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Chemical evolution of the Salton Sea, California: nutrient and selenium dynamics

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Abstract

The Salton Sea is a 1000-km^2 terminal lake located in the desert area of southeastern California. This saline ($\sim$44 000 mg l^{-1} dissolved solids) lake started as fresh water in 1905–07 by accidental flooding of the Colorado River, and it is maintained by agricultural runoff of irrigation water diverted from the Colorado River. The Salton Sea and surrounding wetlands have recently acquired substantial ecological importance because of the death of large numbers of birds and fish, and the establishment of a program to restore the health of the Sea. In this report, we present new data on the salinity and concentration of selected chemicals in the Salton Sea water, porewater and sediments, emphasizing the constituents of concern: nutrients (N and P), Se and salinity. Chemical profiles from a Salton Sea core estimated to have a sedimentation rate of 2.3 mm yr^{-1} show increasing concentrations of OC, N, and P in younger sediment that are believed to reflect increasing eutrophication of the lake. Porewater profiles from two locations in the Sea show that diffusion from bottom sediment is only a minor source of nutrients to the overlying water as compared to irrigation water inputs. Although loss of N and Se by microbial-mediated volatilization is possible, comparison of selected element concentrations in river inputs and water and sediments from the Salton Sea indicates that most of the N (from fertilizer) and virtually all of the Se (delivered in irrigation water from the Colorado River) discharged to the Sea still reside within its bottom sediment. Laboratory simulation on mixtures of sediment and water from the Salton Sea suggest that sediment is a potential source of N and Se to the water column under aerobic conditions. Hence, it is important that any engineered changes made to the Salton Sea for remediation or for transfer of water out of the basin do not result in remobilization of nutrients and Se from the bottom sediment into the overlying water.

Introduction

The Salton Sea, located in the desert area of southeastern California, is a large (1000 km^2) shallow (mean depth = 8 m) saline (about 44 000 mg l^{-1}total dissolved solids) lake whose shoreline is currently at an elevation of 69 m below sea level (Fig. 1). It was formed as a fresh water lake in 1905–07 as a result of accidental flooding from the Colorado River and has subsequently been maintained largely by runoff (currently about 1.7 km^3 annually) from agricultural irrigation in the Salton Sea Basin. Because Salton Sea is a closed-basin lake with minimal ground–water interaction and is located in an arid region (precipitation only 7 cm yr^{-1}) of high evapotranspiration (about 1.8 m yr^{-1}), it has been accumulating soluble salts in its water and insoluble constituents in its bottom sediment for nearly 100 years (e.g. Setmire & Schroeder, 1998). These accumulations together with accelerated eutrophication have been implicated in the periodic deaths of millions of tilapia and over 200 000 migratory water birds (Jehl, 1996; Kaiser, 1999). Restoring

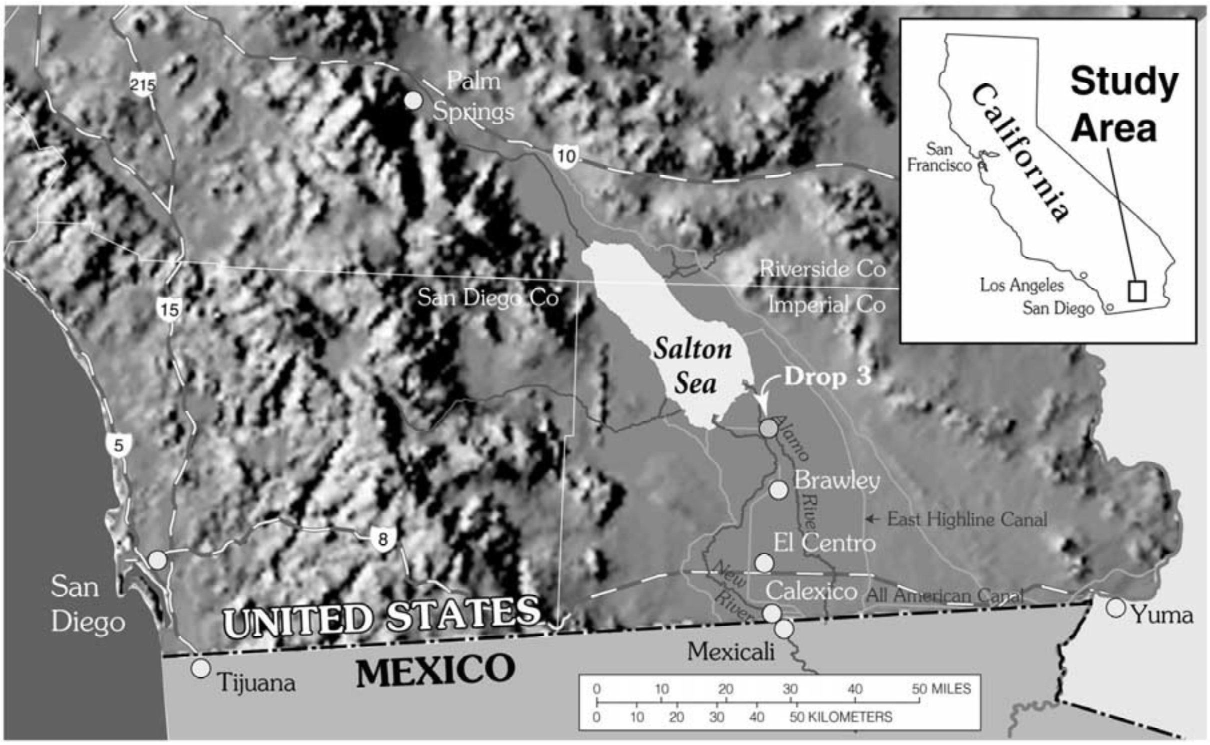

Figure 1. Salton Sea Basin and surrounding area of California, U.S.A. and Mexico.

the ecological health of the Sea is of paramount importance because the Sony Bono Salton Sea National Wildlife Refuge (NWR), a major waterfowl stopover for millions of migratory birds on the Pacific Flyway that also supports five endangered species, is located in the southern end of the Sea (Setmire & Schroeder, 1998). Historical and technical information on the Salton Sea and Salton Sea Basin are available from Dowd (1956), Hely et al. (1966), Setmire et al. (1990, 1993), Tolstrud (1997) and Setmire & Schroeder (1998) and references therein, and from other reports in this volume.

Nutrients (nitrogen and phosphorus) and selenium (Se) are among those constituents that, in addition to water salinity, threaten the health of Salton Sea (Kaiser, 1999; Schroeder & Orem, 2000). The concentration of total nitrogen (N) in irrigation water diverted from the Colorado River is relatively low (1.0 mg l^{-1}as NO$_3$), and fertilizer use is the primary source of N, which is delivered to the Sea with agricultural runoff (e.g. Setmire & Schroeder, 1998). Municipal and domestic wastewater, in addition to agricultural runoff, are the important sources of P (Federal Water Quality Administration, 1970). The addition of nutrients and abundant sunlight are responsible for the excessive biological productivity (eutrophication) of the Salton Sea that is evidenced by the lake's frequent algal blooms, large fish population, and high organic-carbon (OC) content in the water column and bottom sediment (Jehl, 1996; Setmire & Schroeder, 1998; Kaiser, 1999). The initial source of Se is marine pyritic shales that outcrop in the Upper Colorado River Basin and relatively high concentrations of Se (2.5 μg l^{-1}), mainly as selenate, is delivered to the Salton Sea Basin in irrigation water obtained from Colorado River (Engberg, 1999; Kharaka et al., 2001).

In this report, we present new data on the salinity and concentration of nutrients, Se and selected other chemicals in the Salton Sea water, porewater and (or) sediments. These results are combined with historical data from the Salton Sea Basin, results of one laboratory experiment and geochemical computer simulations to investigate the chemical evolution, and the fate and the cycling of N, P and Se in this saline lake. Understanding the physical and chemical evolution of the Salton Sea is important to the success of the various plans being considered to remediate the major ecological problems of the Sea.

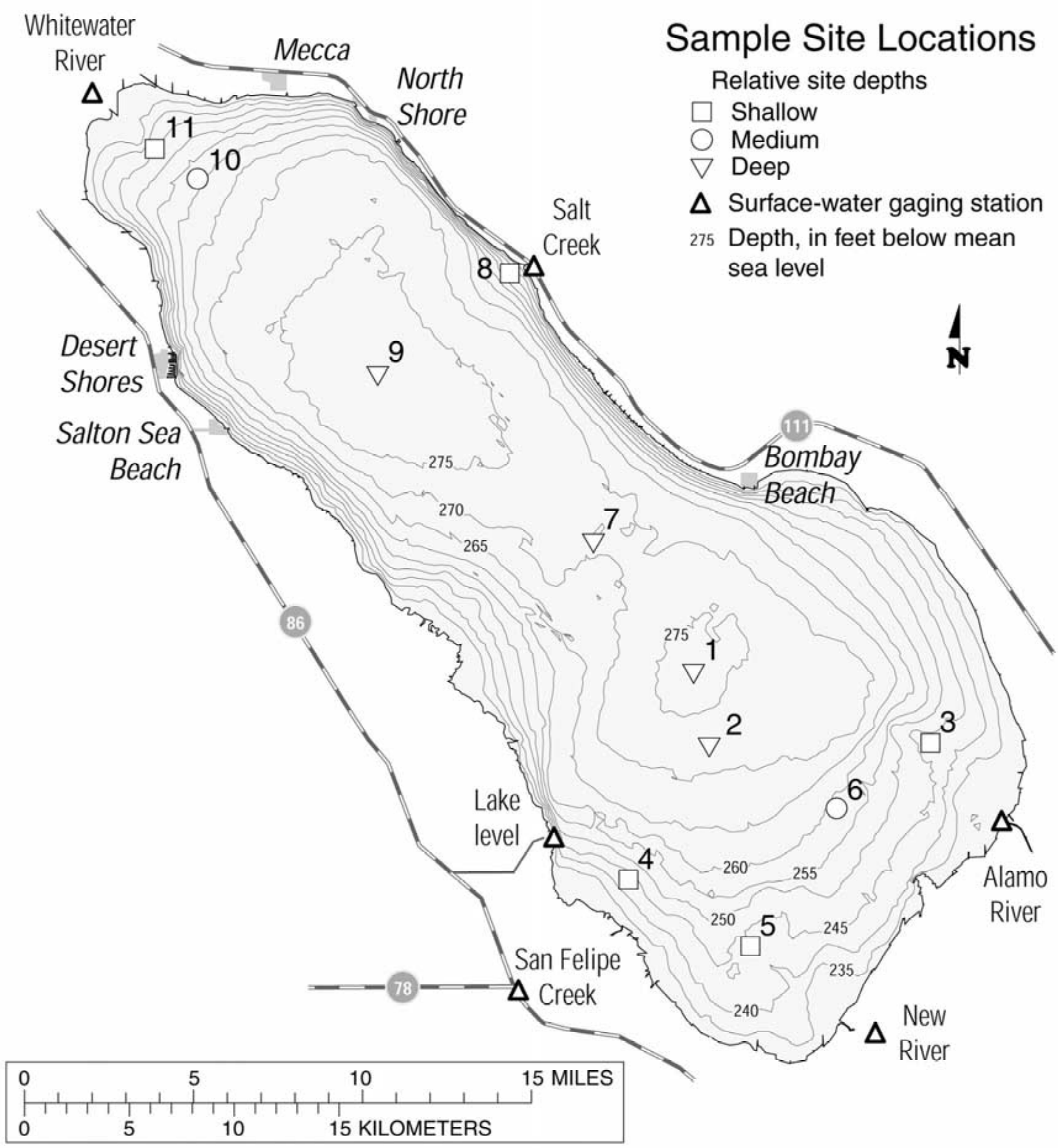

Figure 2. Sampling locations in the Salton Sea, 1998–99.

