the models are predicting.

Although the odor of hydrogen sulfide is pervasive at the Salton Sea, its net release to the atmosphere is unknown, but is likely quite small compared to the total sulfur (S) inventory. However, there may be enough sulfate reduction to generate sufficient alkalinity to precipitate the year's total input of Ca as calcite. There are currently no measurements of sulfate reduction rates at the Salton Sea, although based on published rates of reduction in estuaries (with much lower sulfate concentrations), panel member Parkhurst calculated that the flux of H_2S out of bottom sediment in the Salton Sea could be comparable to the external sulfur (as sulfate) load delivered by discharge to the Salton Sea. Based on Parkhurst's calculations, there could easily be enough sulfate reduction and alkalinity generation such that only small amounts of gypsum are forming, and calcite is the dominant mineral phase.

Not all of the hydrogen sulfide formed in the sediments will make it to the atmosphere. Oxidation of hydrogen sulfide within the water column will consume alkalinity (generate acidity), as represented by the reaction below.

$$H_2S + 2O_2 \rightarrow SO_4^= + 2H^+ \qquad \text{Eq. 3}$$
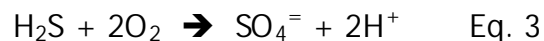
This could be an important mechanism that decreases the alkalinity of the Sea water. Preliminary data collected by researchers at UC Riverside indicates there is no calcite precipitation within the water column of the sea but extensive precipitation within the pore water of the sediments (Anderson and Amrhein, 2002). Thus, the region of active sulfate reduction also favors rapid calcite precipitation. The fate of hydrogen sulfide

released to the water column is probably some out-gassing to the atmosphere and some reoxidation within the aerobic portion of the sea.   Clearly, there exists a need for field data to determine sulfate reduction rates in the sediments and hydrogen sulfide evolution rates to the atmosphere to quantify the extent of alkalinity generation within the sea.

The ultimate limit on sulfate reduction in the Salton Sea is the amount of organic matter, or algal biomass, available for oxidation. Because algal production is phosphate limited in the Sea (Setmire and others, 2001), it is possible to estimate the total amount of biomass produced each year. Assuming all of this biomass decomposes anaerobically via sulfate reduction, alkalinity generation can be estimated. Using only the total mass of P that enters the sea every year (1,339,000 kg/yr; Setmire and others, 2001), panel member Amrhein calculated that sufficient alkalinity is generated to precipitate 98% of the annual Ca load, or 691,000 tons of calcite. This calculation does not take into account internal recycling of P from the sediments. Studies in progress by researchers at UC Riverside (Anderson and others, 2001) have shown that internal loading of P can be significant during the summer months. On average, the internal loading of P is approximately 46% of the total P loading to the Sea (Anderson and Amrhein, 2002). This additional P will increase the estimate of total biomass produced each year.

There is good evidence that the concentration of Ca in the sea is not increasing, and in fact may be decreasing. If there is sufficient alkalinity generation within the sea

via sulfate reduction, the annual Ca load may be precipitating as calcite. If this were true, the total "salt" precipitation as $CaCO_3$ would be 705,000 metric tons.

Reactions other than those involving calcite and gypsum can affect aqueous salinity, but their effect is much less important. Some of the sulfide formed from sulfate reduction is precipitating within the sediments as FeS_2 (pyrite). The source of Fe for this reaction is the dissolution of iron oxides and iron-containing clay minerals in the bottom sediments and suspended solids entering the sea. Based on marine systems, the rate of pyrite formation is probably limited by the rate of dissolution of these iron-containing minerals. The amount of pyrite in the sediments has recently been measured in 80 sediment samples collected throughout the sea (Amrhein, unpublished data, paper in preparation). The concentration of pyrite averaged 4.5 $\pm$ 2.1 g/kg (dry weight basis; $\pm$ 1 standard deviation), or 0.45% by weight.

If these sediments are exposed to oxygen either through dredging, mixing, or retreat of the shoreline, oxidation and release of sulfate is possible. In a laboratory study of sediments from the center of the north basin, oxidation of the mud for 4 days increased the soluble sulfate concentration ~0.7 g/(kg dry sediment), compared to a sample kept under argon (Amrhein, unpublished data). This indicates that approximately 10% of the pyrite had oxidized during this brief exposure to oxygen.

