CHAPTER III

SULFUR REDUCTION IN SEDIMENTS OF MARINE AND EVAPORITE ENVIRONMENTS

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Introduction

Estimates of the earth's current crustal reservoirs of sulfur minerals indicate that 200-250 x 10^{18} moles of sulfur in the form of sulfate occur in evaporite deposits as gypsum ($CaSO_4$). 200-250 x 10^{18} moles of reduced sulfur (as FeS_2) are found in sediment, and only 40-42 x 10^{18} moles of sulfur are found dissolved in the oceans and in the atmosphere (R. Garrels, personal communication). During the Permian Period and at other times during the Earth's history, the development of large basins of restricted circulation, (i.e., evaporite environments,) resulted in widespread evaporite sedimentation ($CaCO_3$, $CaSO_4$, NaCl and potash minerals - see Fig. I-17). A result of this sedimentation was a sequestering of sulfur as $CaSO_4$. Although it is estimated that nearly 50 percent of the total sulfur pool is in the form of sulfate, little is known about the role of sulfur-reducing microorganisms as regards either the deposition or the diagenesis of this sulfate.

The microbial ecology of evaporite environments such as the Persian Gulf, the Great Salt Lake, and the Dead Sea are often characterized by extensive microbial mat communities covering the sediments and/or high biological activity in the plankton of the brines. Although the distribution of microorganisms within these communities has been studied, the interrelationship of microbes and transformations in the sedimentary sulfur cycle environments remains poorly understood.

Geomicrobiological studies of evaporite environments have been retarded by logistical problems including the absence of adequate on-site laboratory facilities. It has been difficult to examine temporal developmental aspects of these environments such as the effects of increasing salinities over time on the geomicrobiology of evaporites.

Solar salt ponds serve as model systems for studying the geomicrobiology of sediments in normal marine and evaporite environments. A solar salt facility maintains seawater-concentrating ponds in a series of brines of increasing density, analogous to a river with a series of dams. Seawater enters the system and flows through the ponds so that $CaCO_3$ and $CaSO_4$ precipitate before the brines reach the stage

of NaCl saturation. The range of salinities in any one pond throughout the year depends on the management procedures of the salt company. These ponds provide opportunities to examine the effects of increases in salinity on the biological processes in the water column and sediments.

The accessibility of the PRME program to the Alviso salt ponds in San Francisco Bay Wildlife Refuge (Map 2) allowed us to examine transformations of sulfur in sediments of ponds ranging in salinities from that of normal seawater to those of brines saturated with sodium chloride.

Our investigations focused on the chemistry of the sediment and pore waters with emphasis on the fate of sulfate and sulfide and on the specific rate measurements of sulfate reduction. The effects of increasing salinity on both forms of sulfur and microbial activity were determined.

Site Description

The Alviso salt ponds, near the east side of the Dumbarton Bridge, are about 80 years old. On the average, brines have a residence time of about 5 years from the time they enter the system from San Francisco Bay until the time the brines are pumped from the NaCl crystallizer ponds to harvest salt. Table III-1 (provided by Leslie Salt Co.) summarizes the brine salinities measured between 25 March, 1983, and 20 July, 1984, in the ponds from which our sediment samples were taken. The data show that pond A2 varied the least (from 30 per mil to 80 per mil salinity). Pond 4 varied from roughly 43 per mil to 180 per mil, pond 5 varied from about 35 per mil to 133 per mil, and pond 1 varied from approximately 105 per mil to 250 per mil.

The ponds support very dense planktonic communities, especially when their salinity is greater than about 42 per mil salinity. Visibility through these brines was about 10 cm.

In ponds with brines ranging up to approximately 3 times seawater salinity, small fish (sticklebacks and topsmelt) are found. In ponds of higher density only a few invertebrates are found (*Ephydra* fly larvae and the brine shrimp *Artemia salina*). *A. salina*, a filter feeder, probably fails to limit phytoplankton both because it is harvested commercially and because of extremely high rates of primary productivity. Brine shrimp growth must also be limited by other factors; the shrimp do not thrive in brines of greater than about 200 per mil salinity. These brines typically have dense blooms of primary producers (the cyanobacterium *Aphanothece halophytica* and the green algae *Dunaliella salina* and *D. viridis*), *Halobacter*, and other halophilic bacteria. Microbial mat development on the surface of sediment occurs in ponds up to about 200 per mil salinity. The extent of mat development is limited by shading by dense plankton communities and rapid chemical precipitation of gypsum (at salinities of greater than 120 per mil) and halite (at salinities of greater than about 250

SALT PONDS
(see Map 2)

NAMES OF PONDS [b] (this study)	Date	Pond A2	Pond 1	Pond 4	Pond 5	S‰
		42	33 [c]	150	90 [d]	
	3/25/83	35	105	42.5	35	13
	4/8/83	35	113	42.5	35	14
	4/15/83	30	113	47.5	37.5	14
	4/29/83	40	115	47.5	42.5	14
	5/6/83	37.5	113	47.5	42.5	15
	5/13/83	40	115	50	45	15
	10/7/83	60	215	125	115	21
	11/4/83	60	200	148	133	19
	11/18/83	55	153	90	90	11
	12/2/83	52.5	158	90	90	11
	12/16/83	47.5	130	62.5	75	14
	1/6/84	45	128	60	67.5	13
	1/13/84	45	128	60	67.5	10
	2/3/84	47.5	130	65	70	12
	2/10/84	47.5	128	65	70	13
	2/24/84	47.5	125	65	67.5	14
	3/2/84	47.5	128	65	67.5	15
	3/16/84	50	128	67.5	67.5	16
	3/23/84	47.5	130	70	70	16
	4/6/84	50	140	80	80	15
	4/27/84	60	168	100	100	14
	5/25/84	80	220 [a]	133	113	16
	6/8/84	65	215	176	123	15
	6/29/84	42.5	225	155	125	19
	7/20/84	37.5	250	150	100	24

a Pond was essentially dry
b Named for quantity.
per mil. of salt measured in July 1984
c Salt marsh mean pond (map 2)
d Same as pond A4 (map 2)

Table III-1. Salinities and temperatures of Leslie Salt Co. concentrating ponds in 1983 and 1984. Salinities as per mil were calculated from salinometer readings.

per mil). Data obtained from sediments at an intertidal environment, the marsh site adjacent to the ponds, were used in comparison with those obtained from the pond sites.

Materials and Methods

Chemical Analyses

Salinities in the overlying water were measured with a hand-held refractometer (American Optical). Values of reported salinities are accurate to within 1 per mil.

Cores were obtained with hand-held extruded polycarbonate core barrels (7.5 cm inner diameters). Cores over 50 cm in length were obtained with the aid of an internal piston to avoid compaction of the core profile. Cores, stoppered and returned to the laboratory at S.J.S.U, were processed within 6 hours of collection.

Pore water from sediments was obtained by extruding the cores in an oxygen-free environment. The latter was obtained by placing a collar over the core and passing oxygen-free N_2 or carbon dioxide over the extruded section. Subsamples of the extruded material were placed in vials (10 cc) pre-flushed with oxygen-free N_2, stoppered with butyl rubber stoppers, and centrifuged for 30 minutes at 12,000 x g in an RG-2 Sorvall centrifuge. Pore water was removed and immediately analyzed for sulfate, sulfide, and chloride. Pore water for analyses such as volatile fatty acids not sensitive to oxygen was obtained by centrifuging larger samples in 50 cc polypropylene tubes.

Sulfate was analyzed turbidimetrically according to the method of Tabathabai (1974); sulfide was analyzed colorimetrically using the methylene blue technique (Cline, 196⁹). Chloride was determined titrimetrically with silver nitrate (American Public Health Assoc., 1976).

Volatile fatty acids were analyzed after the method of Lovley and Klug (1982). Briefly, 10 ml of pore water are made basic (pH 8.2) and slowly dried in a sand bath with a maximum temperature of 50°C to avoid basic hydrolyses of longer chain esters. Dried samples are made acidic with 10 percent phosphoric acid and vacuum steam distilled. The distillates were analyzed on a Hewlett Packard (Avondale, Pa.) HP 3830A gas chromatograph equipped with a flame ionization detector. Acids were separated on a 2 m glass column packed with 10 percent SP-1220 and 1 percent phosphoric acid coated on AWS Chromosorb 100/120 mesh (Suppelco, Avondale, Pa.). Operating conditions were: Column oven 135°C; detector 175°C; Injector 175°C; flow rate (N_2) 18 ml/minute. Output of the column was integrated with a HP 3830A integrator coupled to the above chromatograph.

At each sampling depth subsamples of sediment were also transferred to a preweighed vial and dried for 18 hours at

70°C in order to obtain a wet/dry conversion value. After drying, a subsample of the sediment was transferred to porcelain crucibles and combusted at 540°C for 20-24 hours in a muffle furnace. Organic content of the sediment was calculated as the percent weight loss following ignition.

For the analyses of acid volatile sulfide (AVS) soluble sulfur subsamples of sediments taken from cores including those used for other analyses were treated withe aqua regia (HNO_3-HCl 2:1) and frozen at -70°C in plastic bags. They were processed within one week. Samples were weighed and suspended in 30-50 ml distilled deionized water (ddw) warmed, and sparged with oxygen-free N_2 in a gas train. The train consisted of the flask with the sediment, followed by a flask with a 5 percent H_2SO_4 solution to trap any free chloride during acidification of the sample, and a tube containing 10 percent $AgNO_3$ to trap sulfide as an Ag_2S precipitate. After sparging, 25-30 ml of concentrated HCl was added to the sediment and the reaction was continued until no further Ag_2S precipitation was observed. The flask was again briefly warmed to remove the last traces of AVS. The Ag_2S precipitate was filtered on Whatman 50 paper, washed, dried, and weighed. The HCl-treated sediment was filtered on Whatman 50 paper and washed. The filtrate was analyzed for sulfate. The sediment was subjected to aqua regia oxidation by wetting the sediment with approximately 5 ml ddw and adding 20 ml aqua regia. The sediment was left at room temperature for 16 hours, heated to just below boiling for 2 hours, then filtered on glass fiber GF/A filters (Gelman Instrument Co.), washed with 80 ml ddw. The filtrate was analyzed for sulfate. Sulfate was estimated according to the method of Tabathabai (1974).