Sampling sites, materials and methods

Surface sediment and water-column and bottom-water samples were collected from 11 sites in the Salton Sea during July 20–22, 1998 (Fig. 2). Sediment cores, porewater and water-column samples were collected from two of the 1998 sites (Sites 9 and 10) on April 26–27, 1999. The sites for coring were selected in the center of the north basin (deepest part of the Sea) and between this basin and the Whitewater River delta (Fig. 2). Because of the distance from the major sources of input at the south end of the Sea, the sediment at these sites has uniformly fine texture, allowing for successful recovery of 0.5-m cores. Sediment samples were squeezed for pore water and processed for other tests described below almost immediately after collection. Some core samples, not processed immediately, were stored under anoxic conditions in the sealed core liner. Sediment samples were stored at 4 °C prior to processing to minimize bacterial activity.

Bottom sediment and water

The 11 sites from which grab samples of bottom sediment were collected in 1998 (Fig. 2) were chosen to represent the range in depositional environments and to span lake depths from shallow (4.6 m) to medium (9 m) and to deep (14–15 m). The shallow sampling depth of 4.6 m was chosen because these sites could become the new shore if inflow to the Salton Sea is reduced annually by 0.37 km^3 (300 000 acre-ft), an amount that represents a commonly anticipated water-conservation scenario (Pacific Institute, 2001). Shallow sites were sampled in the deltas at each of the five perennial streams that discharge to the Salton Sea (Sites 3, 4, 5, 8 and 11). Deep sites were sampled at four locations – in the center of the north (Site 9) and south (Site 1) basins, in the saddle between the basins (Site 7) and near the center of the south basin (Site 2). The remaining two sites that were sampled are in the coalesced deltas of the New and Alamo Rivers (Site 6), and between the Whitewater River and the lake's north basin (Site 10). Grab samples of bottom sediment (top 10–15 cm) were obtained with a 23-cm stainless-steel Ekman dredge, which was lowered to within 2–3 m of the bottom then allowed to free-fall into the sediment. The top 3 cm of sediment (about 1.5 kg wet weight) was transferred into a glass bowl and homogenized before transfer into small plastic and glass containers for chemical and particle-size analyses. The remaining sediment was sieved and visually inspected onboard for presence of macroinvertebrates. Sieves and hydrometers were used to determine the grain-size distributions (Guy, 1969).

The sediment grab samples were analyzed for about 50 inorganic elements at the USGS's Analytical Facility in Denver using ICP-MS, and hydride generation for Se. Sediment samples were also analyzed for polycyclic aromatic hydrocarbons (PAHs) and organochlorine compounds by GC-MS at the USGS's National Water Quality Laboratory (NWQL) in Denver. Nutrient analyses on sediment and porewater samples were done by Orem's laboratory in Reston, Virginia, using procedures described in the following section. Sediment analyses were done on material from which large shells and debris had been removed using either 850-μm or 2-mm sieves.

Dissolved oxygen (DO), pH, specific conductance (surrogate for salinity), and temperature profiles were determined electrometrically by lowering a Hydrolab^{TM} containing suitable probes through the water column. In addition, a bottom-water sample was collected at each site using a Van Dorn sampler lowered to a depth about 30 cm above the sediment–water interface. Water samples were filtered through a 0.45-μm capsule membrane and analyzed for alkalinity, silica, orthophosphate (PO_4), dissolved hydrolyzable P, NO_3, NO_2, NH_4, ON, and DOC (using a 0.45-μm membrane silver filter). All bottom water samples collected in 1998 were analyzed by the NWQL in Denver.

Sediment cores and porewater

Sediment cores from the Salton Sea were collected at Sites 9 and 10 (Fig. 2) using a Benthos gravity corer with a 5-cm o.d. plastic core liner. Multiple cores were collected at each site to provide samples for solid phase and porewater analyses. In most instances, the gravity core penetrated through the soft surface mud into the underlying material that predates the 1905–07 creation of the Salton Sea. Once recovered, the core liners were removed, capped on both ends, and taped shut until returned to shore. At the NWR, cores were vertically extruded in 2-cm intervals and stored for analyses. Cores for porewater studies were extruded into a porewater-squeezing barrel using a plastic coupling device (Orem et al., 1997). Filtered (0.45-μm Gelman Acrodisc^{TM}) porewater samples, collected from selected depth intervals, were stored frozen and later analyzed for reactive P and NH_4 within 5 days (Strickland & Parsons, 1973; EPA, 1979). Water-column samples from the core sites were similarly analyzed (Orem et al., 1997). Precision is ± 2% for both.

Sediment grab samples collected in 1998 for analysis of nutrients (C, N and P) were lyophilized and sieved (850 μm) to remove large shells, sand, and rocks. Sediment samples collected by coring in 1999 were sieved (62 μm), which at these sites removed very little material. The sieved samples were milled to a powder, and prior to analysis, were dried overnight at 60 °C to remove adsorbed water. Total C, OC and N were determined using a Leco 932 CHNS Analyzer^{TM} (Leco Corp., St. Joseph, Mich.); OC was determined after removal of carbonates (Orem et al., 1999). Total P was determined by baking ~0.5 g of dried sediment at 550 °C, extracting the residue in 1 M HCl, and analyzing the extracted TP (Strickland & Parsons, 1973; Aspila et al., 1976). Precision is ±1% for TC and TN, ±2% for OC, and ±3% for P.

Results and discussion

Only selected data collected during 1998 and 1999, discussed below, are included in this article because of space limitations. Additional data available but not included herein are: (1) numerous organic compounds whose concentrations were below the method reporting level (MRL) from grab sediment at 11 sites, (2) more than 40 elements in grab sediment from 11 sites and in sediment from about 20 samples at 2-cm intervals in cores from two sites, and (3) profiles of temperature, salinity, DO, and pH at nine of the 11 sites sampled in 1998. These data can be obtained from the NWIS public website (http://water.usgs.gov/ca/nwis/qwdata/), using the station ID numbers listed in Table 1, or directly from the senior author.

Water quality

The specific conductance values (Table 2) measured in bottom water samples collected from the 11 sites sampled in 1998 ranged from 54 300 to 54 800 μS cm^{-1} at 25 °C, a range that is within the measurement error of ±1%, indicating an essentially constant salinity for the bottom water. Measured residue-on-evaporation (ROE) at 180 °C on the same bottom-water samples ranged from 40.8 to 43.1 g l^{-1} (Table 2), indicating constant salinity within the analytical precision of ±3%. Profiles of salinity, expressed as ROE and calculated from field conductance measurements at all 11 sites exhibit considerably more variation with depth at a given site and differences in surface water between sites (profiles from Sites 1 and 9 shown in Fig. 3). Salinity differences in near-surface water between sites illustrate the local effect of dilution from the large freshwater sources (the Alamo and New Rivers) that discharge at the south end of the Sea (Fig. 3). The profiles indicate salinity increases with depth, especially in deeper parts of the Sea, as a result of thermal density stratification that is typical of summertime conditions (Fig. 3).

These results indicate that water samples for lake chemistry should be taken from near the lake bottom and preferably near the center of the lake to minimize the effect of spatial inhomogenity, if the purpose is to ascertain short-term interannual salinity trends. For evaluating trends and validating geochemical-model predictions of mineral precipitation, it would also be helpful to have annual analyses of all the major ions.

Historically there have been numerous chemical analyses of water from the Salton Sea, but these are restricted largely to determination of salinity (total dissolved solids) and major constituents. The Salton Sea started as a fresh water lake in 1905–1907, but water salinities increased (water levels declined after the initial rise) rapidly due to the high evaporation rate, reaching a value of about 50 000 mg l^{-1} in 1935 (Fig. 4). Water salinities decreased substantially between 1935 and 1955 as water levels rose from increased input of irrigation water. Salinities then show a general increase with time (currently about 44 000 mg l^{-1}), even though water levels remain essentially unchanged since about 1980 (Fig. 4), indicating a dynamic steady state between evaporation and irrigation input.

Salinity of the Salton Sea is increasing because it is a terminal lake with minimal ground–water interaction (Hely et al., 1966) and large amounts of salts, ≈4.5 million metric tons annually, are carried in surface-water discharges. However, the salinity increase is significantly less than would be expected on the basis of mass balance, indicating precipitation of some of the less-soluble salts (Tostrud, 1997). Computer simulations were run on chemical data collected in the late 1980s from source waters and from water in the Salton Sea to calculate saturation indices (departure from equilibrium) for minerals using thermodynamic information in the geochemical code PHREEQC (Parkhurst, 1995). Results indicate that precipitation of calcite is likely and that precipitation of gypsum is probable within the lake (Fig. 5). Incorporation of large amounts of calcite in bottom sediment is confirmed by x-ray diffraction on the bottom sediment (B. Jones, 2001, written communication) and by finding as much as 40% by weight in sediment from deepwater sites in the 1998 grab samples (calculated from IC data in Table 4). Gypsum precipitation also is confirmed by x-ray diffraction on the bottom sediment (B. Jones, 2001, written communication). Calcite and gypsum precipitation also are indicated from temporal trends in the concentrations of Ca, HCO_3, and SO_4 relative to Cl, in water from the Salton Sea (Tostrud, 1997).

The effect of biological production and summer stratification is evident on DO profiles (Fig. 3). Oxygen is present in surface water at all 11 sites, but is vir-

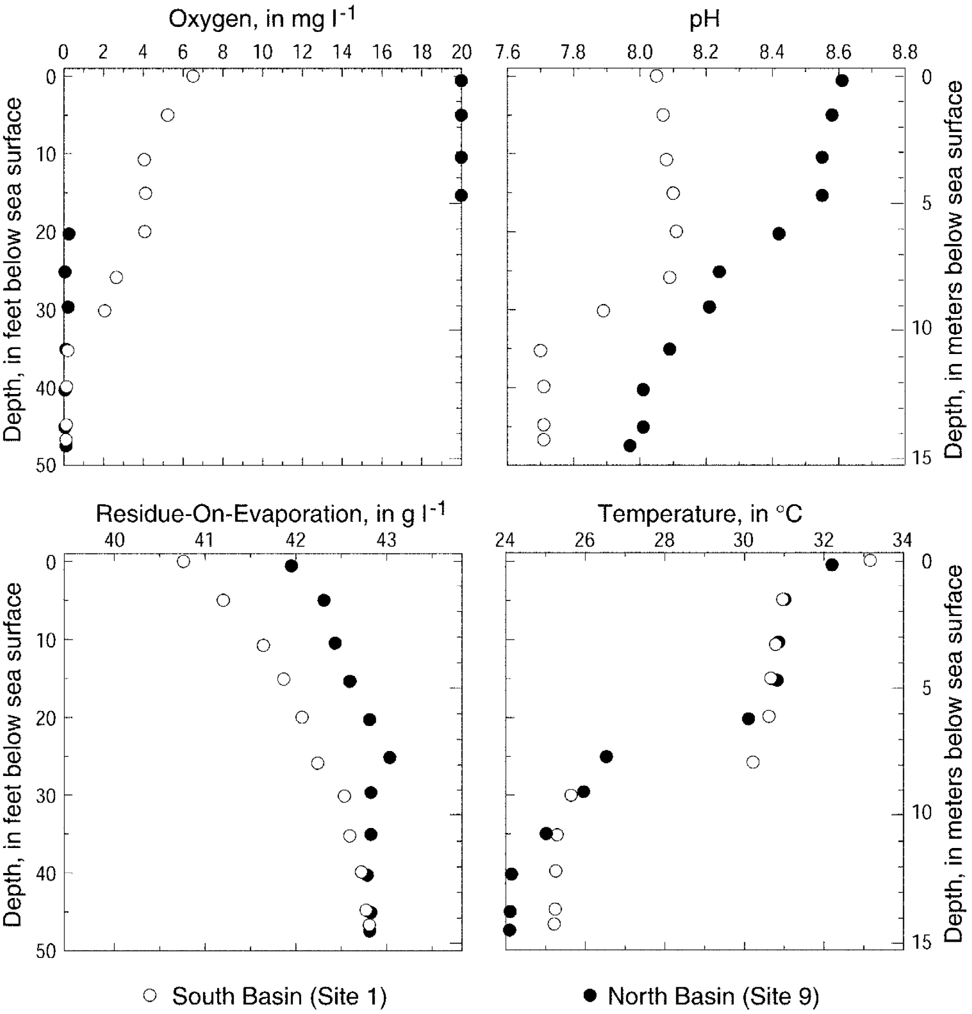

Figure 3. Selected water-quality profiles in the Salton Sea, July 1998.