Based on color changes of the sediments exposed to oxygen and Fe(II) to Fe(III) ratios in acid extracts of the sediments, green rust is an important component in the sediments. Green rust is a mixed oxidation-state iron hydroxide sulfate mineral with an ideal formula of $[Fe^{II}_4 Fe^{III}_2(OH)_{12}][4H_2O?SO_4]$. Extraction of 98 sediment

samples yielded 9.5 ± 3.4 g/kg of sulfate green rust, or 0.95% by weight (Amrhein,

unpublished data). Oxidation of this mineral will also release sulfate and precipitate

Fe(III) oxides, which results in the observed color change. (Green rust is dark greenish

black and Fe(III)-oxides are orange/red/brown.)

Compared to calcite and gypsum, both pyrite and green rust are relatively lesser

components of the Salton Sea sediments. If the major source of Fe for these minerals

is clays that wash into the sea as suspended solids in the rivers, it is possible to

calculate annual Fe-mineral formation. Typically, readily reducible iron in clays will be

1% of the suspended solids load. Using this assumption, a total of 5000 metric tons of

Fe could be precipitating as pyrite and green rust each year. If this were all pyrite, the

mass of FeS_2 would be 10,800 metric tons/yr. Compared to calcite, this is a relatively

small amount.

Magnesium can be removed from solution through substitution for calcium in

calcite. An estimate of the importance of this reaction can be computed using the data

from Mucci and Morse (1983), who studied the coprecipitation of Mg^{2+} into calcite

formed in ocean water. Based on these data and the Mg/Ca molar ratio of the Salton

Sea water, the calcite formed in the sea should have a Mg/Ca mole ratio of 0.054. This

would give an average formula for the calcite mineral as: $Ca_{0.949}Mg_{0.051}CO_3$.

If the calcite contains 5% Mg, the total mass of calcium/magnesium carbonate

would be 735,000 metric tons, compared to 705,000 tons without magnesium.

X-ray diffraction analysis can also be used to determine the extent of Mg

substitution into calcite. Magnesium incorporation into calcite causes a collapse of the

crystal lattice, which can be accurately measured using X-ray diffraction. Using this method, panel member Amrhein has determined that the calcite in the Salton Sea sediment contains between 3.0% and 3.8% $MgCO_3$. This would increase the total tonnage of calcite from 705,000 metric tons/yr to about 725,000 metric tons/yr.

Additional losses of Mg from the sea can be attributed to the precipitation of magnesium silicate minerals like sepiolite and "protosepiolite" (Levy et al., 1995). Dissolved silica also might be precipitated as diatom exoskeletons. A reasonable assumption, based on the date in Table 1, is the annual Si load precipitates every year. If all of the Si precipitates as sepiolite ($Mg_4Si_6O_{15}(OH)_2?6H_2O$), a total of 39,000 metric tons will form. Overall, the precipitation of Mg and Si will have a small, but not negligible effect on salinity.

Ion exchange between dissolved ions and clay minerals also has the potential to alter the salt balance in the Salton Sea. Suspended solids (soil material) that are washed into the sea will have predominately Ca on the exchange phase. After equilibration with the Sea water, the exchange phase will be dominated by Na, and Ca will be released to the water. This has the potential of increasing the total amount of Ca available for precipitation as calcite or gypsum. An approximation assuming a suspended sediment concentration in discharge to the Salton Sea of 300 mg/L, clay content of one-third in the suspended load, and cation-exchange capacity of 100 meq (milliequivalents) per 100 g clay yields an ion exchange capacity of 0.1 meq/L in the average river water input to the Sea. This is equivalent to 0.15 mg/L based on the equivalent weights of 23 for Na and 20 for Ca, the ions primarily involved in exchange,

which translates into less than 0.01% of the dissolved salt load given in Table 1. Panel member Amrhein reached a similar conclusion from direct measurements of cation exchange capacity in bottom sediment from the Salton Sea.