Sulfate Reduction Rates

Sulfate reduction rates were obtained using a modification of the technique of Ivanov (1964). Subsamples of sediments were obtained with 5 ml plastic syringes with the needle end cut off. The subcores were extruded into preflushed (oxygen-free N_2) 30 ml serum vials and stoppered. Each bottle received 3 microcuries (μc) $Na_2{}^{35}SO_4$ in 1 ml of anoxic sulfate-free seawater. Samples were mixed and incubated at *in situ* temperature (23°C) for 6-8 hours. The reaction was stopped by injecting 1 ml of 5 percent zinc acetate; then the samples were frozen (-70°C) until processing. All experiments were done in duplicate for each core section. Samples were assayed and rates determined using the procedure described by Smith and Klug (1981). These methods only accounted for the recovery of reduced sulfate in the free S^{2-} and AVS pool. Rates therefore should be considered underestimates of total sulfate reduction.

Results and Discussion

Chemical Profiles

Values measured for the sulfate, sulfide, and acid volatile sulfide (AVS) pools in sediments collected from an intertidal marsh site near pond 1 (33 per mil), pond A2 (42 per mil), pond A4 (90 per mil), pond 4 (150 per mil), and pond 1 (300 per mil) are shown in Tables III-2 through III-6 and Figures III-1 through III-5. Hereafter, sampling sites will be referred to by their salinities.

The percent sediment dry weight generally increased as a function of pond salinity due to the precipitation of gypsum and halite which are relatively dense constituents of hypersaline sediments. The organic content of the sediments (measured as a loss of weight upon ignition) was very high, ranging from about 10 percent to 20 percent of the dry weight. The lowest value recorded was 7.8 percent (300 percent salinity) and the highest value recorded was 23.1 percent (90 per mil site). Organic carbon content appeared to increase with salinity in sediments to a maximum in 90 per mil sediments, and then to decrease somewhat with continued concentration of brine. In all cases the organic content was higher than that found in the intertidal marsh sediment (33 per mil).

The salinity of the superficial brines in the salt ponds was estimated with a refractometer. Because calcium precipitates primarily as $CaSO_4$ in brines concentrated greater than four-fold (about 140 per mil) and NaCl precipitates when brines are concentrated to greater than about 250 per mil, the actual ion content of concentrated brines in the study sites could not be calculated by simply multiplying the concentration of each ion by the factor of concentration measured with the refractometer. With the exception of the 300 per mil site, estimates of seawater concentration were possible by measurements of Cl^- concentration, since this ion is conservative until the brine reaches the stage of NaCl saturation. For this reason, the calculation of sulfate/chloride ratios in sediment pore waters shown in Tables III-2 through III-6 and Figures III-1 through III-5 give a reasonable estimate of the amount of steady state sulfate reduced as a function of salinity and depth below the oxygen interface.

In every site except the 300 per mil site, the sulfate/chloride ratio decreased with depth in a manner typically found in marine sediments. The sediment profile in the 300 per mil site (Table III-6) may be complicated by the fact that although the chlorinity decreased with depth somewhat continuously, gypsum precipitation in various layers increased both the solid and soluble sulfate pools in localized horizons. Sulfate reduction rates (discussed on the following pages) were significant in this core; therefore the absence of biological activity can not explain the unpredictability in the pore water

Depth (cm)	S^{2-} mM	SO_4^{2-} mM	Cl^- M	$\frac{SO_4^{2-}}{Cl^-}$	% dry wt	% org matter	µmol[a] AVS	µmol[b] ARS
overlying water		27.5	0.345	0.080				
0-1	1.39	19.1	0.455	0.042	24.0	11.7	148	181
1-2	0.88	18.8	0.444	0.042	29.6	9.9	177	221
2-3	1.27	16.4	0.424	0.039	31.2	9.8	180	196
3-5	1.11	19.1	0.403	0.047	32.1	9.7	242	181
5-7	2.35	16.4	0.378	0.043	31.2	9.9	186	193
9-11	2.47	11.7	0.355	0.033	30.4	11.4	155	357
11-13	1.48	11.7	nd	nd	32.3	9.6	107	375
13-15	1.24	7.8	nd	nd	34.1	9.5	195	254
17-19	2.29	7.8	0.335	0.023	33.4	9.0	108	347
21-23	2.22	6.3	nd	nd	34.5	8.3	57	574
23-25	2.84	10.5	0.339	0.031	35.9	8.1	44	478
26-28	2.84	8.6	nd	nd	37.9	8.2	41	446
28-30	2.72	8.0	nd	nd	38.5	8.1	31	549
30-32	2.16	12.5	nd	nd	39.5	8.6	26	488

[a] acid volatile sulfur per g dry weight
[b] aqua regia soluble sulfur, per g dry weight

Table III-2. Chemical profiles of 33 per mil sediments.

Depth (cm)	S^{2-} mM	SO_4^{2-} mM	% dry wt	µmol[a] AVS	µmol[b] ARS
overlying water		21.9			
0-1	1.7	24.1	20.0	97	179
1-2	3.4	33.6	24.	156	187
2-3	3.4	28.9	26.5	161	155
5-7	5.0	24.5	23.3	124	206
9-11	5.0	18.2	26.6	108	315
13-15	nd	16.4	23.2	156	209

[a] acid volatile sulfur per g dry weight
[b] aqua regia soluble sulfur, per g dry weight

Table III-3a. Chemical profiles of 42 per mil sediments, 7/23/84.

Depth (cm)	SO_4^{2-} mM	Cl^- M	$\frac{SO_4^{2-}}{Cl^-}$	% dry wt	% org matter
0-3	28.1	0.818	0.035	25.1	14.9
3-6	20.9	0.656	0.027	24.7	17.7
6-9	17.8	0.930	0.023	37.6	10.8
9-12	13.5	0.975	0.019	30.9	14.1
12-15	11.1	0.980	0.017	27.3	16.3
15-18	9.2	0.988	0.009	27.3	16.3
18-21	8.6	0.975	0.009	28.5	19.4
21-24	4.3	0.978	0.004	26.2	19.8
27-30	4.8	0.973	0.005	27.7	17.2
3-36	3.9	0.973	0.004	32.1	13.4
39-42	3.9	nd	nd	26.2	15.8
45-48	4.3	0.983	0.004	32.2	15.4
51-54	4.5	nd	nd	30.6	15.9
57-60	3.9	nd	nd	31.1	15.6
63-66	2.5	0.980	0.003	29.6	15.9
69-72	3.9	0.963	0.004	29.2	15.0
72-72	5.2	0.955	0.006	30.6	14.6
78-81	3.7	0.968	0.004	36.2	13.5
83-86	4.1	0.968	0.004	34.9	12.9
86-89	5.3	0.949	0.006	38.3	11.9

Table III-3b. Chemical profiles of 42 per mil sediments, 7/28/84.

Depth (cm)	S^{2-} mM	SO_4^{2-} mM	Cl^- M	$\frac{SO_4^{2-}}{Cl^-}$	% dry wt	% org matter
0-1	0.9	61.7	1.17	0.053	17.9	20.9
1-2	2.3	46.9	1.19	0.039	23.2	15.1
2-3	8.7	46.9	1.24	0.038	23.1	17.2
3-5	10.2	32.8	1.28	0.026	22.5	17.9
5-7	9.9	25.8	nd	nd	19.2	23.1
7-9	12.0	16.4	1.29	0.013	19.	22.5
9-11	12.9	13.7	1.26	0.011	22.8	17.3
11-13	18.0	10.9	nd	nd	23.5	18.1

Table III-4. Chemical profiles of 90 per mil sediments.

Depth (cm)	S^{2-} mM	SO_4^{2-} mM	Cl^- M	$\frac{SO_4^{2-}}{Cl^-}$	% dry wt	% org matter
overlying water		105	2.25	0.047		
0-1	3.60	84.0	2.06	0.041	nd	nd
1-2	4.65	87.8	2.25	0.039	27.4	16.2
2-3	4.87	74.0	2.00	0.037	26.4	17.6
3-5	5.04	64.6	2.38	0.030	28.3	18.2
5-7	5.81	68.7	1.64	0.042	36.6	15.0
7-9	6.75	60.2	1.50	0.040	38.9	12.4
9-11	6.43	55.8	1.50	0.037	42.2	12.1
11-13	5.25	50.8	1.38	0.037	33.2	14.7
15-17	6.37	49.5	1.31	0.038	40.2	9.7
17-19	4.87	42.9	1.13	0.038	44.7	8.3
19-21	5.67	45.1	1.13	0.040	43.9	9.4

• gypsum layer in this sediment interval

Table III-5. Chemical profiles of 150 per mil sediments.