Table 1. Physical characteristics of bottom sediment from the Salton Sea. Initial 13 digits in ID are site latitude and longitude, grain size is in percent by weight and depth is in meters

Site no.	Station ID	Depth	Clay	Silt	Sand	Visual field observations
1	331600115453001	14.6	86	13	1	Olive-gray organic muck
2	331400115450001	13.1	62	18	15	Olive-gray organic muck
3	331400115380001	4.6	<1	1	99	Medium fine sand
4	331023115473701	4.6	20	27	53	Many barnacle shells
5	330835115434501	4.6	14	10	76	Some barnacle shells
6	331215115410001	9.1	33	33	34	Some worm tubes
7	331930115484001	13.1	64	19	17	Olive-gray organic muck
8	332637115512001	9.1	32	35	33	Abundant live barnacles and pileworms
9	332400115553001	15.2	81	13	6	Olive-gray organic muck
10	332908116011501	9.1	49	50	1	Dark gray clay + organic muck
11	332958116023501	4.6	29	68	3	Black clay

Table 2. Selected aqueous data from bottom water in the Salton Sea, July 1998. Concentrations in mg l^{-1}, SC in dS m^{-1}, and ROE in g l^{-1}

Constituent Site no.	1	2	7	9	6	10	3	4	5	8	11
	(Deep)				(Medium)		(Shallow)				
Temperature, °C	25.2	25.5	24.8	24.1	26.4	31.1	29.3	28.7	29	31.1	31.5
Dissolved oxygen	0.1	0.1	0.1	0.1	0.1	15	1.1	<0.1	<0.1	16	9.3
Ammonium-N	1.7	1.7	1.8	2.2	1.8	0.7	1.1	1.4	1.3	0.74	0.78
Organic-N	3.2	3.1	2.8	3.2	3.4	2.9	3.0	2.9	2.9	3.0	2.9
Nitrite-N	<0.01	<0.01	<0.01	<0.01	<0.01	0.03	0.02	<0.01	<0.01	0.04	0.03
Nitrate-N	0.05	<0.05	0.05	0.05	0.05	0.11	0.07	0.05	<0.05	0.08	0.09
Orthophosphate-P	0.044	0.054	0.043	0.04	0.044	0.028	0.029	<0.010	0.022	0.016	0.011
Silica	14	14	15	16	15	7.7	9.7	11	11	7.6	7.3
SC at 25 °C	54.7	54.8	54.3	54.8	54.7	54.5	54.4	54.6	54.7	54.8	54.6
ROE at 180 °C	43.1	43.1	42.6	42.0	41.3	43.2	43.2	40.8	42.5	41.2	43.1
DOC	44	-	42	42	40	42	43	42	43	43	44
Alkalinity as $CaCO_3$	210	210	210	210	210	210	210	200	220	190	190

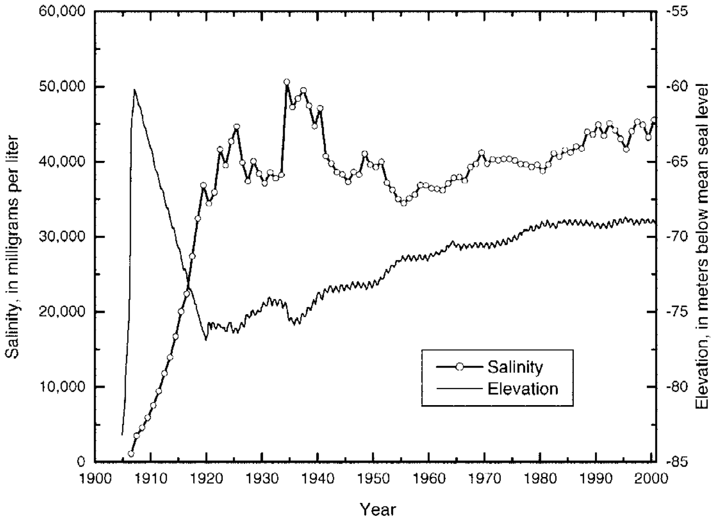

Figure 4. Historical averaged annual Salton Sea salinity and monthly surface water elevations (at Fig Tree John). Data before 1929 from Tostrud (1997), the rest from Imperial Irrigation District files.

tually absent in bottom water from the deep sites, and even from shallow sites in the south basin (Table 2). However, bottom water at Site 8, 10 and 11 is supersaturated (9–16 mg l^{-1}), creating conditions, especially at Site 8, near Salt Creek (Fig. 2), for numerous live pileworms and barnacles in bottom sediments. Just as DO decreases with increasing depth, so also does pH, reflecting the dominance of respiration and organic-matter degradation over primary biological production (Fig. 3).

Bottom water from the 11 sites was analyzed for the nutrients C, N and P. The results (Table 2) compare favorably with those from a single sample collected in the late 1980s (Schroeder, 1996). Virtually all of the aqueous nitrogen is in reduced forms. Ammonium concentration ranges from 0.74 to 2.2 mg N l^{-1} (highest at the deepwater sites) and organic nitrogen ranges from 2.8 to 3.3 mg N l^{-1}. Concentrations of both reduced species are far higher than are concentrations of nitrate, which ranges from <0.05 to only 0.11 mg N l^{-1}, and nitrite, which is detectable (>0.01

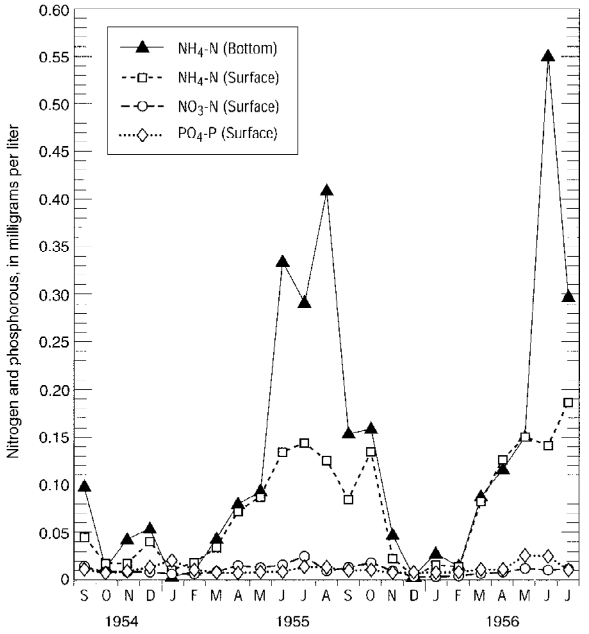

Figure 5. Historical nutrient concentrations in the Salton Sea (from Carpelan, 1961). (Compare to current concentrations given in Table 2).

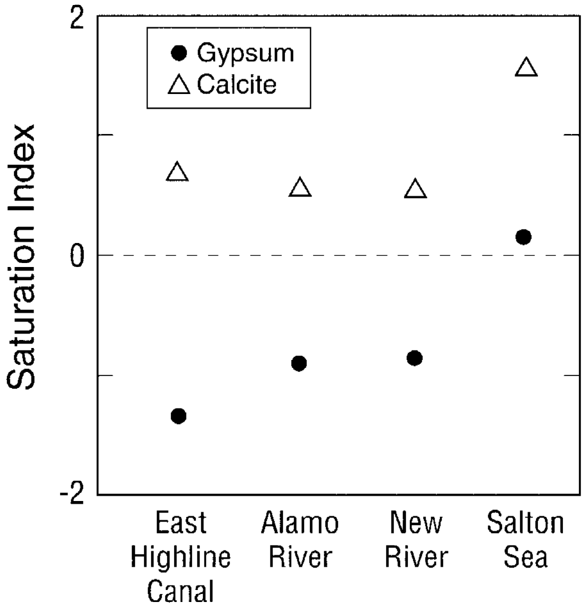

Figure 6. Saturation indices (departure from equilibrium) for calcite and gypsum in the Salton Sea and its source waters.

mg N l^{-1}) only at those sites where nitrate also is present (Table 2) .

Orthophosphate and dissolved hydrolyzable P concentrations were found to be low (0.01–0.05 mg P l^{-1}) and so near the MRL that results are subject to large uncertainties (Table 2). Comparison of these nutrient concentrations with levels that existed in the mid-1950s (Fig. 6, reproduced from Carpelan, 1961), only a few years after the heavy use of chemical fertilizers began, indicates a several-fold increase in NH_4, and little or no change in P. Possible explanations for the low P are discussed later in the section, 'Phosphorus Removal'.

Dissolved organic carbon (DOC) concentration in bottom water ranges from 40 to 44 mg C l^{-1}, which is within the analytical precision. This yields a C:N:P atom ratio of about 4000:400:1 for water in the Salton Sea, which can be compared to 800:15:1 in the ocean and 80:15:1 in soft biological tissue (Broecker, 1974). The classical interpretation of this nutrient concentration and ratio data is that the Salton Sea is highly eutrophic and that P is by far the limiting nutrient relative to N, although the possible role of micro-organisms and detritus on light attenuation and mixing within the water column as limiting factors also is recognized. The fact that the aqueous C/N ratio is somewhat higher in the Salton Sea ($\sim$10) compared to biological tissues (5–6) suggests that a large fraction of the high DOC is derived from biological production within the lake (is autochthonous), but that external (allochthonous) loading also is substantial.

Bottom sediment

Visual observations and grain-size data from the sampling in 1998 (Table 1) show an increase in the fine-particle content at sites more distant from shore, especially away from the large rivers located at the south end of the lake. Concentrations of organic carbon, selected trace elements, nutrients, and xenobiotic (synthetic) organic compounds are positively correlated with clay plus silt content, and hence, generally increase with distance from shore.