Future Data Needs

Material in the preceding sections illustrates the importance of additional information in two areas: monitoring and historical reconstruction. Confidence in the effect that salt precipitation has on salinity trends in the Salton Sea will be achieved only after there is agreement between model simulations and field data. Accordingly, there exists a need for better, as well as additional kinds of data to constrain the models. Given the importance of monitoring, it would probably be useful to compile all historical water-quality (salinity) records from the Salton Sea, and the associated lake stage (volume), in an electronic spreadsheet. Information on previous lake conditions, especially as they relate to the early history of the Salton Sea, should also be sought from two additional sources: the anecdotal accounts of older residents and their descendents, and the biogeochemical changes that are recorded by the sediment that has accumulated beneath the Salton Sea.

There are three issues with respect to measuring salinity that need to be addressed: analytical precision (and accuracy), sample location and sample handling, and reporting units. The current analytical precision of about 5% in estimates of the Salton Sea's salinity is approximately equivalent to 5 times the annual discharge of dissolved salt to the Sea. Accordingly, the determination of average annual salinity trends and the early detection of major changes in salt precipitation in the Salton Sea

now requires the averaging (or cumulative accounting) of measurements over a period of at least a decade—far too insensitive an indicator to be useful. The precision on salinity (either from gravimetric or from sum of individual constituents) analyses could be greatly improved, but it would require special efforts not generally provided by broad-service laboratories. However, specific conductance can routinely be measured with a precision of ±1% in the field, if accurate temperature measurements and suitable standards are used. The collection and analysis of this surrogate for salinity should be repeated at least every 6 months. The resulting conductance data would itself certainly lead to a marked improvement in the determination of short-term annual salinity trends, and might even provide the sensitivity needed to detect major changes in annual salt deposition within a few years after they occur. Comprehensive chemical analyses also are certainly desirable for determination of trends and are essential for use in geochemical models, but the need for high-precision data becomes less frequent if good conductance information is available.

Profiles shown in Figure 2 illustrate the fact that surface-water quality is very dependent on location in the Salton Sea. The approximately 3% difference in salinity between the center of the north and south sub-basins becomes even greater closer to the south shore, where most of the freshwater discharge occurs. It is likely that nearly all of the published historical salinity data on the Salton Sea are from water samples taken from the lake's surface, near shore. Panel member Schroeder (unpublished data) found a range of only 1% (within the limit of precision) for specific conductance @ 25°C in bottom water from 11 locations scattered throughout the lake. The narrow

range occurred in bottom water spanning a depth from 15 to 50 feet, and at a time of maximum thermal stratification in July. A salinity-monitoring program should therefore be based on sampling of the sea at several depths near the center of the Salton Sea. Water samples collect from the near-shore are subject to wide variations due to local heating and evaporative concentration and influence from the river inflows.

Salinity (and chemical concentrations) for the Salton Sea has usually been expressed in volumetric units as mass of salt per liter of solution. As such, the values are density dependent (oceanographers use grams of salt per kilogram of solution to eliminate this effect) and the density information is rarely available. Panel member Amrhein has measured the density of Salton Sea water and found a range from 1.028 to 1.032 g/mL, with an average of 1.030 g/mL.

Reasonable adjustments to specific conductance measurements if the temperature at which the salinity measurement was made is known. But the temperature must be known to within about ±0.1°C because the thermal dependence for specific conductance is about 2% per degree. Precise values for temperature will become increasingly important as future measurements are made by lowering instruments through the water column to obtain profiles. Therefore, laboratory data for conductance over the range in temperature that occurs in the Salton Sea should be obtained so that anyone can then make the necessary adjustments to convert the conductance data to a temperature of 25°C.

Sample handling in the field and transport to the laboratory are also important. The common practice of refrigerating water samples could cause the immediate

precipitation of gypsum. Ideally, samples should be diluted in the field to reduce the level of saturation, and the potential for calcite and gypsum precipitation. For calcium analysis, acidification using HCl or HNO_3 may be effective in stopping precipitation if the pH is <2. Sulfuric acid should never be used because it leads to rapid gypsum precipitation.

Water samples for alkalinity determination should be diluted at least 50% with deionized water, preferably in the field or immediately upon return to the lab. The most reliable and accurate method is to use an electronic balance to add 100 g of deionized water to 100 g of Sea water. Inexpensive, portable electronic balances make it possible to do this dilution in the field. Dilution of samples prior to alkalinity determination has the added benefit of improved pH measurement at the endpoint due to the lower salinity. It is widely recognized that pH measurements in high Na waters are problematic. The measured pH of the diluted samples has no relevance to the actual pH of the sea.