Depth (cm)	S^{2-} mM	SO_4^{2-} mM	Cl^- M	$\frac{SO_4^{2-}}{Cl^-}$	% dry wt	% org matter	µmol[a] AVS	µmol[b] ARS	mM $CaSO_4$
overlying water		196	6.38	0.0307					
0-1	2.01	162	6.0	0.0270	48.6	12.1	9.3	41.8	0.90
1-2	3.24	172	6.0	0.0287	43.7	14.0	38	46.4	1.10
2-3	3.55	162	5.81	0.0279	45.0	13.2	71	62	0.71
3-4	4.09	149	5.5	0.0271	46.0	13.5	62	88	1.61
4-6	6.10	122	4.56	0.0268	44.3	15.1	59	71	0.93
6-8	6.49	148	4.88	0.0303	44.6	15.2	62	10	.21
8-10	6.25	119	3.63	0.0328	44.6	16.0	67	163	0.99
10-12	8.73	108	2.63	0.0411	45.2	15.0	57	368	2.05
12-14	10.27	204	10.63	0.0192	40.1	14.5	70	203	0.38
14-16	10.81	117	4.44	0.0264	40.3	11.0	64	249	0.51
18-20	8.03	87	2.63	0.0331	39.4	10.9	78	185	0.28

[a] acid volatile sulfur per g dry weight
[b] aqua regia soluble sulfur, per g dry weight
[c] gypsum layer in this sediment interval

Table III-6. Chemical profiles of 300 per mil sediments, 7/28/84.

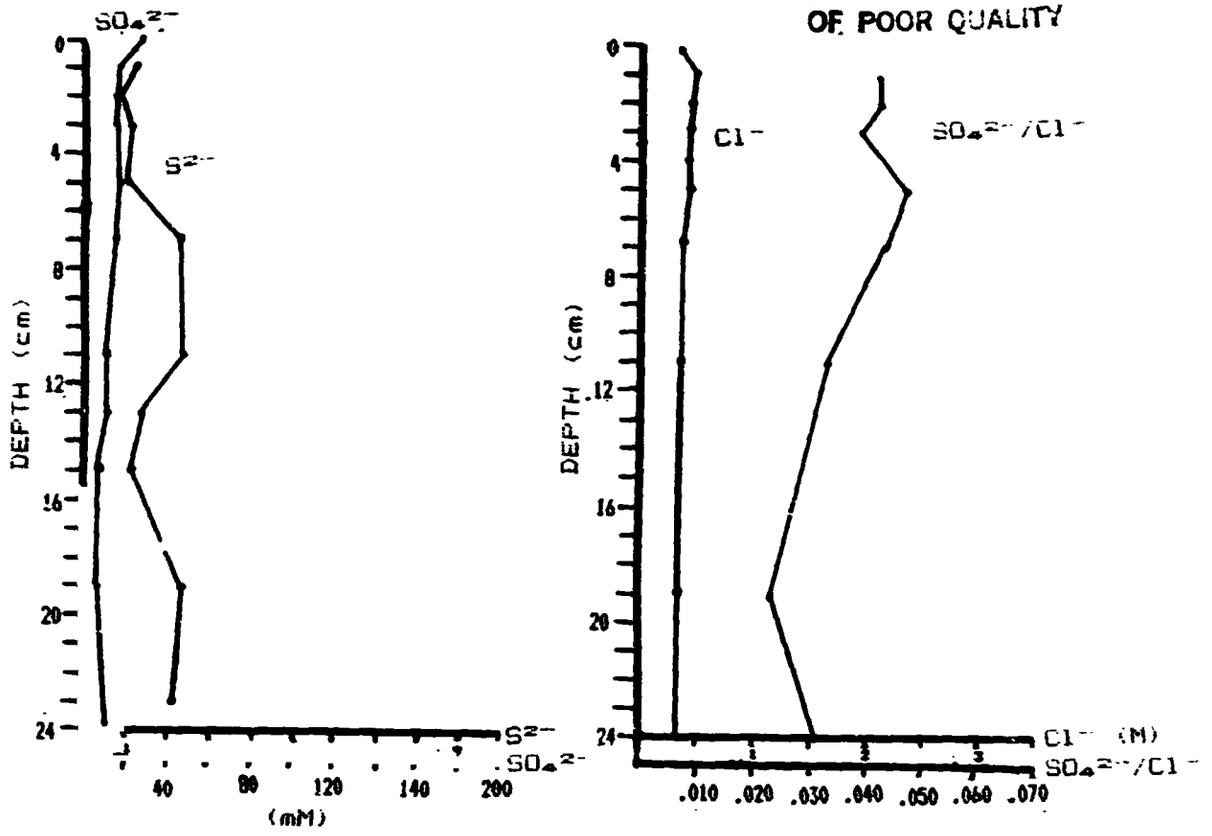

Figure III-1. (a) Sulfate and sulfide pool sizes in sediments from the 33 per mil site; (b) sulfate/chloride ratio and chloride pool size in sediments from the 33 per mil site.

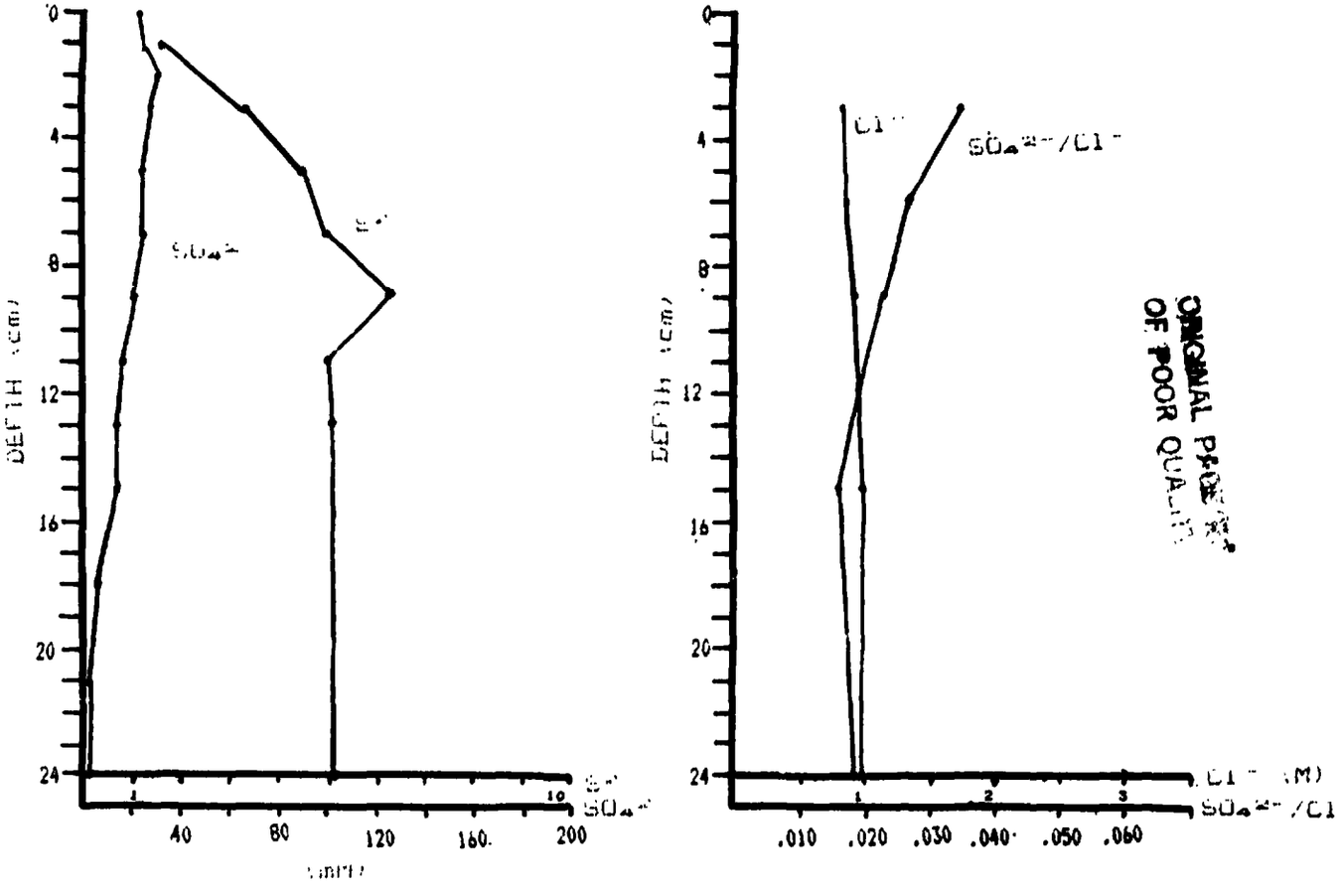

Figure III-2. (a) Sulfate and sulfide pool sizes in sediments from the 42 per mil site; (b) sulfate/chloride ratio and chloride pool size in sediments from the 42 per mil site.