Organic compound data for which concentrations exceed the MRL ($\approx$5 μg kg^{-1} for aromatic hydrocarbons and $\approx$1 μg kg^{-1} for organochlorines) are summarized in Table 3. The sites are listed from deep to shallow across the table and the relation to distance from shore and with grain size is evident. Combustion of hydrocarbons and other organic matter from large urban centers, such as Mexicali, are commonly sources of PAHs; however, their concentrations are low in the Salton Sea (Table 3), because of dilution by relatively clean suspended sediment in irrigation runoff (R. Schroeder, 1995–6, unpublished data). The

Table 3. Selected organochlorine and aromatic hydrocarbon concentrations in surface sediment grab samples from the Salton Sea. Concentrations are in μg kg^{-1} dry weight; E = estimated value, close to the detection limit

Constituent Site no.	1	2	7	9	6	10	3	4	5	8	11
	(Deep)				(Medium)		(Shallow)				
Monocyclic and Polycyclic Aromatic Hydrocarbons											
Phenol	140	38	98	69	8.7	11	E3.8	8.1	5.3	30	16
p-Cresol	35	19	110	34	7	E8.2	<5	6.6	E3.1	15	9.3
2,6-Dimethylnaphthalene	630	300	1,100	460	43	66	E4.4	38	25	90	58
1,6-Dimethylnaphthalene	51	22	110	36	E3.9	E5.6	<5	E3.1	E2.5	6.4	E4.7
Phenanthrene	46	<10	<10	<10	<5	<10	<5	<5	<5	<5	E2.1
Anthracene	47	<10	<10	<10	13	<10	<5	<5	<5	<5	E2.3
Fluoranthene	E4.0	E2.7	12	E6.2	E1.6	E2.3	<5	<5	<5	E1.1	E3.8
Pyrene	E3.4	E2.5	16	E5.2	E1.3	E2.0	<5	<5	<5	E1.1	E3.5
Organochlorine Compounds											
Dieldrin	<1.5	<1.5	<1.5	<1.5	0.55	<1.0	<0.5	0.47	<0.5	0.59	0.7
DDE	14	10	39	24	4.1	6.0	0.24	1.5	0.67	3.0	4.4
DDD	E0.92	<1.5	<1.5	1.9	<0.5	<1.0	<0.5	<0.5	<0.5	<0.5	E0.46
DDT	<1.5	<1.5	<1.5	<1.5	<0.5	<1.0	<0.5	<0.5	<0.5	<0.5	<0.5
PCBs	<15	<45	<45	<15	<15	<5	<15	<15	<15	<15	<15

higher values for 2,6-dimethylnapthalene may reflect petroleum combustion sources (boats) within the lake or in the basin.

DDE (the predominant DDT metabolite), though of an agricultural rather than urban origin, also follows the aforementioned spatial pattern, with enrichment in the fine-grained organic-rich sediments from central parts of the Salton Sea (Table 3). Organochlorine concentrations are comparable to those reported in bottom sediment from drainage channels and rivers in the Salton Basin (Setmire et al., 1990) and, therefore, do not indicate any unusual enrichment within bottom sediment of the Sea. PCBs were not detected in any of the samples from the Salton Sea.

Concentrations of C, N and P, were determined in the <850-μm fraction of surface sediment from the 11 sites sampled in 1998 to evaluate the spatial distribution of these nutrients. Results on dry weight basis (Table 4), display the same spatial pattern already described, with highest concentrations found in the finest sediment far from shore. Inorganic carbon (IC) concentration ranges from about 1% in the Alamo River delta (Site 3) to about 5% in the center of the north basin (Site 9); these values indicate 10–40% calcite, since abundant calcite but no dolomite or magnesite were detected in x-ray diffraction analysis of bottom sediment (B. Jones, 2001, written communication). Organic carbon (OC) concentration at these two sites yields the full range of 0.08 and 6.3%, respectively.

Total N concentration exhibits a spatial pattern similar to that of OC and ranges from 0.06 to 0.97%. Total nitrogen is almost entirely composed of ammonium plus organic nitrogen because nitrate and nitrite are negligible in the reducing sediment. The relatively low OC/TN ratios of 6–8 (Table 4) indicate that the dominant source of sedimentary organic matter in the Salton Sea probably is from algae that use N from agricultural runoff (Meyers & Ishiwatari, 1993). The very low OC/TN ratios, below even that in living tissue, at Sites 3, 5 and 8 near the Alamo River, New River, and Salt Creek outlets, respectively, all occur in coarse-grained sediment with very low organic content. These ratios could reflect a greater relative contribution of inorganic nitrogen (ammonium) at these particular sites, or errors inherent in the analysis at these low concentrations.

Atomic OC/total P ratios (Table 4) fall into two groups; those >120, which generally occur in deep sites, and those <60. The higher values are somewhat larger than is typical for living algae, the major source of organic matter in sediment, suggesting recycling of P-rich organic detritus in the water column before deposition (Summons, 1993). Atomic N/P ratios also fall into two groups, with the deep sites having ratios >20

Table 4. Selected element concentrations in surface sediment grab samples from the Salton Sea. C, N and S concentrations are in percent dry weight; others are in mg kg^{-1}

Constituent Site no.	1	2	7	9	6	10	3	4	5	8	11
	(Deep)				(Medium)		(Shallow)				
Inorganic carbon	3.5	3.8	4.2	5.1	2.4	3.7	1.2	1.4	1.3	3.7	1.3
Organic carbon	5.2	4.7	3.8	6.3	1.30	3.4	0.08	0.65	0.39	0.68	1.6
Nitrogen	0.90	0.79	0.66	0.97	0.26	0.51	0.06	0.10	0.11	0.26	0.27
Phosphorus	790	850	670	660	580	690	180	530	330	560	700
Sulfur	3.6	3.5	4.3	4.6	1.5	2.2	1.4	2.5	2.1	5.6	1.4
Organic C/Total N	6.7	7.0	6.7	7.6	5.8	7.9	1.5	7.2	4.3	3.1	6.8
Organic C/Total P	170	190	150	250	58	130	12	32	30	31	58
Total N/Total P	25	27	22	32	10	16	8.0	4.4	7.1	10	8.5
Molybdenum	36	34	31	75	2.0	27	0.73	1.4	1.4	2.8	6.2
Selenium	8.8	5.8	8.0	9.7	1.5	11	0.58	0.90	1.0	1.8	2.7
Uranium	14	14	14	20	3.0	14	2.4	2.7	2.5	5.0	5.3

and the near-shore sites having ratios <10. Ratios that are higher than in soft tissue indicate N enrichment relative to P in the Salton Sea, as was noted earlier in the discussion on aqueous concentrations. In fact, the solid-phase data actually 'understate' the N/P ratio of sedimentary organic matter because a large proportion of the total P is natural input from soils, as discussed in later sections.

Sulfur (S) data (Table 4), exhibit a spatial pattern that is only partially similar to that of OC and various trace elements for which higher concentrations are generally associated with finer material. Site 8, near Salt Creek, is the most obvious exception in that it has the highest reported S concentration (Table 4) despite a relatively high coarse content (Table 1). As noted earlier, the bottom sediment at this site contained numerous live barnacles and calcareous concretions, together with gypsum. The S/Se ratios (Table 4) in near-shore sites are generally higher (S is enriched relative to Se) compared to deep sites. Apparently, Se-depleted gypsum makes a greater contribution within the coarse sediment closer to shore.

The earliest Se concentrations in bottom sediment collected by the USGS from the Salton Sea was from a grab sample obtained in 1986 along an arc between the center of the south basin and the outlets of the Alamo and New River (Schroeder et al., 1988). The Se concentration on the sieved silt + clay fraction was 3 mg kg^{-1}, which is about 10 times higher than average Se concentrations in soil from the Imperial Valley (Schroeder et al., 1993). Sixteen samples taken closer to shore in the Alamo River delta had Se concentrations of 0.2–2.9 mg kg^{-1} (Schroeder et al., 1993; Setmire et al., 1993). On the basis of the apparent relation to distance from shore, a single grab sample was collected from near the center of the lake in May 1996 that yielded the highest Se concentration of 9 mg kg^{-1} (Setmire & Schroeder, 1998). Data from the 11 sites sampled in 1998 (Table 4) confirm the anticipated spatial pattern of lower concentrations for Se and other trace elements in the coarser sediment near the riverine sources, and higher concentrations in the finer sediment from interior parts of the Sea.

Nitrogen and selenium mass balance

Understanding the fate and cycling of Se in the Salton Sea Basin is of special importance because: (1) Se is present in relatively high concentrations (2.5 μg l^{-1}), essentially all as selenate, in irrigation water delivered from Colorado River (Engberg, 1999; Kharaka et al., 2001); (2) Se concentrations in subsurface drainwater, present mainly as selenate, are much higher (generally 10–100, and up to 300 μg l^{-1}) than in irrigation water, primarily due to high evapotranspiration in the desert conditions (Setmire & Schroeder, 1998; Kharaka et al., 2000); and (3) the present USEPA chronic water-quality criterion that is protective of wildlife and aquatic life is only 5 μg l^{-1}; furthermore, many aquatic biologists believe the criterion value should be lowered to 2 μg l^{-1}, because Se is rendered more toxic by bioaccumulation in the food chain of fish and avian populations (Presser et al., 1994; Engberg et al., 1998).

Selenium occurs in four oxidation states, at the redox conditions that exist in the Salton Basin, that determine Se partitioning between water, sediment and air and thus determine its bioavailibility and toxicity (Schroeder et al., 1993; Setmire & Schroeder, 1998). Irrigation drainwater is aerobic in nearly all parts of the Salton Basin: hence, Se occurs dominantly as the highly soluble selenate (+VI) in both irrigation water and subsurface drainwater (Kharaka et al., 2000). The concentration of Se in the imported Colorado River water is high ($\sim$2.5 μg l^{-1}) and Se values are further concentrated in subsurface drainwater, with a median value of $\sim$30 μg l^{-1}, and ranging up to 300 μg l^{-1}. Stable water isotopes (Michel & Schroeder, 1994) and the ratio of conservative chemical components, Se/Cl and Se/B, indicate that the high Se concentrations in drainwater as well as water salinities that average 5000 mg l^{-1} total dissolved solids, result primarily from the extremely high evapotranspiration rates ($\sim$1.8 m yr^{-1}) in the desert environment of the Salton Basin (Setmire & Schroeder, 1998; Kharaka et al., 2000).

The biogeochemical cycle of Se in anoxic environments such as those encountered in the deeper water and bottom sediment of the Salton Sea result in the reduction of selenate to selenite (+IV), Se° (0) and ultimately to metal and organically bound selenide (-II) (Cooke & Bruland, 1987; Oremland, 1994; Setmire & Schroeder, 1998). Dissolved Se concentrations in anoxic environments are low because selenite and Se° have a high affinity for sorption onto sediments, especially organic matter, clay minerals and iron oxyhydroxides and the solubility of metal selenides, including $FeSe_2$ and $CuFeSe_2$, is extremely low (White & Dobrovsky, 1996; Kharaka et al., 2001). Also, some of the end products of Se reduction, such as the hydrogen and alkyl selenides, are gases and could potentially be volatilized to the atmosphere (Cooke & Bruland, 1987). The environmental geochemistry of Se is detailed in a recent volume edited by Frankenberger & Engberg (1998).