The simulations reported herein used PHREEQC and PHRQPITZ. Other geochemical models exist and each is likely to yield slightly different results; however, the differences are much less important than is our lack of quantitative information on the biological and chemical processes that govern precipitation and dissolution. Furthermore, these processes must be determined not only in the water column, but also where they are most important—within the bottom sediment itself where they occur. Required information includes rates of oxidation and reduction within the sediment (including any role that iron might play in the reactions); flux (from porewater

chemical profiles) for sulfide, as well as for the other nutrients, major ions, and alkalinity; and complete chemical and mineralogical analyses of the bottom sediment.

Response to Questions

The response to several questions posed by members of the audience and the Salton Sea Science Office is given below. Some of the questions and answers repeat topics addressed in more detail above.

Q Are dissolved salts being precipitated and(or) being biologically reduced in the Salton Sea?

A Yes.

Q If so, which salts are they and to what extent is precipitation occurring? What percent of the TDS in inflow waters is precipitating on an annual basis?

A Calcium salts, as carbonate and sulfate, are precipitating. The extent of precipitation is uncertain, partly because quantitative information on the extent of biological reduction is not available. Estimates of salt precipitation in this paper range from 330,000 to 1.5 million metric tons annually, with a range between 0.7 and 1.2 million thought to be the best estimate. At the upper end of the range, salt precipitation represents about one third of the annual salt load.

Pyrite and green rust are also forming in the sediments. At this time we have insufficient data to accurately calculate the annual precipitation rate but the sediment concentrations are typically <1% by weight of each. Compare this to the average calcite content of the sediments (24%) and gypsum content (6.9%).

Q Will salts re-dissolve if salinity is reduced, and what should be the salinity goal for remediation?

A. Dissolution will not occur until dilution is sufficient to reduce the constituent aqueous-ion concentrations below saturation (SI = 0). Panel member Holdren used PHRQPITZ to conclude gypsum dissolution will not begin until salinity was decreased to 31,000 mg/L. Calcite will never re-dissolve. Hence, reducing salinity to "oceanic" levels would not result in re-dissolving salts. There are no obvious benefits (as regards any salt exchange between the sediment and water) to lowering salinity below current levels.   In fact, it could be argued that allowing salinity to remain near the current higher level is beneficial in that it results in the need to dedicate less land for evaporation ponds and in less salt to dispose. (Our assessment does not consider any possible ecological ramifications from a salinity that differs compositionally and is somewhat higher than oceanic levels as the panel does not have expertise on that topic.)

Oxidation of pyrite and green rust will occur in sediments exposed to oxygen. This reaction will precipitate Fe(III) oxides and generate sulfate and acidity that will go to reducing the alkalinity of the porewater. Quantification of this reaction has not been attempted although it is believed to be small because of the high calcite content relative to Fe-mineral content.

Q Are there other sources of salt to the Salton Sea, such as ground-water seepage?

A Ground-water seepage, geothermal fluxes, and magmatic CO_2 fluxes through the lake bottom are two additional direct sources that were considered. Hely and others

(1966) estimated that ground water is 3.6% of total inflow and Schroeder and others

(1993, Table 10) measured dissolved-solids concentration of about 14 g/L in regional

ground water (below the depth affected by irrigation drainage) at the north end of the

Imperial Valley near the south shore of the Salton Sea. This yields a value for salt

inflow from ground water that is about 20% of the surface-water load—not large, but

not insignificant either. However, most of the ground-water seepage probably occurs

along the (east and west) sides and at the north end of the Salton Sea adjacent to the

Coachella Valley, areas where the soils are more permeable and the ground water likely

is much less saline. Hence, the ground-water contribution to salt loading is likely only a

few percent.

Panel member Kharaka postulated an annual magmatic CO_2 flux of 10^6

moles/km^2 to calculate an annual gas flux of 44,000 metric tons for the whole lake. If

the CO_2 simply evolves (volatilizes), there would be no effect on salinity. Because the

sea is so highly oversaturated with respect to calcium carbonate, elevated levels of CO_2

will decrease the pH of the sea but not result in calcite dissolution. The venting of

geothermal water within the sea could contribute an indeterminate amount of salt.