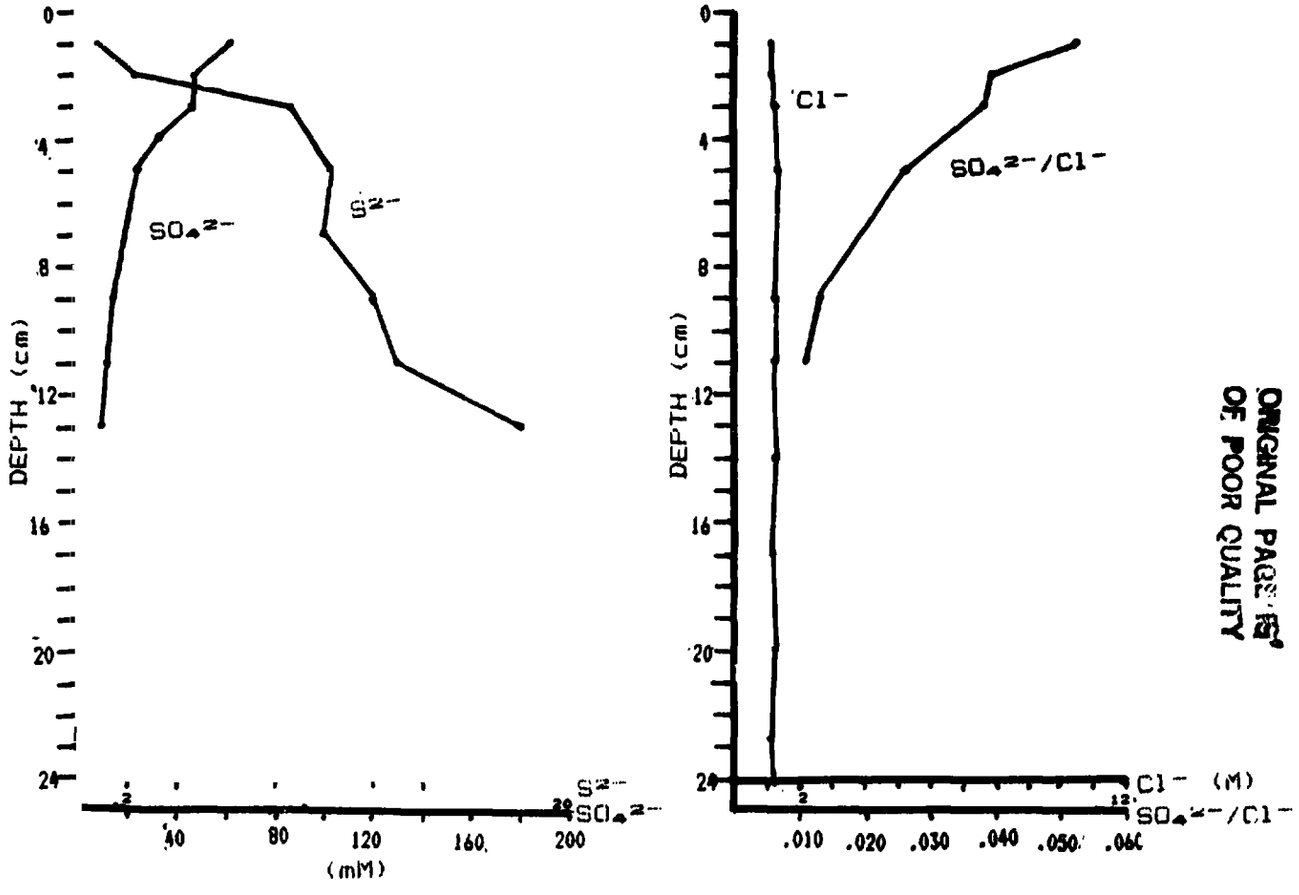

Figure III-3. (a) Sulfate and sulfide pool sizes in sediments from the 90 per mil site: (b) sulfate/chloride ratio and chloride pool size in sediments from the 90 per mil site.

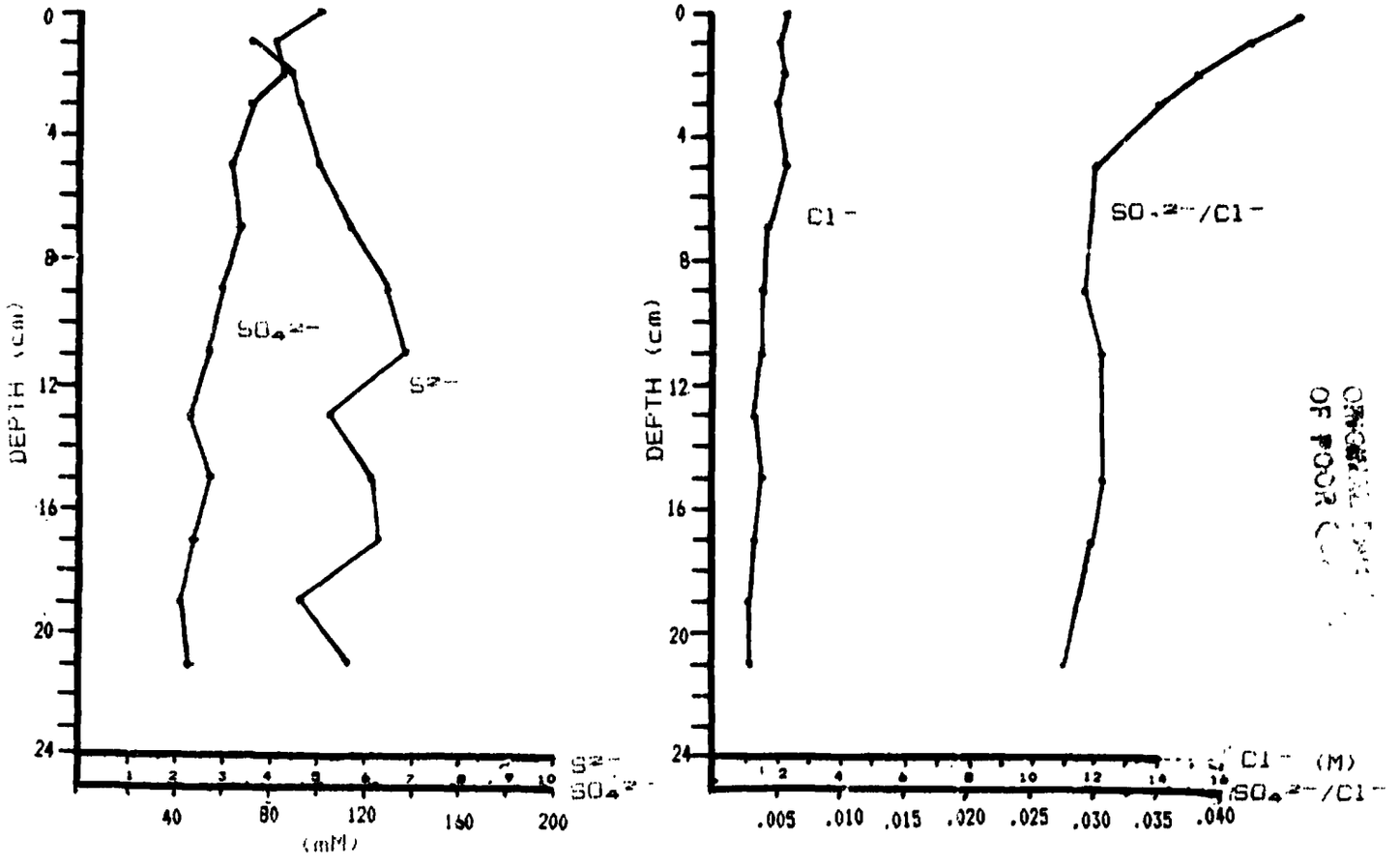

Figure III-4. (a) Sulfate and sulfide pool sizes in sediments from the 150 per mil site; (b) sulfate/chloride ratio and chloride pool size in sediments from the 150 per mil site.

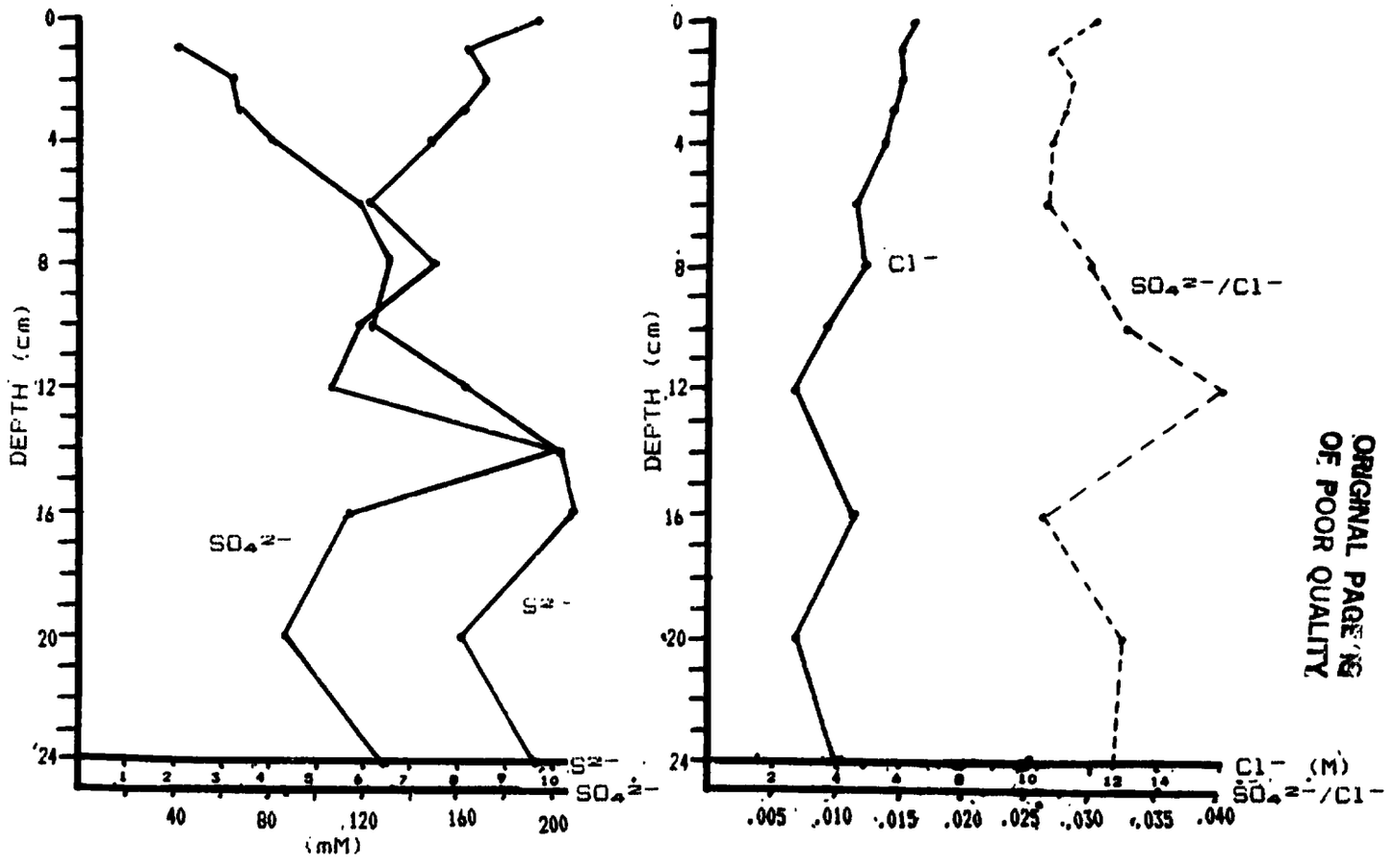

Figure III-5. (a) Sulfate and sulfide pool sizes in sediments from the 300 per mil site; (b) sulfate/chloride ratio and chloride pool size in sediments from the 300 per mil site.