Dissolved Se concentrations in Salton Sea water are low (0.5–2 μg l^{-1}) and Cl values are about 17 000 mg l^{-1}, resulting in Se/Cl ratios (about 0.006×10^{-5}) that are much lower than those of the drainage water in Salton Basin or the roughly equivalent value for the Colorado River water (2.2×10^{-5}), indicating that Salton Sea is a major sink for Se (Cooke & Bruland, 1987; Setmire & Schroeder, 1998; Kharaka et al., 2001). Were Se to continue accumulating in the water, as has the conservative Cl, the Se concentration in the Salton Sea would have risen to about 400 μg l^{-1} (Schroeder & Orem, 2000). This analysis shows that more than 99% of Se that has entered the Salton Sea is no longer present in the water column. The missing Se may be sequestered in bottom sediment, in biota, and (or) may be lost by volatilization. Results discussed below strongly suggest that virtually all of the Se in the Salton Sea is present in the bottom sediment.

The amount of Se in the lake's biota can be estimated from the concentration of Se in different organisms that reside in the water column reported in Schroeder et al. (1993). It is estimated that the lake contains 10^8 fish (Riedel et al., 2001). Using an average weight of 1 kg per fish and a Se concentration of 2 μg g^{-1} (wet weight) (Setmire & Schroeder, 1998), yields 200 kg of Se in fish tissue. This compares with about 10 000 kg of Se in the water column, estimated by multiplying the lake's volume of 10^{13} l (7.6 million acre-ft), calculated from the dimensions of the Salton Sea given in the introduction) times an aqueous Se concentration of 1 μg l^{-1}. Thus, the Se in fish tissue is only 2% of Se in solution. Additional Se is present in organisms from lower trophic levels, but the exact amount of this Se is not known at this time. The total Se from lower organisms probably is not likely to significantly exceed the total Se in fish, even though the mass of these likely is an order of magnitude or more greater than the mass of fish, but the Se content of these organisms is lower than that of fish, by a factor of 10 for algae (Setmire & Schroeder, 1998; Fig. 5, p. 219).

The loss of Se from the water column by volatilization can be studied by examining its speciation data, which show no selenate, even in the oxygenated surface waters of Salton Sea, and show that selenite comprised 33% of total Se in the upper 4 m, but selenite was not detected in deeper water. The bulk of Se (58–81%) is in the form of nonvolatile organic selenides, but the volatile dimethyl selenide (DMSe) comprised 2–11% and showed increased percentages with depth, possibly indicating degassing at the lake surface (Cooke & Bruland, 1987; Setmire & Schroeder, 1998).

Estimation of Se and N loss from the Salton Sea water by volatilization to the atmosphere or sequestration within bottom sediment can be made through a comparison of Se and N concentrations with those of two other elements, (molybdenum) Mo and (uranium) U. These four elements (though to a lesser extent for N) exhibit similar geochemical behavior; they occur as highly soluble species in aerobic environment, such as the rivers that deliver them to the Salton Sea, and as insoluble species in anaerobic conditions, such as the bottom sediments, where they are sequestered (Calvert, 1976; Setmire et al., 1993). Because Mo and U, unlike Se and N, do not occur as gases during reduction, they can be used to 'normalize' for the possible loss by volatilization of Se and N. Therefore, any decrease in the ratio of Se and N to Mo and U between rivers that discharge to the Salton Sea and bottom sediment within the Sea itself is a measure of net removal from the system. Because of the environmental importance of Se and N, it is important to know whether the Se and N discharged to the Salton Sea are removed as a result of volatilization, or whether they are retained within its bottom sediment.

In order for the conclusions from the simple calculations that follow to be valid, the amount of each element contained within the Salton Sea's water must be negligible compared to that element's total input. It has already been noted that less than 1% of the total Se ever discharged to the Sea now resides in its water. Concentrations of Mo and U in the Salton Sea are only a few micrograms per liter and also represent less than 1% of the total amount in surface water discharged to the Sea (Schroeder et al., 1993; Schroeder, 1996). If N discharge has remained about the same for the past 50 years (the period during which use of chemical fertilizers has been widespread), aqueous N concentration in the Salton Sea would be about 20 times higher (Schroeder & Orem, 2000) than the approximately 5 mg l^{-1} now present. The DOC contained in the Salton Sea equals about 20% of total input from surface-water discharges, based on current DOC concentrations in the Alamo and New Rivers – an amount that is still minor, but not negligible.

Validity of this calculation is also dependent on condition that the data must be representative of conditions over at least the previous 10–15 years – a period that matches the top 2–3 cm of deposition for the sediment grab samples collected in 1998. River concentrations are obtained from monthly monitoring (single sample from each river for U) for one year (1988–89) from the two major rivers that convey irrigation runoff, the Alamo and the New, at their outlets to the Salton Sea (Schroeder et al., 1993). The two rivers represent almost 80% of total water discharge to the Sea. About half of the remaining water discharged to the Salton Sea is from surface drainage channels, which have chemical concentrations similar to those of the two major rivers, and from the Whitewater River, which also carries substantial irrigation drainage (Michel & Schroeder, 1994). The remaining sources have little additional influence on element ratios of surface water discharged to the Sea.

Although the aqueous data used in the subsequent calculation are from monitoring for one year (1988–89) only, long-term monitoring values reported for salinity and Se (Iwatsubo, 1993), and compiled for N (Fig. 7), the element that exhibits the highest variability in the rivers, can be used to establish the fact that mean annual chemical concentration in surface water discharged to Salton Sea has not changed significantly during the last 30 years. The N data are from the Alamo River at Drop 3 (Fig. 1), about 10 km upstream from the river's outlet to the Salton Sea. Nearly all of the water in the Alamo River is from agricultural runoff in the Imperial Valley and its chemical composition changes little between Drop 3 and the river's outlet.

Calculations for 5 elements, using 1988-89 river data in Schroeder et al (1993) and apportioning 60% to the Alamo and 40% to the New River, yields the following mean input concentrations:

Element	Weighted concentration
Nitrogen	9.3 mg l^{-1}
Selenium	6.3 μg l^{-1}
Uranium	15.8 μg l^{-1}
Molybdenum	12.3 μg l^{-1}
Organic carbon	10.4 mg l^{-1}

The RSD on these values is about 20% (ranges from 17% for Mo to 23% for N). Note that for U the value is based only one sample from each river. Because of the small number of samples, U data are used only to substantiate results calculated using Mo.

The mean mass ratios of Se:Mo:U:N:C are 1:2.0:2.5:1500:1700 in river input. The analogous ratios are 1:3.0:2.3:1100:5400 in surface sediment from the Salton Sea (data in Table 4). The RSD values for element ratios from bottom sediment are lower when normalized for U than for Mo; the values, as expected are higher (about 50%, with a range from 32% for Se/U to 74% for OC/Mo) for bottom sediment than for river inputs. Using the above elemental ratios, the calculated values obtained by normalizing for Mo yield the following results: 33% loss for Se, 51% loss for N and 112% gain for OC. The calculated values obtained by normalizing for U are: 10% gain for Se, 20% loss for N and 247% gain for OC. Results obtained with

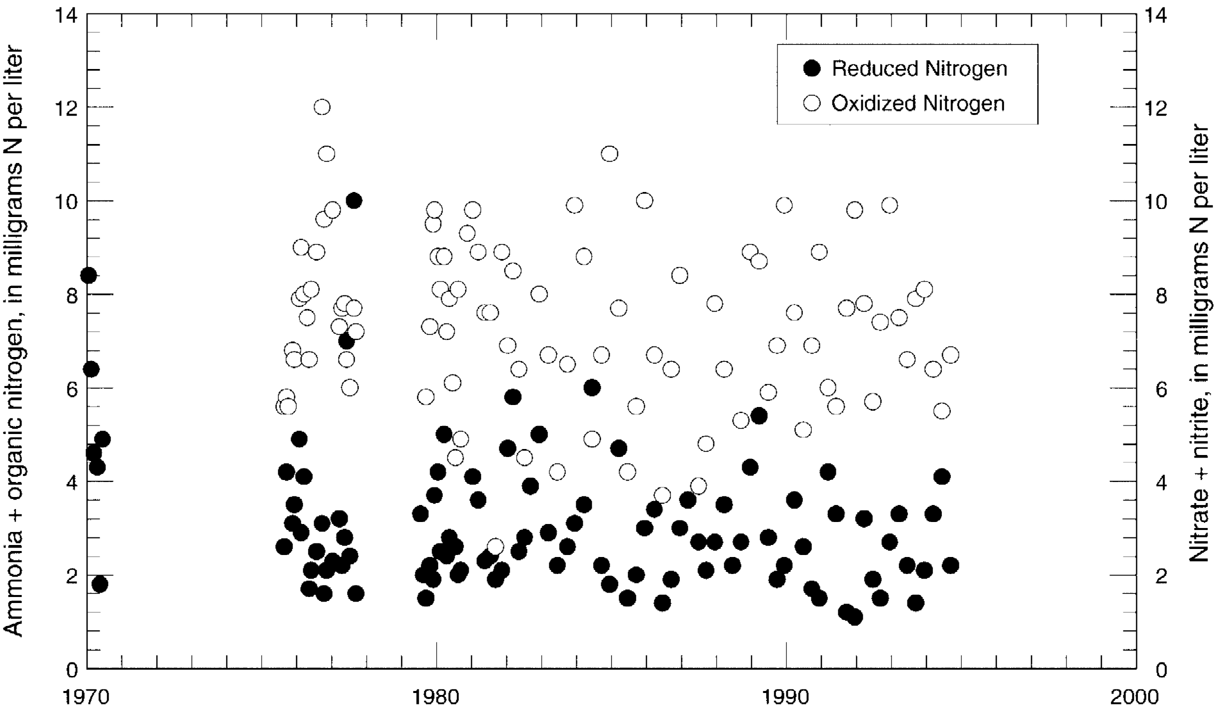

Figure 7. Nitrogen concentrations in the Alamo River at Drop 3 (shown in Fig. 1) since 1970.

Mo and U are comparable within data limitation, and indicate major net production of OC, some loss of N and possibly minor loss of Se within the Sea itself. The calculated gain for OC is a 'net' value; and hence, does not account for any recycling of carbon within the water column or at the water–sediment interface, which could be quite extensive in this eutrophic lake. Significant production of OC within the Salton Sea also was inferred (and discussed elsewhere in this paper) on the basis of low C/N ratios in water and sediment. The losses calculated for Se and N carry large uncertainties as a result of slight differences in the geochemical behavior of these elements, data limitations and spatial differences, but imply that most, if not all, the Se and N discharged to the Salton Sea remains within the Sea's sediment where the elements are potentially available to the benthic biota, or for remobilization into the overlying water. Detailed measurements of mass balances and fluxes for all compartments of the geochemical cycle, including all biota and wind deposition, for each element has the potential to yield improved estimates for net fluxes of Se and N.

Nutrient profiles in cores

Vertical profiles of C, N and P in cores from Site 9 in the north basin and from Site 10 in water of medium depth between the north basin and Whitewater River delta are shown in Figure 8. Nutrient and inorganic element profiles suggest that the depositional history recorded from Site 10 may not be continuous (slumping or episodic redistribution), and therefore results from this core are discussed in less detail than are those from Site 9.