Q Do we need to look at TDS, only at NaCl, or at individual components?

A All of the major ions need to be considered to gain a complete understanding of the

processes that affect the salt budget of the Salton Sea.

Q Are organisms generating bicarbonate over what is brought in with inflows?

A Biological generation of alkalinity via sulfate reduction is substantial. Estimates

based on potential biomass production indicate an additional 50% of the inflow

alkalinity could be generated in the sea. However, there are no quantitative

measurements of processes and the net production is unknown. Any excess alkalinity

that is generated will increase the amount of calcite that is precipitating. The amount

of calcite that precipitates is currently limited by alkalinity.

Q What if processes are not at "steady state" or at "equilibrium" in the Salton Sea?

A One indication of the magnitude of effects is provided by the range in annual salt

precipitation that is computed by simulations with various assumptions. Another is to

note that the amount by which gypsum exceeds saturation at SI = 0.18 is equivalent to

about a decade of discharge to the Salton Sea. These observations illustrate the

necessity of regular and careful monitoring as well as studies to quantify the chemical

and biological processes that affect precipitation and dissolution. All of the precipitation

reactions are sensitive to temperature. Because the temperature of the sea is

constantly changing, there never is a true steady state condition. Equilibrium can never

be reached because of the dynamic nature of inflow, evaporation, mixing events,

temperature changes, and rising salinity.

Q Will seasonal and spatial variability in the Salton Sea affect processes in such a way

that understanding and projecting trends from simple models will not be

representative?

A Models, and simulations, could be made more complex to account for variability if

sufficient data were available but it not readily apparent that the greater complexity

that would result is important for discerning trends and calculating lake-wide salt

budgets over periods of several, or even a few, years.

Q If biological reduction, rather than chemical precipitation, is the dominant process affecting precipitation, wouldn't an imbalance in salt inflow and salt inventory show up as a gradual effect, rather than an abrupt change, in the Salton Sea's salinity trend?

A Biological reduction leads to chemical precipitation, so the two are linked. The following equations show how this occurs:

$$SO_4^{2-} + 2CH_2O_{(org.\ matter)} \rightarrow 2HCO_3^- + H_2S(g)$$

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3(s) + CO_2 + H_2O$$

Precipitation will always be a gradual process so no abrupt change is likely. The rates of precipitation and biological reduction change with the season, mostly due to temperature changes, photosynthetic activity, and concentrations of dissolved organic carbon.

Q Will diurnal (photosynthesis/respiration) cycles have an effect on TDS measurements as $CaCO_3$ precipitates and dissolves in response to changes in CO_2 levels.

A The effect on salinity would be far too small to measure. It does not appear that significant amounts of calcite are precipitating within the water column; i.e. there is very little "calcite fallout" due to photosynthetic activity in the surface water. The mechanisms blocking the precipitation of calcite in the surface water are not known, although dissolved organic compounds and phosphate have been implicated in other lakes. Virtually all of the calcite precipitation appears to be occurring within the pore water of the sediments. The concentration of CO_2 could never change enough to dissolve calcite in the sea. Calcite will not dissolve in the Salton Sea, even with extensive dilution.

Q Did massive fish die-offs since the 1980's cause a change in salinity trends.

A There is no obvious direct effect as the amount of mineral matter, as skeletal material, tied up in fish (assuming 10^8 fish with 0.05 kg bone per fish) is at least 5 orders of magnitude less than the amount of salt that is precipitating annually.

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Table 1. Chemical composition of various waters in the Salton Basin.