(at 14 cm) but the variation may be due to a combination of a localized halite lamina and analytical error.

Sulfate is reduced to sulfide by sulfate-reducing bacteria, but sulfide may then react either biologically or non-biologically. Thus the sulfide pool is not an absolute indicator of the degree of sulfate reduction. It is therefore useful to measure the various sulfide pools as well as the sulfate/chloride ratios in order to evaluate the effects of bacterial sulfate reduction on the cycling of sedimentary sulfur.

In all sediment pore waters, sulfide was present in millimolar concentrations, typically between 1 and 10 mM. Sulfide typically increased with depth in all the salt pond sites. In the 42 per mil and 150 per mil sites, sulfide levelled off below about 10 cm depth, and in the 300 per mil site, it leveled off below around 14 cm. In the 90 per mil sediment sulfide increased with depth to at least 13 cm; no further profiles were measured below this point. Sulfide remained low with no general increase in the 33 per mil marsh sediment down to 32 cm. This type of profile may be typical of an intertidal marsh from which pore water is constantly pumped in and out with tidal changes in the nearby tidal creek. The steady-state values recorded for the salt pond sediments reflect sulfide concentrations that result from *in situ* sulfide production and passive diffusion in the absence of tidal pumping.

In anaerobic sediment in which Fe^{2+} is present, free sulfide reacts with Fe^{2+} to produce FeS and FeS_2. FeS is primarily responsible for the black color of reduced sediments. FeS is somewhat refractory to redissolution by microorganisms but it is readily oxidized by O_2. FeS reacts in an unknown way to form FeS_2 (pyrite), an extremely recalcitrant mineral that is not significantly oxidized non-biologically by O_2. Analyses of FeS and pyrite in sediment profiles through a wide range of salinities would indicate whether well-described trends in pyrite formation for marine sediments hold true for organic-rich evaporite sediments as well. For this study AVS and aqua regia-soluble sulfur profiles were determined in the 33 per mil, 43 per mil, and 300 per mil sediments. Pyrite was the major iron sulfide phase found in all three sediments (Figs. III-6 and 7). In the 42 per mil salinity site, the pyrite pool was nearly twice as large as the AVS pool within the top cm of the sediment. Pyrite content in all three sediment cores increased with sediment depth. In the 33 per mil core, as is typical for marine sediments, AVS decreased with sediment depth down to at least 32 cm. Because the 42 per mil sediment profile was only measured down to 14 cm no definite trend could be ascertained. The AVS pool increased with depth to at least 24 cm in the 300 per mil salinity sediment. These findings may be of importance in evaluating the mechanisms of FeS-FeS_2 transformations especially since the soluble and solid sulfate pools in this core were extremely large.

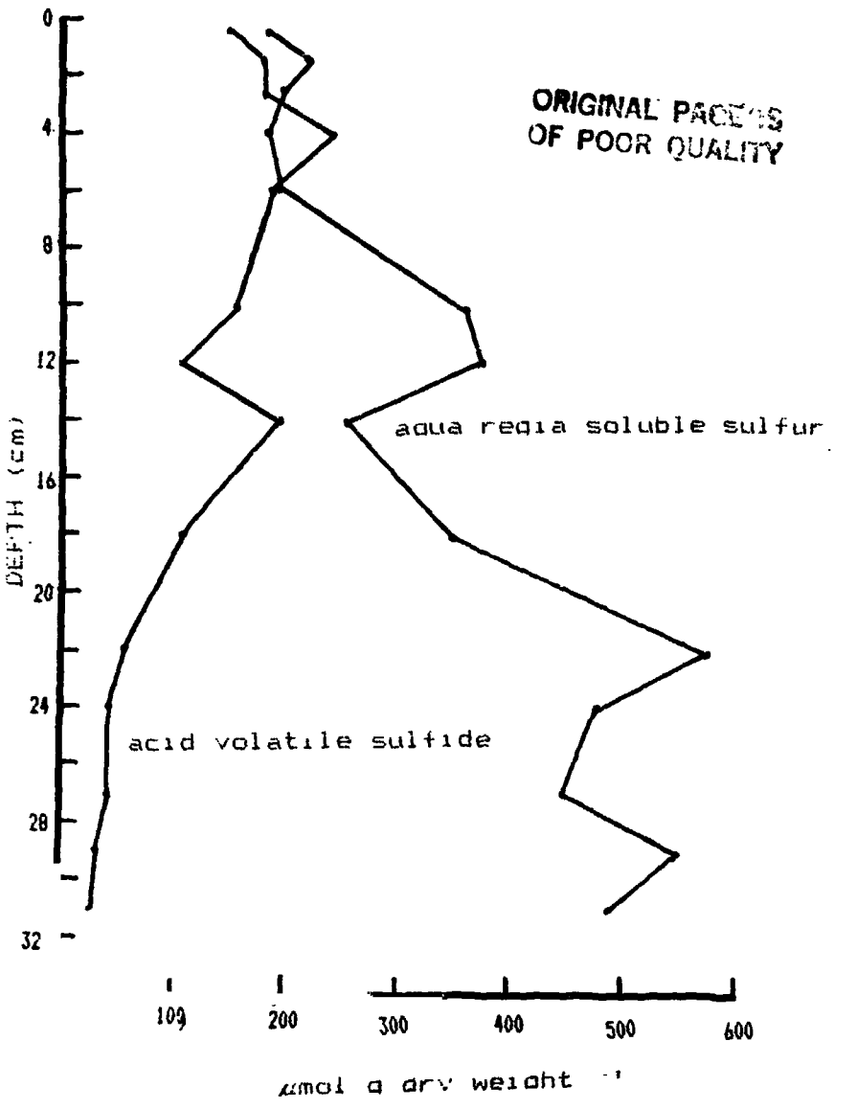

Figure III-6. Pool sizes of acid volatile sulfide and aqua regia soluble sulfur in sediments from the 33 per mil site.

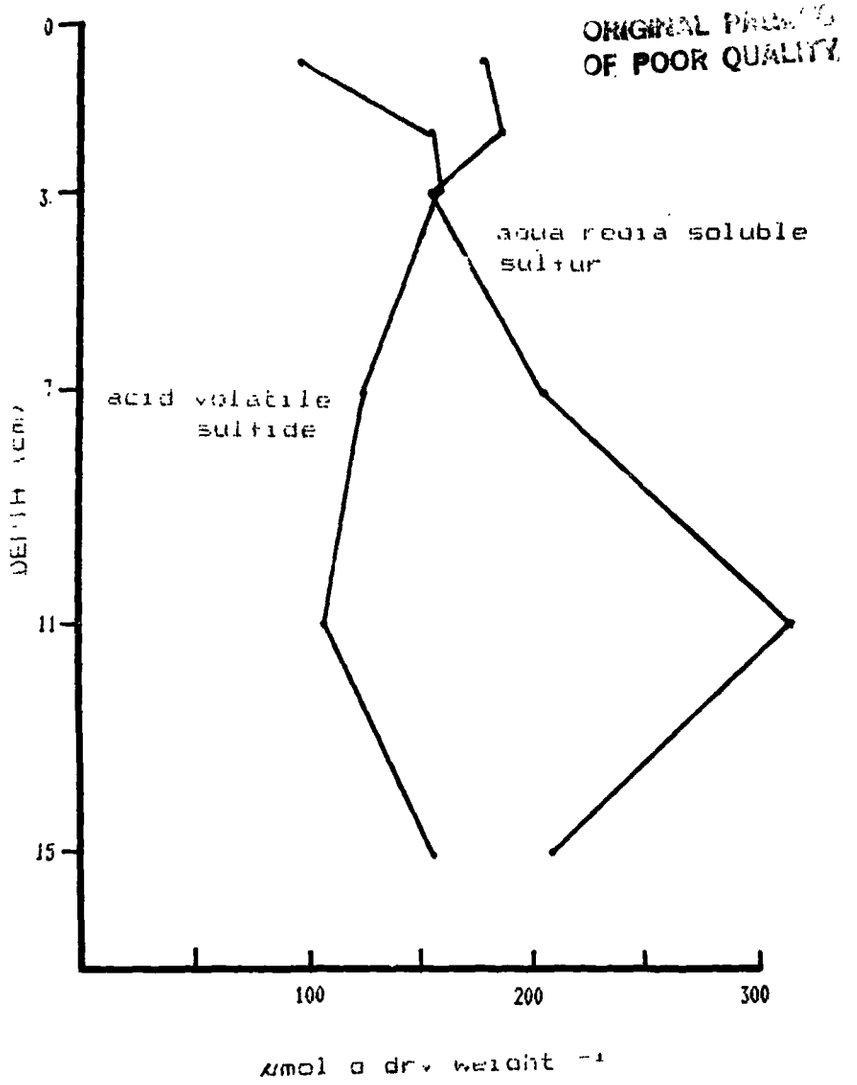

Figure III-7. Pool sizes of acid volatile sulfide and aqua regia-soluble sulfur in sediments from the 42 per mil site.