Concentrations of OC and N decrease by almost an order of magnitude with increasing core depth in the center of the north basin (Site 9) and reach a relatively constant concentration a little below 20 cm (Fig. 8). These OC and N profiles are used to delineate the horizon that represents formation of the Salton Sea and implies an average sediment accumulation rate of 2.3 mm yr^{-1}. Additional element data (Ca, S, Al, Se and Mo) that support this sedimentation rate are discussed later in the section, "Historical Record from Cores". Analysis of a single Ekman dredge sample collected in 1996 had indicated low activities for ^{137}Cs and for excess ^{210}Pb, probably because of inefficient scavenging from the atmosphere in this extremely arid environment. Radiometric analyses on cores collected in 1999

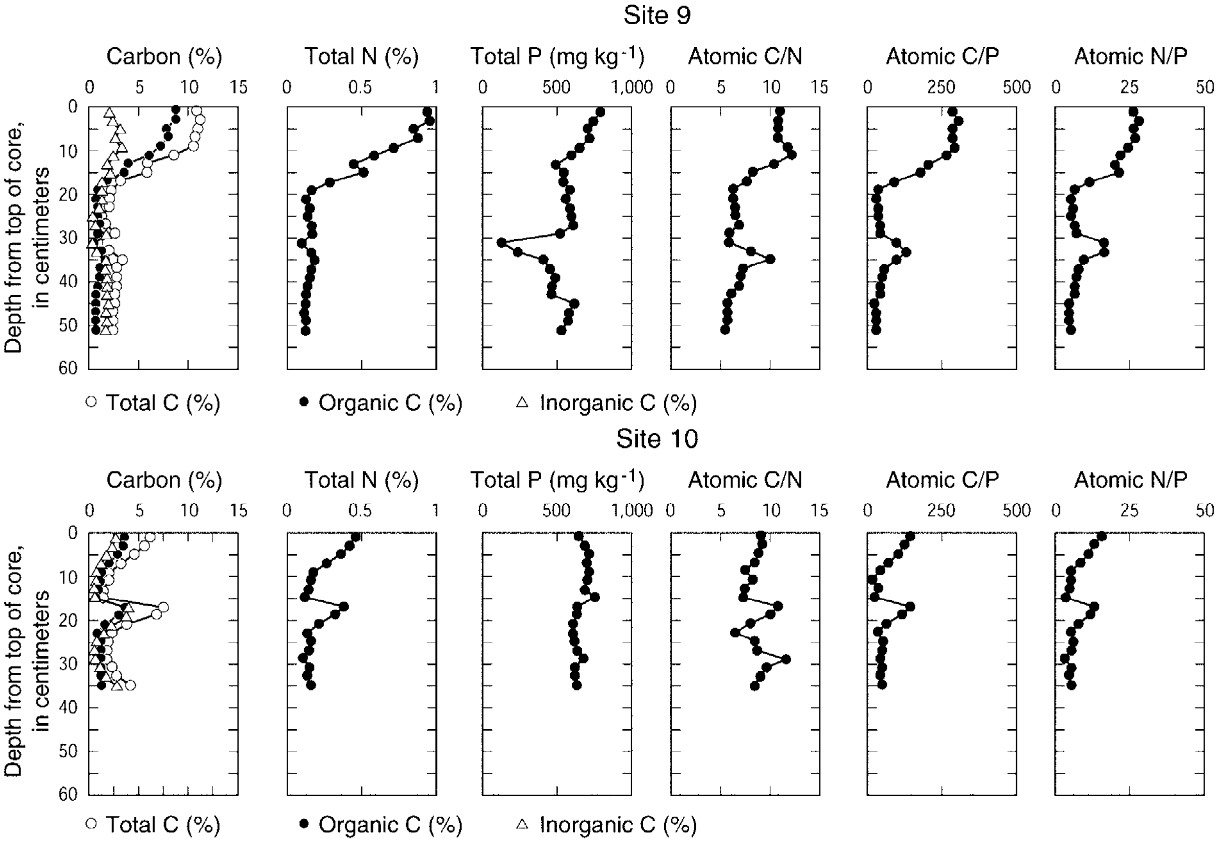

Figure 8. Nutrient profiles in core sediment from the Salton Sea.

confirmed the earlier result (J. Holmes, pers. comm.) and indicate that this method of dating will require larger diameter cores (more material) to be used. An alternative method to determine sediment ages is to match DDE profiles to the historical pattern of agricultural DDT use. Data on DDE in Table 3 indicate that this method would likely be successful in the Salton Sea, and could be used to date cores in the future.

The shapes of the OC and N profiles (Fig. 8) in the upper 20 cm do not approximate theoretical curves of diagenesis (Berner, 1980) and, therefore, suggest an increasing load of both OC and N over time. The slope of both curves declines above about 8 cm, suggesting a rapid increase in the load of both elements prior to about 1965 and only a modest increase since then. Inorganic carbon (IC) concentration varies much less than that of OC, presumably because calcite deposition has been occurring in the Salton Sea throughout its history. As a result, IC gradually increases as a proportion of total carbon (TC) from 19% at the surface to 77% near the bottom of the core from Site 9.

Phosphorus profiles, discussed in more detail later, show that P concentration decreases from about 800 mg kg^{-1} at the surface to 500–600 in depths that predate formation of the Salton Sea. The decrease in concentration, which is much less than for OC and N, implies that about two-thirds of the total P at the sediment surface derives from a natural (eroded soil) as opposed to an anthropogenic source and, therefore, may be in a refractory form.

Dry bulk density (DBD) information is needed to calculate element accumulation rates from concentrations and, as expected, DBD values increase with increasing core depth as water is expelled by the weight of the overlying sediment (Fig. 9). Current accumulation rates for C, N and P are calculated using the estimated sedimentation rate of 0.23 cm yr^{-1}, DBD data, and element concentrations from the 0 to 2-cm interval for the cores shown in Figure 8. The calculated accumulation rates likely represent minimum values, since the sedimentation rate is an average throughout the history of the Salton Sea and recent

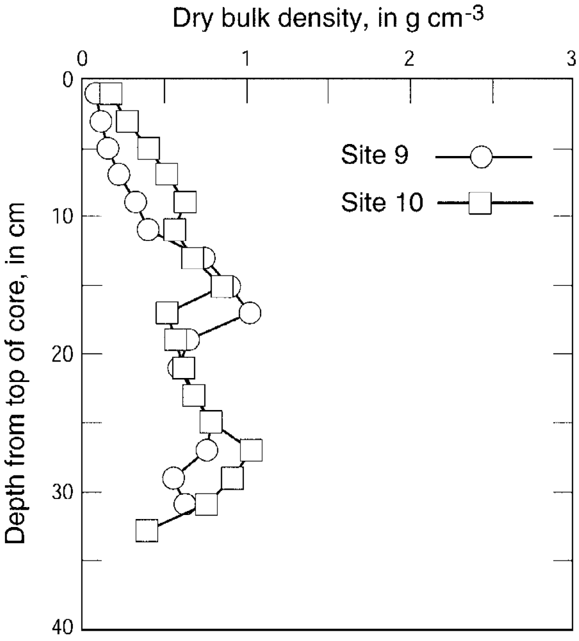

Figure 9. Density profiles in cores from the Salton Sea.

sedimentation rates may be higher because of eutrophication. Estimated minimum accumulation rates are as follows:

Element	Site 9	Site 10
Total C (g C cm^{-2} yr^{-1})	2.2×10^{-3}	2.3×10^{-3}
Organic C (g C cm^{-2} yr^{-1})	1.7×10^{-3}	1.3×10^{-3}
Inorganic C (g C cm^{-2} yr^{-1})	4.2×10^{-4}	9.8×10^{-4}
Total N (g N cm^{-2} yr^{-1})	1.9×10^{-4}	1.7×10^{-4}
Total P (g P cm^{-2} yr^{-1})	1.6×10^{-5}	2.4×10^{-5}

The estimated accumulation rates from the two sites are about the same for TC, OC and N and are reasonably comparable for IC and P.

Nutrient fluxes

The concentration of ammonium and dissolved reactive phosphorus (DRP) in overlying water and in porewater at Sites 9 and 10 are shown in Figure 10. Concentrations of both ammonium and DRP are much higher in porewater than in the overlying water, reflecting the recycling of labile sedimentary N and P (Berner, 1980). Higher concentrations of ammonium and DRP in porewater relative to the overlying water indicate a flux of these nutrients out of the porewater. The flux of ammonium and DRP from the porewater into the overlying water at Sites 9 and 10 was calculated from Fick's Law of Diffusion:

$$F_i = -\phi D_i \theta^{-2} (dc/dz),$$

where F_i is the diffusion flux of species i, ϕ is sediment porosity, D_i is the diffusion coefficient for species i, θ is tortuosity of the sediment, and dc/dz is the linear slope of the concentration *versus* depth curve of the species of interest in porewater. Porosity is approximated from a water content of 90% by volume, and an average dry bulk density (DBD) of 0.493 g cm^{-3} for sediment from the upper 24 cm at Site 9 and 0.554 g cm^{-3} for the upper 26 cm at Site 10 (Fig. 9). Tortuosity is assumed to be 1. Diffusion coefficients for ammonium and DRP in the Salton Sea are taken from Krom & Berner (1981). Calculated fluxes are then:

	Site 9	Site 10
Ammonium	2.5×10^{-6} $\mu g\ cm^{-2}\ s^{-1}$	1.4×10^{-6} $\mu g\ cm^{-2}\ s^{-1}$
DRP	3.2×10^{-7} $\mu g\ cm^{-2}\ s^{-1}$	1.2×10^{-7} $\mu g\ cm^{-2}\ s^{-1}$

Estimated flux of both ammonium and DRP is higher at Site 9 than at Site 10. This reflects the steeper increase (higher gradient) in porewater concentrations with depth at Site 9. The estimated fluxes are comparable to those reported for near-shore marine sediments (McCaffrey et al., 1980; Klump & Martens, 1981).

Nutrient flux from the bottom sediment, derived from these two cores, can be compared with discharge from surface water to determine relative contribution from each. Using an average value for fluxes listed above and a lake area of 1000 km^2 yields annual loads by diffusion out of the bottom sediment of about 6×10^5 kg yr^{-1} for N and about 7×10^4 kg yr^{-1} for P. Annual discharge from rivers and surface drains carrying mostly irrigation drainage is computed from a water discharge of about 1 km^3 and average N and P concentrations at the outlet to the Salton Sea of approximately 10 and 1 mg l^{-1} yielding 10^7 and 10^6 kg yr^{-1}, respectively. The conclusion is that nutrient loading from surface water discharged to the Salton Sea exceeds that from diffusion out of its bottom sediment by about an order of magnitude.