Constituent	Irrigation water[1]	Drainwater[1]	River Water[2]	Salton Sea[2]
Temperature (°C)	--	--	22.6	23
Dissolved oxygen (mg O_2/L)	--	--	6.41	5.48
Specific conductance (µS/dm)	1.06	8.29	--	--
Dissolved solids (g/L)	0.69	4.86	2.28	43
pH	8.3	7.2	7.6	8.1
Ammonium (mg N/L)	0.03	0.18	--	--
Nitrate (mg N/L)	0.22	12	--	--
Calcium (mg/L)	76	310	168	944
Magnesium (mg/L)	29	330	80.8	1,400
Sodium (mg/L)	110	1,420	454	12,400
Potassium (mg/L)	4.3	19	9.9	258
Chloride (mg/L)	92	1,200	543	17,240
Sulfate (mg/L)	270	3,000	734	10,500
Alkalinity (as mg $CaCO_3$/L)	145	383	274	247
Silica (mg/L)	10	15.5	14	9.84
Selenium (µg/L)	~2	24	--	--

[1] From Schroeder (1996, Table 1), with a corrected value for drainwater sodium based on charge balance and specific conductance measurements. The original Na was 2,000 mg/L, which as been shown to be in error.
[2] Values used by Parkhurst and Holdren for model simulations reported herein.

Table 2. Projected chemical concentrations in the Salton Sea from model simulations.

Constituent	After 1 year[1]	After 50 years[1]	After 1 year[2]	After 50 years[2]	No ppt 50 yrs[3]
Dissolved Solids (mg/L)	43,830	57,900	43,872	57,950	63,400
pH	8.12	8.16	7.50	7.54	~9.0
Calcium (mg/L)	933	820	933	820	2,450
Magnesium (mg/L)	1,420	2,130	1,420	2,130	2,130
Sodium (mg/L)	12,520	16,510	12,520	16,510	16,510
Potassium (mg/L)	261	347	261	347	347
Chloride (mg/L)	17,410	22,180	17,410	21,280	21,280
Sulfate (mg/L)	11,030	15,620	11,030	15,630	17,100
Alkalinity (as mg $CaCO_3$/L)	246	292	291	342	2,700
Calcite precipitated (mg/L)	35.1	1,890	38.8	1,893	0
Gypsum precipitated (mg/L)	97.3	3,060	93.7	3,052	0

[1]Evolves CO_2 and precipitates calcite and gypsum to maintain pCO_2 = -3.01, $SI_{calcite}$ =1.15, and SI_{gypsum} = 0.18 throughout the simulation.
[2]Based on decreasing pH to 7.5 with same initial alkalinity, then maintaining the resulting pCO_2 = -2.29, $SI_{calcite}$ = 0.63, and SI_{gypsum} = 0.18 throughout the simulation.
[3]Chemical composition of the Salton Sea after 50 years if no precipitation (No ppt) were to occur and the River water composition remains the same as given in Table 1 and the annual inflow is 1.36 MAF.
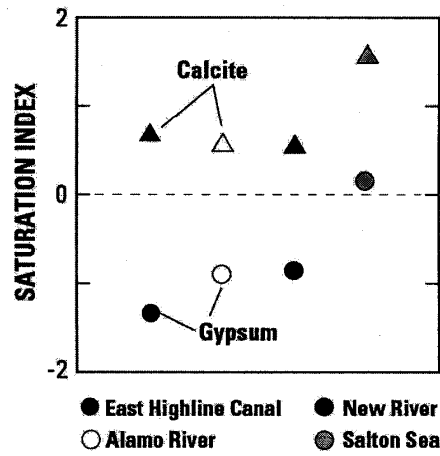
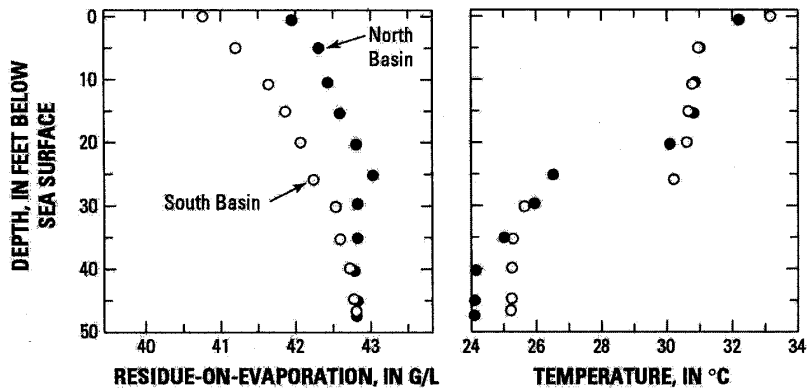**Figure 1.** Saturation indices for waters in the Salton Basin.

Figure 2. Profiles from the North and South subbasins in the Salton Sea.