Total iron sulfides, estimated from the sum of AVS plus aqua regia soluble sulfide in the 33 per mil, 42 per mil, and 300 per mil salinity sediments, were compared. Total iron sulfides decreased with increasing salinity. The one anomalous point at 10-12 cm in the 300 per mil sediment corresponds to the sediment underlying a several mm-thick gypsum crust at this horizon. The relatively high concentration of iron sulfides at this sediment interval may have resulted from incomplete solution of gypsum in the HCl treatment which caused additional sulfate to appear after aqua regia treatment. Total iron was not measured in any of the sediments in this part of the investigation. The lack of iron in hypersaline sediments in combination with lower sulfate reduction rates may account for the lower abundance of iron sulfides in the evaporite sediments.

Sulfate Reduction

The rates of sulfate reduction were determined in duplicate samples at six different horizons in sediments of each pond (Figures III-8 and III-9). In all sediments except those from the 300 per mil salinity site, the greatest rates of sulfate reduction were recorded in the top first centimeter. Sulfate reduction measured in the first centimeter sediment of the 300 per mil pond may have been low because the surface, intermixed with halite crystals, was capped by a several mm-thick halite crust.

In sediments below 1 cm sulfate reduction rates were somewhat similar in most of the samples. In the 33 per mil salinity sediment, where the highest sulfate reduction rates were measured in the surficial 1 cm, negligible sulfate reduction was recorded below a depth of 7 cm. There was less than 1 mmol of dissolved sulfate in the pore water per gram wet weight, indicating that the sulfate reduction was most likely sulfate-limited.

Sulfate reduction rates in the top 1 cm of the 42 per mil salinity sediment were nearly ten-fold less than those recorded for the 33 per mil salinity sediment; both ponds harbored extensive microbial mat communities. However without data on the mat community productivity and on differences in bioturbation, an explanation for these differences is most likely not due to an increase in salinity since the values for reduction in the lower horizons are more comparable.

The higher rate of sulfate reduction recorded in the 13-15 cm interval of the 42 per mil sediment corresponds to the relatively high concentration of AVS and the low abundance of pyrite in this horizon. This is just below a point where sulfide reaches a maximum concentration.

Sulfate reduction rates in the 90 per mil salinity sediment were very high in the surficial 1 cm, and much lower below the

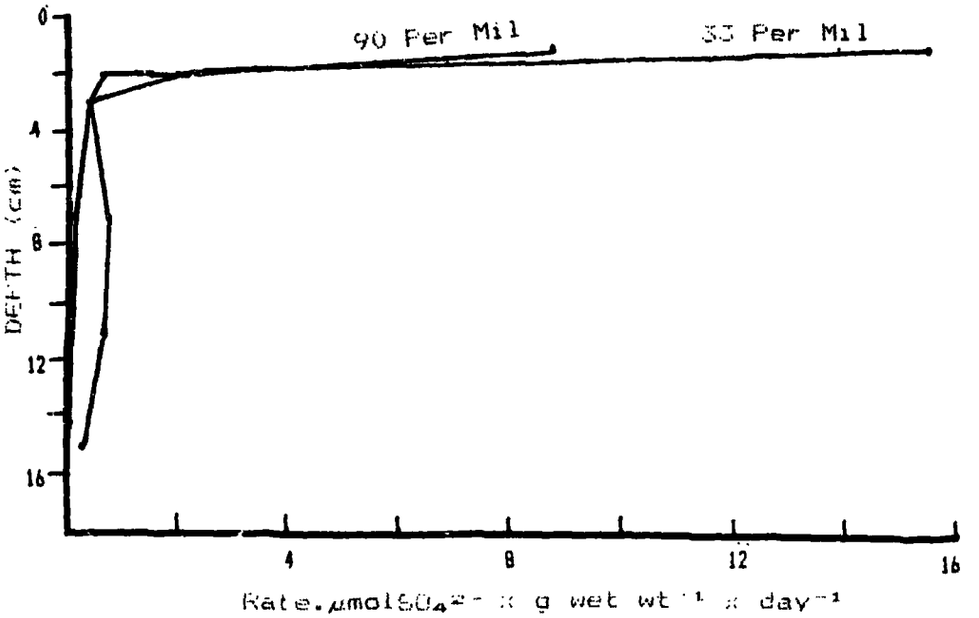

Figure III-8. Sulfate reduction rate in sediments from the 33 per mil site and 90 per mil sites.

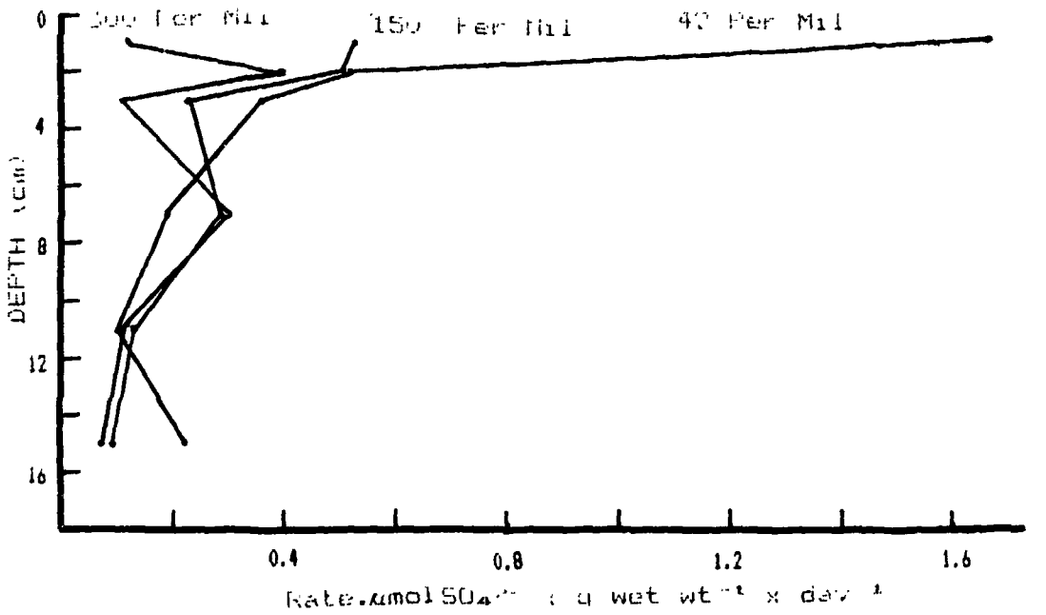

Figure III-9. Sulfate reduction rate in sediments from the 42 per mil, 150 per mil and 300 per mil sites.

surface, although they were never completely attenuated. The dissolved sulfate pool remained high in subsurface sediment, and was never less than 19 mM per gram wet weight in contrast to those measurements recorded for the 33 per mil sediment.

Gypsum deposition may have altered the typical sulfate reduction profiles in both the 150 per mil and 300 per mil salinity sediments. Gypsum precipitation probably precluded the local accumulation of organic-rich sediment found in lower salinity sediments, and increased the potential pool of soluble sulfate in adjacent horizons by acting as a sulfate reservoir.

In all but the 33 per mil site sulfate concentration did not seem to limit sulfate reduction. Organic matter content and concentrations of volatile fatty acids (Tables III-7 through III-11) increased in relation to increased salinity. When the sulfate reduction rates are compared on the basis of salinity, at depths below the top 1 cm a general trend of decreased activity is observed from ponds with a salinity greater than 70 per mil. To determine relationships of salinity to rates of sulfate reduction more studies are required.

Volatile Fatty Acids

Acetic acid was found in the greatest concentration of any volatile fatty acid (VFA) from the pore waters of sediments of any site (Tables III-7 through III-11). Isobutyric acid was the second most predominant VFA identified. It was followed by an unknown "acid volatile" compound which eluted between isovaleric and n-valeric acid at a retention time of 7.35 minutes. Another unknown acid eluted between butyric and isovaleric acids at a retention of 5.25 minutes. Figure III-10 (a-c) compares the chromatograms obtained for a standard series of VFA's (Fig. III-10a); chromatograms obtained from the depth interval of 19-20 cm in the 70 per mil site (Fig. III-10 b); and the composite chromatogram illustrating the elution pattern of the 7.35 minute peak (Fig. III-10c).

The number of identifiable VFA's increased markedly with an increase in salinity. No clear trend was noted in the concentrations of acetate to increased salinity except for the large increase noted in the 300 per mil site.

Acetate concentration generally followed that of sulfate in pore water (the 33 per mil and 42 per mil sites, Figures III-11 and III-12). This relationship did not strictly hold (Tables III-9, III-10, III-11). The concentration of acetate reached a minimum at the sulfate concentration minimum and subsequently increased with depth. These data strongly imply that acetate is a major precursor of sulfate reduction and that the reduction of sulfate and acetate consumption are linked. They further suggest that sulfate reducers are the major sink for acetate in these sediments. Another acetate-consuming process, methanogenesis, was examined in the 42 per mil site. The methane vs sulfate

Depth (cm)	a	b	c
0-1	19.7	-	0.12
1-2	20.39	0.14	0.12
2-3	19.62	0.83	0.51
4-5	9.62	-	-
7-8	10.44	-	-
10-11	10.44	-	-
14-15	8.69	0.68	0.45
18-19	8.20	0.581	0.37
23-24	5.47	0.028	0.99

a = acetic acid μmol/liter pore water
b = isobutyric acid μmol/liter pore water
c = volatile fatty acid 7.35 arbitrary unit/liter pore water

Table III-7. Volatile fatty acids in pore waters from the 33 per mil site. 7.35 refers to the retention time in relationship to acetic and isobutyric acids.