A second mechanism, in addition to diffusive flux, whereby N can potentially be reintroduced into the water column is by oxidation of sedimentary ammonium and organic nitrogen in parts of the Salton Sea where high-DO bottom water is in contact with the sediment surface. To test this hypothesis, a covered and continuously stirred mixture of sediment from the

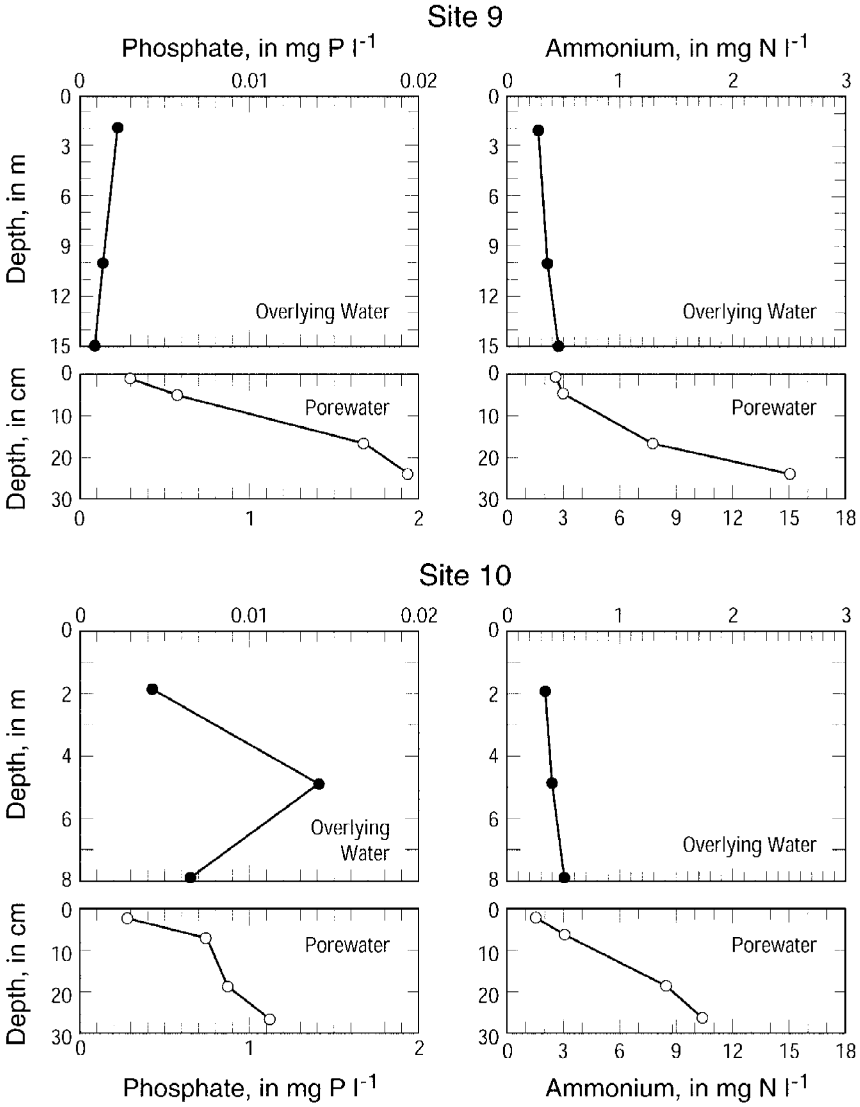

Figure 10. Nutrient profiles across the sediment–water interface in the Salton Sea. (Note changes in scale.)

center of the north basin (Site 9) plus filtered surface water (four parts water added to one part wet sediment by volume) was infused with oxygen by bubbling with filtered air. Aliquots were periodically withdrawn for filtration and chemical analysis and results are shown in Figure 11. The sediment changed color from olive gray to reddish brown, indicating oxidation of iron sulfides, within a few days. Soon thereafter, nitrite, an intermediate species in N oxidation, appears, followed by nitrate that then continues to increase, reaching a value of 35 mg -N l^{-1} and becoming the dominant N species, for the remainder of the 70-day experiment. These results clearly show oxidation and mobilization of N from bottom sediment under aerobic conditions.

Selenium determinations were not attempted on these samples because Se concentrations were expected to be below detection limit after the dilution required (1:100) to lower the high salt content of water to values acceptable for the ICP-MS analysis. A modified ICP-MS method (Gil Ambats, pers. comm., 2001), involving lowering water salinity by ionic exchange and precipitation of AgCl and AgBr, made it possible to determine Se in a water sample kept in contact with sediment in sealed container after completion of laboratory experiment. The high concentration of

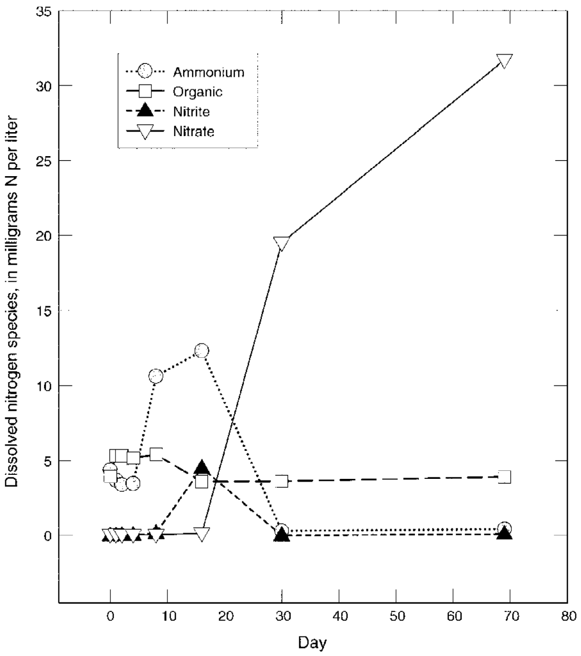

Figure 11. Nitrogen transfer from Salton Sea sediment to water in a laboratory simulation.

Se (15±4 μg l^{-1}, compared to ~1 μg l^{-1} in Salton Sea water) obtained in oxygenated water reacted with sediment, also suggest the possibility for oxidation and mobilization of Se from bottom sediment, as observed in many field investigations and column experiments (Presser et al., 1994; Kharaka et al., 2001).

It is noted that only the sites from shallow and medium depths shown in Figure 2 contain detectable, albeit very low, nitrate and nitrite concentrations in the bottom water (Table 2), where oxygen is generally present at higher concentrations than in deeper parts of the Salton Sea. This pattern could result from some minor oxidation of bottom sediment at these sites, oxidation of dissolved and particulate material within the water column itself, or both.

Phosphorus removal

A detailed understanding of the factors that control P concentration is important because of this element's role as a limiting nutrient in the Salton Sea. Aqueous N concentration appears to have increased by almost an order of magnitude since the early 1950s, but there seems to have been little change in aqueous P concentration. A similar historical trend is revealed by the concentration profiles in sediment cores (Fig. 8). The aqueous N:P atom ratio of 400 in the Salton Sea is nearly 10 times higher than the ratio in the Alamo River (N from Fig. 7 and P from Fig. 12). The New River at its outlet to the Salton Sea will likely have a little lower N:P ratio than the Alamo River because several percent of its flow consists of domestic and municipal wastewater from Mexico (Setmire, 1984). Clearly, aqueous and sediment data indicate P is being effectively scavenged from the water in the Salton Sea when compared to N.

One possible explanation for the apparent lack of a temporal increase in P is that most of the P that arrives at the Salton Sea is sorbed to sediment so strongly that it is not biologically available. Information on the physical and chemical forms of P on solid-phase material, which could be used to infer biological availability, is not currently available, and clearly is needed. In contrast to N, most of the P that is present in the Salton Sea is of natural, as opposed to anthropogenic, origin. In fact, the P concentration in core material beneath the 1905–07 boundary that marks formation of the Salton Sea at about 600 mg kg^{-1}, is about the same as the P concentration in Imperial Valley soil (Schroeder et al., 1993).

Lakes undergoing increasing eutrophication commonly owe the trend to recycling of P from anaerobic, organic-rich bottom sediment into the overlying water column. Yet, this does not seem to be occurring as rapidly in the Salton Sea, possibly because a substantial proportion of the P may be irreversibly sequestered within the bottom sediment as highly insoluble apatites (Schroeder & Orem, 2000). Apatite minerals form the skeletal material of vertebrates and the frequent die-off of as many as 10^{6} fish during single epizootics in the Salton Sea (Riedel et al., 2001) might be providing an efficient mechanism for removal of P from the water into the sediment. Sorption and incorporation in sedimentary calcite is another possible mechanism for sequestration of P. Estimates of the fish population and their skeletal P content along with mineral composition of the sediment are needed to ascertain the relative importance of each mechanism.

Historical record from cores

Analysis of cores from receiving water bodies can be a useful method to reconstruct historical changes (trends) in water quality where long-term monitoring data are scant or nonexistent (Schroeder, 1985; Callender & Van Metre, 1997; Van Metre et al., 1997). Selected major-element (Ca, S, and Al) concentrations from a core depicted in Figure 13 are used to

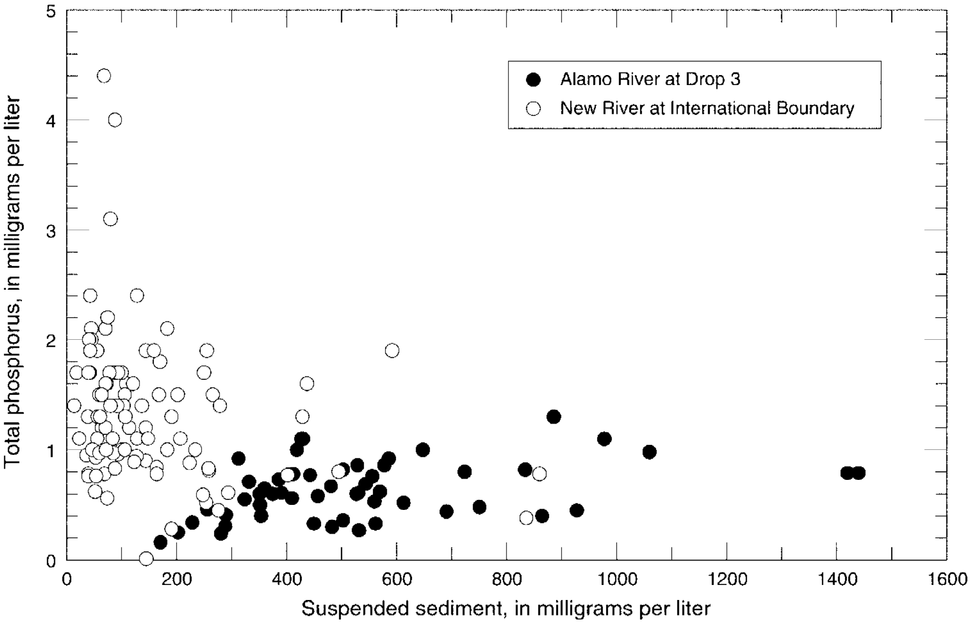

Figure 12. Relation between total-phosphorus and suspended-sediment concentrations in the New and Alamo Rivers since 1970.

infer the 1905–07 boundary that marks formation of the Salton Sea. The profiles show a distinct discontinuity at 22–24 cm, with high Ca and S and low Al relative to concentrations in sediment above and below this interval. (We observed that P concentration also drops markedly in this same interval.) These results likely are due to accumulation of efflorescent minerals, including gypsum, on the dry lakebed that preceded massive flooding which formed the Salton Sea. The gypsum, in effect, dilutes Al in this interval because it replaced much of the aluminosilicate material that composes the local soil. This 'gypsum dilution' also results in much lower concentrations for about 20 other elements (but increases for Mo and As) that typically are associated with the aluminosilicate phase.

Since the Colorado River is the source of irrigation water and Se that reach the Salton Sea, it is possible that chemical profiles in cores obtained for this study might reveal historical trends in the level of Se in the Colorado River itself. Measurements of concentration and discharge in the Colorado River and its tributaries indicate that Se behaves like a conservative ion as it moves downstream (Engberg, 1999). Selenium is transported to the Colorado River from weathering of seleniferous deposits in the Upper Colorado River Basin. Presently about 80% of dissolved Se load and 53% of total salinity are attributable to anthropogenic (mostly agricultural development) activities (Mueller & Osen, 1988; Trueman, 1999; Kharaka et al., 2001), but Se concentrations also may have been higher in the past from initial leaching as extensive undeveloped areas came under cultivation. Hamilton (1999) presents evidence for such higher historical exposures to Se locally within the Colorado River. The Se profile (Fig. 14) wherein concentration increases from about 9 mg kg^{-1} at the surface to about 15 at 10–12 cm, could indicate that Se in Lower Colorado River water diverted to the Salton Basin might have reached 4 μg l^{-1} in the past, compared to 2.5 μg l^{-1} today. The Se maximum at 10–12 cm (Fig. 14) could result from other geochemical processes, but its location in the core corresponds to a date of about 1950 in the Salton Sea, and allowing for the residence time of Se in the Colorado River system, translates to 1930–1940 in the Upper Colorado River basin (Michel & Schroeder, 1994).

