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Geochemistry of sulfur in the Florida Everglades: 1994 through 1999

By

Anne L. Bates, William H. Orem, Judson W. Harvey, and Elliott C. Spiker

U.S. Geological Survey, National Center, Reston, VA 20192

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Abstract

In this report, we present data on the geochemistry of sulfur in sediments and in surface water, groundwater, and rainwater in the Everglades region in south Florida. The results presented here are part of a larger study intended to determine the roles played by the cycling of carbon, nitrogen, phosphorus, and sulfur in the ecology of the south Florida wetlands. The geochemistry of sulfur in the region is particularly important because of its link to the production of toxic methylmercury through processes mediated by sulfate reducing bacteria.

ediment cores were collected from the Everglades Agricultural Area (EAA), Water Conservation Areas (WCAs) 1A and 2A, from Lake Okeechobee, and from Taylor Slough in the southern Everglades. Water collection was more widespread and includes surface water from WCAs 1A, 2A, 3A, 2B, the EAA, Taylor Slough, Lake Okeechobee, and the Kissimmee River. Groundwater was collected from The Everglades Nutrient Removal Area (ENR) and from WCA 2A. Rainwater was collected at two month intervals over a period of one year from the ENR and from WCA 2A. Water was analyzed for sulfate concentration and sulfate sulfur stable isotopic ratio (34S/32S). Sediment cores were analyzed for total sulfur concentration and/or for concentrations of sulfur species (sulfate, organic sulfur, disulfides, and acid volatile sulfides (AVS)) and for their stable sulfur isotopic ratio.

Results show a decrease in total sulfur content (1.57 to 0.61 percent dry weight) with depth in two sediment cores collected in WCA 2A, indicating that there has been an increase in total sulfur content in recent times. A sediment core from the center of Lake Okeechobee shows a decrease in total sulfur content with depth (0.28 to 0.08 percent dry weight). A core from the periphery of the lake (South Bay) likewise shows a decrease in total sulfur content with depth (1.00 to 0.69 percent dry weight), however, the overall sulfur content is greater than that near the center at all

depths. This suggests input of sulfur in recent times, especially near the lake margins. Sediments show a general decrease in sulfur concentration with depth, probably because of increases in sulfur input to the marshes in recent times. Regional differences in the concentrations and stable isotopic ratios of sulfate sulfur in surface water show that sulfur contamination to the northem Everglades likely originates from canals draining the EAA.

Introduction

The Everglades region of south Florida is the subject of investigations to determine the effects of agricultural and water management practices, and of urban development on the geochemistry of the ecosystem. The geochemistry of sulfur is of particular interest because of the link between the reduction of sulfate to sulfide and the production of toxic methylmercury (Hurley et al., 1998; Lambou et al., 1991), which is known to be a problem in some areas of the Everglades. Our purposes have been to determine if sulfur content has increased in recent times, to find the sources of sulfur contamination to the northern Everglades, and to determine its relationship with methylmercury content in sediments. To this end, sediment cores were collected and analyzed for sulfur speciation and sulfur stable isotopic ratios ($^{34}S/^{32}S$, expressed as $\delta^{34}S$ in per mil units). We also collected water (surface, ground, and rainwaters) to determine sulfate content and $\delta^{34}S$ values.

The Everglades ecosystem encompasses a large area, including the Kissimmee River basin, Lake Okeechobee, the freshwater northern Everglades, the Everglades National Park, and Florida Bay (Figs. 1 and 2). Most of our sampling for sulfate in water was conducted in the northern Everglades, with emphasis on the Water Conservation Areas (WCA 1A, 2A, 2B and 3A), the Nutrient Removal Area (ENR), the Everglades Agricultural Area (EAA), Lake Okeechobee, and the Kissimmee River. Solid sediment was collected in the EAA, WCA 1A and 2A, and Lake Okeechobee. To a lesser extent, sediment and water was also collected from the southern Everglades in Taylor Slough (part of the Everglades National Park) and from Florida Bay (Fig. 2).