Depth (cm)	a	b	c	d
0-3	43.64	0.69	2.27	2.73
3-6	59.30	-	2.62	2.49
6-9	19.17	-	3.22	3.23
9-12	13.06	-	2.24	2.14
12-15	15.86	-	1.57	1.60
15-18	14.51	1.02	0.99	
18-21	9.34	-	0.82	0.96
21-24	30.64	-	0.71	0.68
27-30	40.73	2.13	1.90	1.69
33-36	39.78	0.71	1.21	0.90
39-42	26.09	0.95	0.67	0.52
51-54	34.38	-	0.07	0.28
57-60	20.72	-	0.55	0.57
63-66	29.47	-	1.57	1.50
69-72	13.82	-	0.31	0.3.
72-75	13.97	-	0.40	0.60
78-81	11.75	-	0.30	0.42
83-86	13.63	-	0.54	0.57
86-89	8.19	-	0.12	0.23

a = acetic acid μmol/liter pore water
b = isobutyric acid μmol/liter interstitial water
c = propionic acid μmol/liter interstitial water
d = volatile fatty acid 7.35 arbitrary unit/liter interstitial water

Table III-8. Volatile fatty acids in pore waters from the 42 per mil site. 7.35 refers to the retention time in relationship to acetic and isobutyric acids.

Depth (cm)	a	b	c	d	e
0-1	5.67	0.-	-	0.13	-
1-2	16.98	0.03	-	0.21	-
2-3	21.56	2.0	-	2.50	-
4-5	37.38	6.64	-	8.25	0.17
7-8	20.76	2.51	-	2.91	-
10-11	31.76	4.59	-	5.14	0.15
13-14	37.64	3.43	-	5.01	0.04
16-17	42.62	9.7	-	9.73	0.24
19-20	45.62	10.67	-	9.09	
22-23	16.79	5.67	-	4.73	0.18
25-26	32.34	8.68	-	8.33	-

a = acetic acid μmol/liter pore water
b = isobutyric acid μmol/liter interstitial water
c = n butyric acid μmol/liter interstitial water
d = volatile fatty acid 7.35 arbitrary unit/liter interstitial water
e = volatile fatty acid 5.25 arbitrary unit/liter interstitial water

Table III-9. Volatile fatty acids in pore waters from the 90 per mil site.

Depth (cm)	a	b	c	d	e
0-1	16.00	1.61	-	1.77	0.09
1-2	22.24	3.82	0.30	3.81	0.27
2-3	36.60	3.16	0.28	3.29	0.27
2-3	36.00	3.16	0.28	3.29	0.27
4-5	20.63	4.73	-	7.16	0.21
7-8	35.87	7.35	-	11.09	0.77
10-11	40.70	8.90	0.61	7.37	0.06
13-14	19.80	1.22	-	1.27	-
16-17	18.65	1.27	-	1.15	-
19-20	45.76	3.81	-	4.27	-
22-23	30.63	1.90	-	1.95	-
25-26	35.30	1.68	-	1.91	-

a = acetic acid μmol/liter pore water
b = isobutyric acid μmol/liter interstitial water
c = n. butyric acid μmol/liter interstitial water
d = volatile fatty acid 7.35 arbitrary unit/liter interstitial water
e = volatile fatty acid 5.25 arbitrary unit/liter interstitial water

Table III-10. Volatile fatty acids in pore waters from the 150 per mil site.

Depth (cm)	a	b	c	d	e	f	g
0-1	802.33	9.95	128.76	5.88	5.92	85.92	4.70
1-2	736.97	4.66	150.40	2.46	3.85	114.06	2.88
2-3	309.66	-	34.53	1.07	-	26.43	1.77
4-5	288.94	0.73	65.05	2.65	2.30	32.96	2.00
5-6	248.94	0.73	65.05	2.65	2.30	32.96	2.00
12-13	45.31	-	14.68	-	-	6.78	0.28
20-21	27.47	-	7.05	-	-	3.15	-
24-25	39.25	6.84	-	-	3.03	-	
28-29	57.36	-	7.3	-	-	3.71	-

a = acetic acid μmol/liter pore water
b = propionic acid μmol/liter interstitial water
c = isobutyric acid μmol/liter interstitial water
d = n butyric acid μmol/liter interstitial water
e = isovaleric acid μmol/liter interstitial water
f = volatile fatty acid 7.35 arbitrary unit/liter interstitial water
g = volatile fatty acid 5.25 arbitrary unit/liter interstitial water

Table III-11. Volatile fatty acids in pore waters from the 300 per mil site.

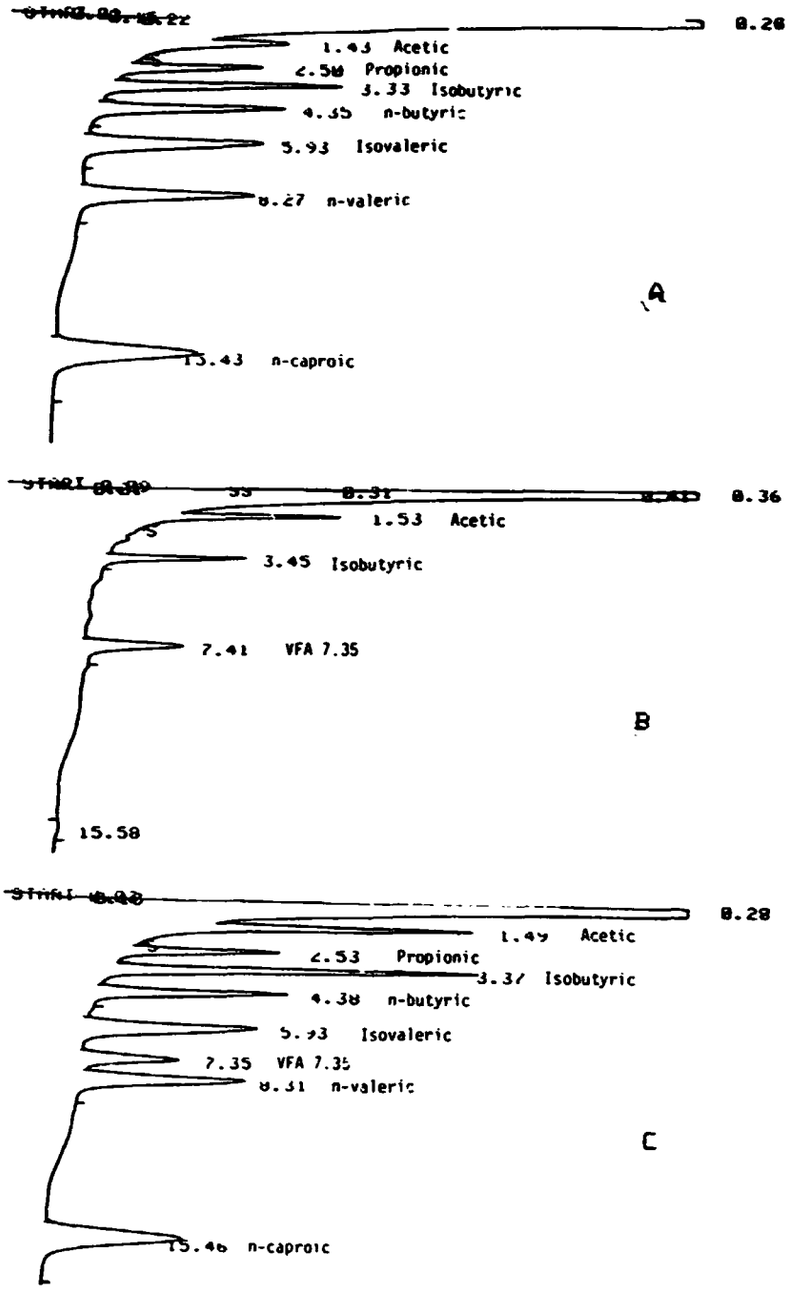

Figure III-10. (a) Chromatogram of standard volatile fatty acid mixture; (b) chromatogram of volatile fatty acids in the 19-20 cm profile of sediments from the 70 per mil site; (c) composite chromatogram of (a) and (b).

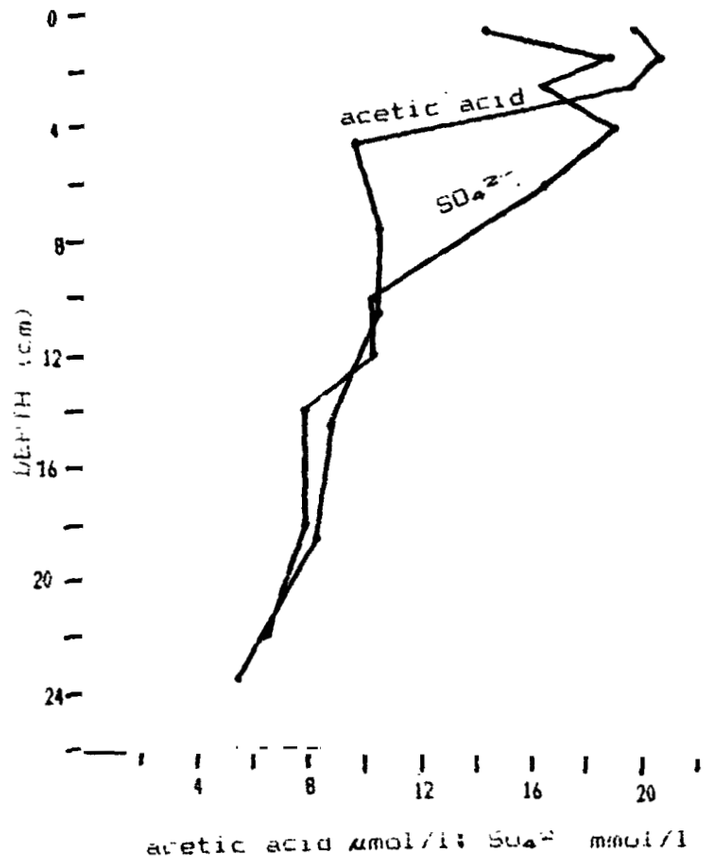

Figure III-11. Pool size of acetic acid and sulfate in sediments from the 33 per mil site.