Long-term implications for the Salton Sea

Protection of the ecological resources and enhancement of the economic value of the Salton Sea has recently stimulated a restoration effort. A part of that effort has produced an environmental impact report that evaluates the effect proposed remediation or 'no-action' will have on the Sea (Cohen et al., 1999). In

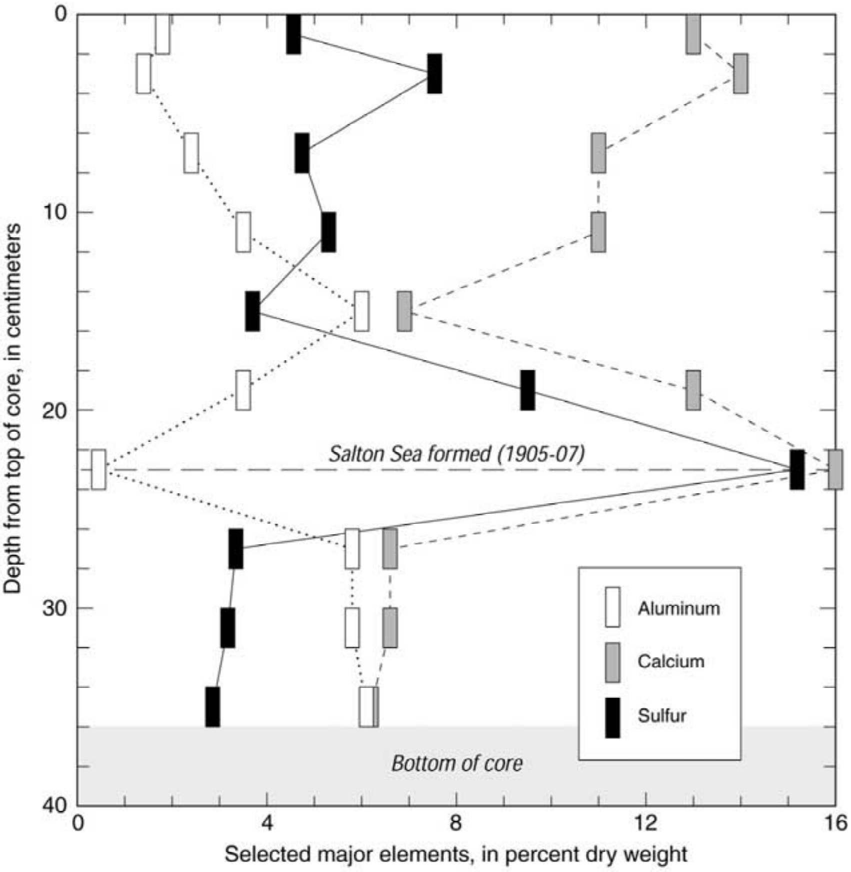

Figure 13. Selected major-element profiles in a core from Site 9 in the Salton Sea.

making predictions, it is wise to recognize how different current conditions are from what might have been anticipated 100, or even 50 years ago. The effects of intentional alteration (restoration) are even more difficult to predict. Therefore, we make only limited projections herein, and they apply to what might happen with no intervention.

The most obvious projection is that increasing salinity will eventually eliminate saltwater fish from the Salton Sea. The major-ion chemistry of the Sea will evolve by increased salinity and the precipitation of calcite, gypsum, sepiolite, and magnesite and/or dolomite, toward a relative increase in Na, Mg, Cl, and, SO_4, and a decrease in the proportion of Ca and HCO_3. In arid environments, as salinity increases pH also typically increases, but, this trend will not occur in the Salton Sea as long as water from Colorado River, with low HCO_3 and higher Ca and Mg, continues to be supplied to the basin.

Transfer of water currently used for irrigation in the Imperial Valley to the urban areas of southern California will convert submerged parts of the Sea to shoreline. If the decrease in lake elevation is about 4.6 m, texture and contaminant concentrations of the newly exposed sediment will not differ greatly from the current near-shore environment. However, bottom sediment from medium water depths (about 9 m) is higher in N and Se than from shallower depths, and this sediment would be exposed to more oxic conditions that generally prevail at shallower depths, increasing the possible remineralization (solubilization by oxidation) of these elements. Whether or not this causes an increase in concentration of these constituents within the water column will then depend on whether reducing conditions remain effective at transferring these elements to the bottom sediment in deeper parts of the Sea, as they appear to do now.

Removal of fish from the Salton Sea may have the most significant effect on aqueous P concentra-

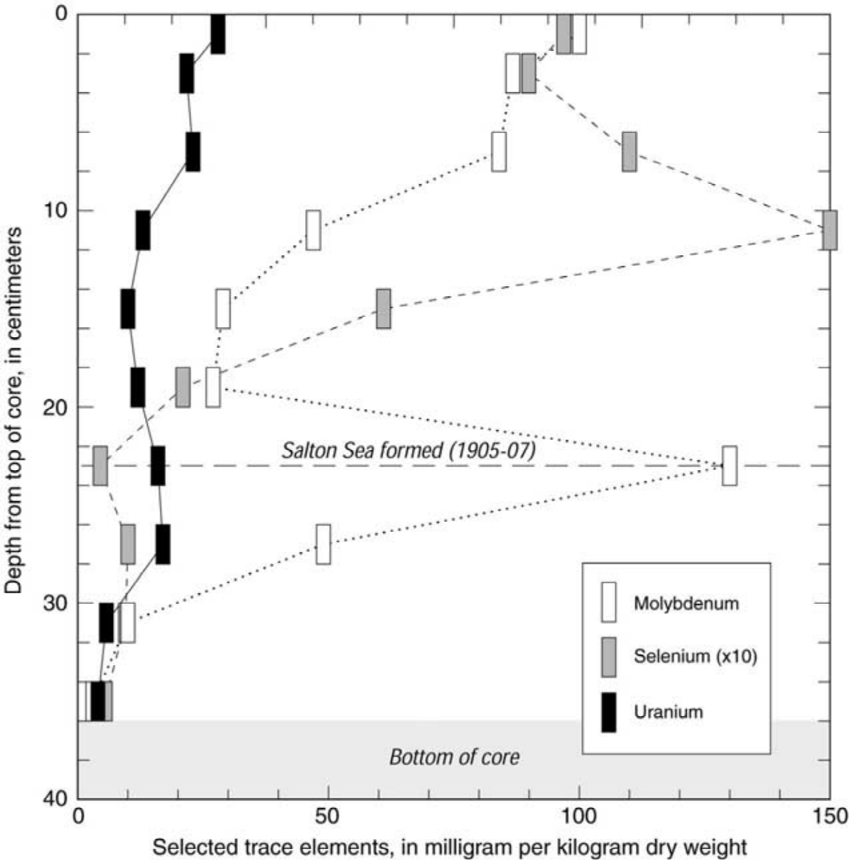

Figure 14. Selected trace-element profiles in a core from Site 9 in the Salton Sea.

tions. Since frequent fish die-offs are a significant mechanism for transfer of P into insoluble apatite minerals from water into bottom sediment, removal of fish will decrease the rate of this transfer. Furthermore, if fish become entirely absent, it is possible that greater recycling of P from anaerobic sediment into the overlying water may accelerate the Salton Sea's rate of eutrophication.

Finally, monitoring by the USGS on the New River at the international border has confirmed the transboundary transport of contaminants typical of urban centers, and their substantial dilution at the river's outlet to the Salton Sea. Long-lived DDT degradation products present on both sides of the border also are transported to and accumulate in the Salton Sea's bottom sediment. However, any of the anticipated changes at the Salton Sea are unlikely to have a significant effect on these contaminants, either because their concentrations are low or because there exists no extraordinarily effective mechanism for their enrichment in sediment and biota.

Summary and conclusions

The Salton Sea has been accumulating chemical constituents delivered by its tributary streams for nearly 100 years because it has no outlet. The buildup of soluble and unreactive chemicals, such as Cl, has resulted in the development of a quasi-marine lake. In contrast, chemicals that react to form insoluble phases ultimately enter the sediments that accumulate on the floor of the Sea. Solubility and sorption properties are especially relevant for two important contaminants, Se and N. The Se is contained in Colorado River water used for irrigation, and N is derived mostly from chemical fertilizer. Both are delivered to the Salton Sea as highly soluble oxyanions by the aerobic Alamo and New Rivers, but are removed as reduced species in anoxic sediment on the Sea's floor. Without this removal mechanism, Se values would be about 400 μg l^{-1} and N would be about 100 mg l^{-1} in the Salton Sea's water, rather than the observed concentrations of only about 1 μg l^{-1} and 5 mg l^{-1}, respectively.

Ironically, anoxic conditions responsible for producing the noxious odors and leading to periodic die-offs of large numbers of fish in the Salton Sea have prevented aqueous Se and N from reaching levels that could indeed pose an extreme environmental hazard. Thus, it is important that any engineering changes made to the Salton Sea do not change the circulation pattern or alter the food chain in such a way as to cause rapid reintroduction of these contaminants from sediment into the overlying water.

It is known that bacteria are capable of converting Se and N into gases that can then be volatilized to the atmosphere (Cooke & Bruland, 1987; Oremland, 1994). By comparing concentrations of Se and N with those of Mo and U that are not effected by volatilization, we estimate that loss from this process may have been about 10% for Se and a one-third loss for N, but this estimation has large uncertainties, especially for results obtained by normalizing to U.

Dissolved-N concentration in the Salton Sea is several times higher today than it was in the mid-1950s; yet dissolved phosphorus (P) concentration has changed little; P is by far the limiting nutrient, based on N:P ratios in the Salton Sea. One possible explanation for minor changes in P is that phosphate is efficiently removed from the water column by incorporation with calcium as apatite minerals – the material that composes fish bone. If so, attempts to slow or reverse excessive biological productivity (eutrophication) through large-scale harvesting of fish may not result in lowering the dissolved P concentration that would thereby improve the trophic status of the Salton Sea. An alternative explanation is that the geochemical cycle for P remains primarily controlled by the same water–sediment ‘equilibrium’ relations over time because P is predominantly of natural origin, and most of it may be recalcitrant.

Bottom sediment from 11 locations distributed throughout the Salton Sea is dominated by sand near the mouths of large rivers and by organic-rich clay in deeper parts of the Sea. The high organic content results from burial of organic matter produced by biological activity under eutrophic conditions. Calcium carbonate content increases with distance from shore to about 40% in surface sediment from the center of the Sea. The sediment in most locations was highly anaerobic and devoid of macroinvertebrates, but these were abundant at places such as near the mouth of Salt Creek, where DO in bottom water was high. The presence of DDE, a degradation product of DDT, at concentration as high as those reported for bottom material from agricultural drains is noteworthy. The presence of DDE suggests its potential value for dating event horizons in future cores from the Salton Sea.

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