There is widespread sulfur contamination in the northern Everglades. Marsh areas near to canal discharge have surface water sulfate concentrations that average about 0.50 meq/L and often exceed 1.0 meq/L, in contrast to background sites which typically have surface water sulfate concentrations of about 0.05 meq/L or less. The sources of water that are potentially major contributors of this sulfur contamination include groundwater, rainwater, and water channeled from Lake Okeechobee through canals traversing the Everglades Agricultural Area and released into the Water Conservation Areas at pumping stations and spillways (Fig. 1). Sulfur enters the wetlands as sulfate ($SO_4^{=}$) contained in groundwater, rainwater, and canal water. The canal water consists of both irrigation drainage from the EAA and water from Lake Okeechobee. Since 1995, we have collected surface water from the following areas: the Hillsboro, North New River, and Miami Canals in the EAA, a buffer wetland constructed on former agricultural land (the Everglades Nutrient Removal Area or ENR), from WCA 1A, 2A, 2B, 3A, and from the canals bordering or within these areas (Fig. 1). Nutrient-impacted WCA 2A was intensely investigated because it receives direct discharge from the Hillsboro Canal that drains the EAA. More recently (since May 1997), we collected rainwater in the ENR, groundwater in WCA 2A and in the ENR, and surface water from Lake Okeechobee and the Kissimmee River near where it empties into the lake (Fig. 1).

The interpretation of stable isotope values ($\delta^{34}S$) of sulfate is complicated by isotopic fractionation during bacterial reduction of sulfate to sulfide under anoxic conditions, primarily in sediments. The sulfide products are enriched in the isotopically lighter ^{32}S, relative to sulfate (Goldhaber and Kaplan, 1974), and the $\delta^{34}S$ values of residual sulfate increase (Nakai and Jensen, 1964). Negative sulfide $\delta^{34}S$ values are usually obtained where there is an essentially unlimited amount of sulfate available (as in seawater); the $\delta^{34}S$ values in freshwater are usually positive. The $\delta^{34}S$ values of the residual sulfate can become very high when the sulfate reservoir is limited. The amount of sulfide produced and the rate of its production through bacterial reduction are controlled by the availability of sulfate and biodegradable organic matter (Berner, 1980; Berner and Raiswell, 1984; Boudreau and Westrich, 1984; Canfield, 1991). Another complicating factor is that oxidation of isotopically light sulfide to sulfate will add isotopically light sulfate to a reservoir, thus decreasing the $\delta^{34}S$ value of the sulfate in that reservoir (without changing the $\delta^{34}S$ values of the residual sulfide). The formation of disulfide minerals (mostly pyrite) from sulfidic sulfur is limited by reactive iron availability, assuming excess precursor sulfide availability. Sulfidic sulfur can also react with organic matter, forming organic sulfur compounds, or it can diffuse out of the sediments into the water column where it can become oxidized to sulfate. If this is the case, the sulfate reservoir in the water column will increase and its $\delta^{34}S$ values will become lighter.

Study Area

Since implementation of the Central and Southern Florida Project for Flood Control and Other Purposes, passed by the United States Congress in 1948, the historic Everglades has been divided by canals and levees into three major areas: the Everglades Agricultural Area, the Water Conservation Areas, and Everglades National Park (Fig. 1). Water in the northern Everglades (the EAA and WCAs) is fresh and derived from rainfall and outflow from Lake Okeechobee. Water from Lake Okeechobee irrigates the EAA and then flows into the WCAs via a network of canals and pumping stations where it is impounded in wetlands and eventually released for flood control and water supply needs. Recent studies (Craft and Richardson, 1993; Koch and Reddy, 1992; DeBusk et al., 1994) indicate that agricultural runoff has increased the input of nutrients in parts of the WCAs adjacent to canals draining the EAA. Increased nutrient loading has resulted in changes in the type and amount of vegetation growing in the impacted areas.

The surficial and ground waters of the freshwater Everglades are components of a continuous, non-confined aquifer system, the uppermost unit of which is the Biscayne Aquifer (Sonntag, 1987). Limestone bedrock underlies the Everglades peat (Gleason and Stone, 1994). Recharge to the aquifer is mostly from rainwater, with lesser amounts supplied by drainage from Lake Okeechobee and other areas to the west and north (Fish, 1988; Waller and Earle, 1975). Groundwater flow patterns in the WCAs vary seasonally and are not well known, although the WCAs and the canals are known to be hydrostatic high points on a regional scale (Fish, 1988). The surface waters are circum-neutral with pH values generally near 7 (unpublished data, Orem).