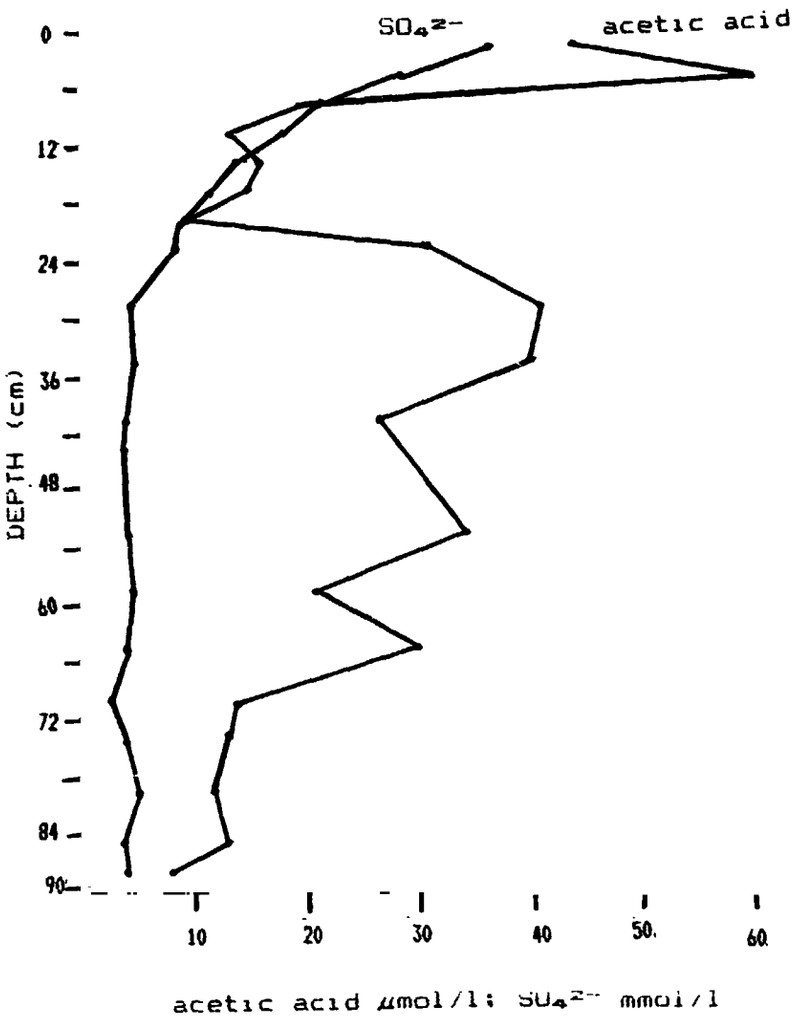

Figure III-12. Pool size of acetic acid and sulfate in sediments from the 42 per mil site.

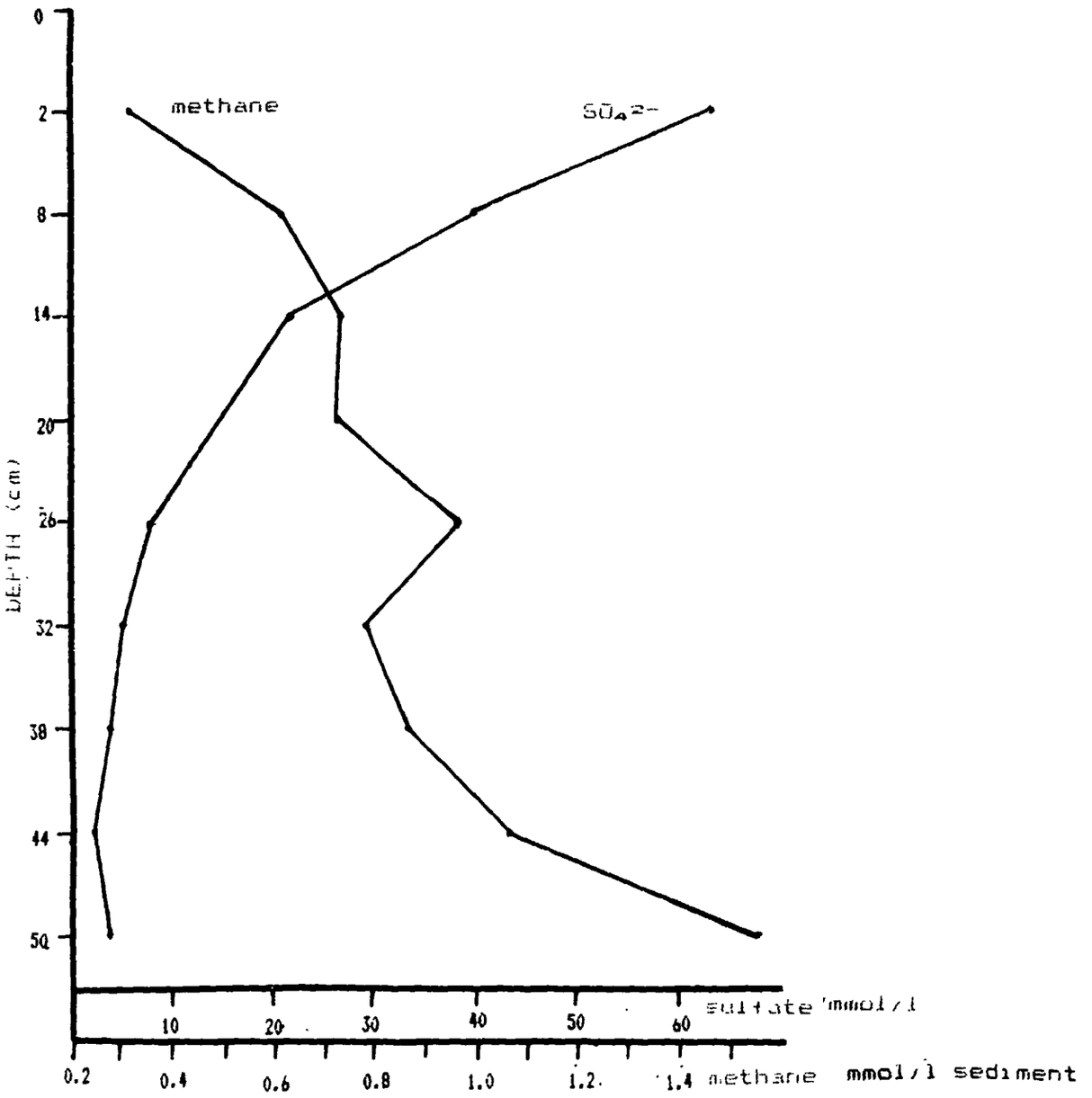

Figure III-13. Pool size of methane and sulfate in sediments from the 42 per mil site.

profiles are illustrated in Figure III-13. Although a steep gradient of methane was observed, no production of methane could be measured within a 60 cm profile from this site. Without further data, based on the observed profiles of sulfate, acetate, and sulfate reduction rates, we can only speculate that the major acetate consuming process is sulfate reduction.

The concentration and increase in diversity of total VFA's in relation to salinity suggests that the production of these compounds through fermentation exceeds their consumption. The general increase in chain length of the acids would be predicted if the products of fermentation, such as acetate are not consumed (Wolin, 1976). The presence of sulfate and acetate at concentrations well above the Km for sulfate reducers for sulfate and acetate down to 20 or more centimeters in sediments of the 90 per mil, 150 per mil, and 300 per mil sites, suggests that something other than low sulfate and acetate concentration inhibited sulfate reducers.

Conclusions

A unique set of chemical profiles and sulfate-reducing activity was found for the sediments of each of the sites examined. The quantity of organic matter in the salt pond sediments was significantly greater than that occurring in the adjacent intertidal site. The total quantitative and qualitative distribtion of volatile fatty acids was also greater in the salt ponds. Volatile fatty acids increased with salinity; the maximum quantitative and qualitative spectra of acids were found in the 300 per mil site. The general decrease in sulfate reduction rate in sediments of ponds of increasing salinity lead us to believe that organic matter was accumulating in these ponds because of the limited consumption of the fermentative intermediates.

Our sulfate reduction rates in sediments from the hypersaline ponds were comparable to those recorded in other evaporite environments (Skyring, 1984; Lyons et al., 1984). Sulfate reduction rates in surficial sediments of 33 per mil salinity were at least 2 and up to 50 times greater than those measured in other temperate salt marshes associated with microbial mats and in *Spartina* marshes. Howarth and Teal (1979) measured sulfate reduction rates of 0.25-6.0 μM per cm^{-3} per day in marsh sediments. In another study by Skyring et al. (1979), in a *Spartina* salt marsh, sulfate reduction rates were about 1 μM per gram per day in surficial sediments. Thus our rates of sulfate reduction were at least an order of magnitude higher than those in other salt marshes. Without knowledge of the extent of the surface mat development, organic production, and bioturbation in the sediments our results are difficult to extrapolate. The major point is that sulfate reduction in the pond sediments was apparently inhibited by salinity (or factors which accompanied the increases in salinity) since adequate sulfate and precursors (i.e., acetic acid) were available as metabolites for sulfate reducers. Iron sulfide

decreased in sediments of ponds of increasing salinity. Since sulfide values were generally higher than those recorded in the marsh site, iron limitations may limit iron sulfide accumulations. Iron limitations would also limit the activity of sulfate reducers, and thus sulfate reduction.

Although preliminary, these results indicate patterns which may serve as a basis for the examination of the chemical and microbiological changes occurring during the developmental stages of evaporite deposits.

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