Taylor Slough in the southern Everglades (Fig. 2) has freshwaters in its northern region. The head of the Slough is adjacent to agricultural fields and is nutrient impacted (Orem et al., 1999). The dominant plants in the northern part of the Slough are sawgrass, waterlily and periphyton algae. Marine water influence is felt in the mangrove swamps in the near-coastal areas of the Slough. Freshwater flows from the Slough into the marine waters of Florida Bay (Fig. 2).

Figure 1. Study Areas in the Northern Everglades of South Florida

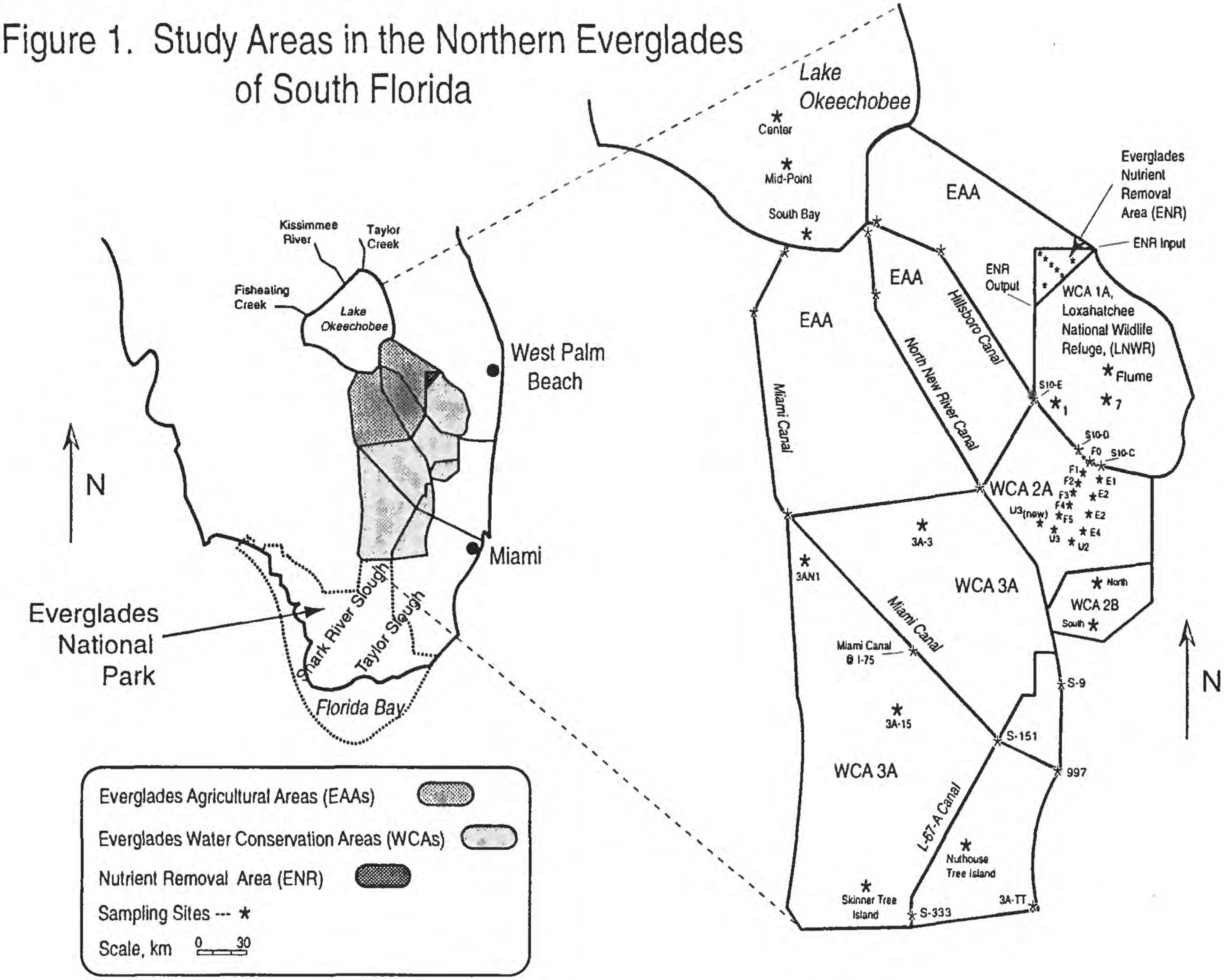
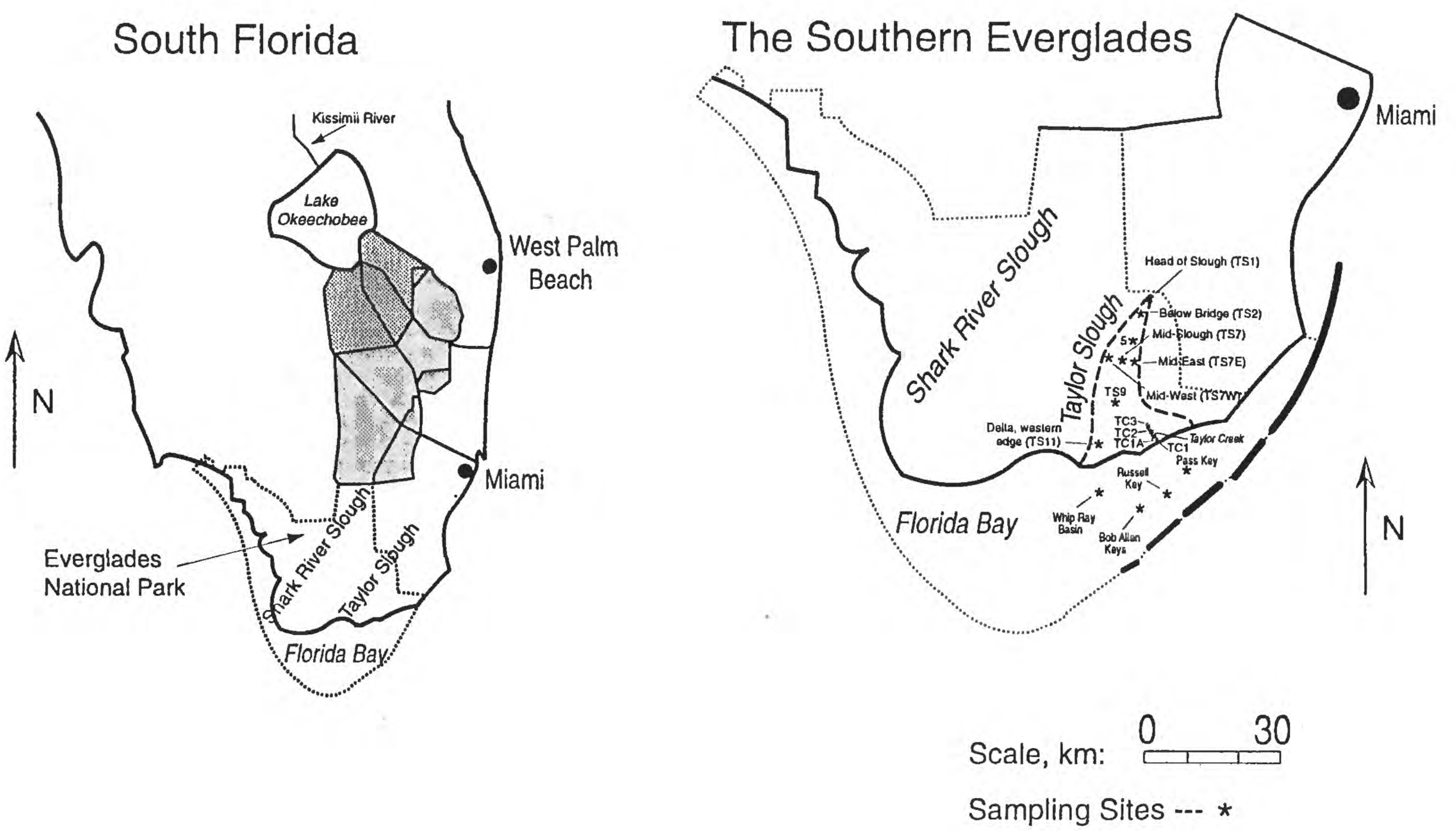


Figure 2. Study Areas in the Southern Everglades of South Florida



Analytical Methods

Sediment Sampling. Sediment cores were collected by piston coring using 9 cm inner diameter Plexiglas core tubes (Orem et al., 1997). The cores were sectioned into segments ranging from 2-10 cm thick. The core segments were placed in zip-lock plastic bags, returned to the lab, and were then frozen until analysis. There was brief exposure to air when the samples were transferred between containers.

Sulfur Speciation. Aliquots of selected freshly thawed core segments were assayed gravimetrically for disulfides (DS), acid-volatile-sulfides (AVS), sulfate and organic-sulfur (OS) after separation of these sulfur fractions by an HCl-$CrCl_2$-Eschka sequential extraction scheme (described in detail by Bates et al., 1993), similar to methods were used by Tuttle et al. (1986) and Canfield et al. (1986). A brief description is given here: acid-volatile sulfides were extracted from the samples using hot 6N HCl under a nitrogen atmosphere in a sealed reaction vessel and then reprecipitated as silver sulfide in a separate test-tube filled with 5% silver nitrate. Disulfides within the HCl-insoluble residue were then reduced by chromous chloride in hot 6N HCl under nitrogen and reprecipitated as silver sulfide. The sediment residue was then filtered. Sulfate in the filtrate (including sulfate derived from both pore-water and solid-phases in the sample) was precipitated as barium sulfate. Organic-sulfur in the residual sediment was oxidized to sulfate by fusion with Eschka's mixture (magnesium oxide and calcium carbonate) and then precipitated as barium sulfate. The percentage by weight of each sulfur fraction in the sediment was determined gravimetrically from the silver sulfide or barium sulfate recovered.

Water Sampling. All water samples were collected in clean, dry 500 milliliter Nalgene bottles. Surface water was collected from about midway between the water surface and the sediment surface. Most water sample bottles were topped off and did not contain any air space. Samples were kept on ice during transit to the laboratory, where they were continuously refrigerated. Usually no more than two weeks elapsed between collection and the beginning of analysis.

Analysis of Sulfate Concentration. Water was filtered through 0.4 micrometer Nuclepore filter pads before analysis in order to remove particulates. The volume of the filtrate was measured to the nearest milliliter. The samples were then transferred to volumetric flasks, and the contents were acidified to pH 4 with concentrated HCl. Samples were then heated on a hot plate, ant barium chloride (10%) was added after they began to boil. After the sample volume had been reduced to about 100 ml, the samples were filtered through 0.4 micrometer Nuclepore filter pads collect the precipitated barium sulfate. Recovery was determined after drying the filter pads in a desiccator. The sulfate concentrations of the samples were calculated from the mass of sulfate recovered and the measured volume of the water sample.

Analysis of Total Sulfur in Sulfur Fertilizer. Sulfur in elemental sulfur fertilizer was oxidized to sulfate by fusion with Eschka's mixture for two hours at 800^{o} C. The dry fusion mixture was then slowly cooled and then suspended in boiling distilled-deionized water for 30 minutes. The suspension was filtered to remove solid residue, and the recovered solution was then treated as described above for water samples.

Sulfur Isotopic Ratio Determination. The recovered barium sulfate was converted to SO_2 by combustion on a vacuum line and was then isolated by vacuum line methods. The $^{34}S/^{32}S$ of SO_2 was determined using a Finnigan MAT 251 stable isotope mass spectrometer, and the results are reported in delta notation ($\delta^{34}S$) as parts per thousand deviation from Canyon Diablo Triolite (CDT) reference standard (Thode et al., 1961). Smaller samples (less than 1 milligram of sulfur) were concentrated using liquid nitrogen for mass spectrometric analysis.

Results and Discussion

Solid Phase Sulfur Geochemistry

Solid phase cores were collected in the EAA, WCA 2A, WCA 1A (Loxahatchee National Wildlife Refuge), Taylor Slough, and Lake Okeechobee (see Figures 1 & 2).

WCA 1A. WCA 1A is a "pristine" area protected from canal discharge. Two sediment cores were obtained from this area in April 1995, one near the Hillsboro Canal at site 1, and one away from the canal at site 7 (Fig. 1). Sulfur species contents for these sampling sites were obtained only on a percent by wet weight basis (Table 1, Fig. 3). These data shows that sulfur contents are about the same at both sites except that organic sulfur is much higher at site 1. The $\delta^{34}S$ values are positive at both sites (Table1, Fig. 3), indicating freshwater levels of sulfate.

WCA 2A. Total sulfur content (percent dry weight) is similar in sediment collected in 1994 at two sites: one near the Hillsboro Canal (E1) and another far from the canal (U3) (Table 2, Fig. 4). At each site, total sulfur shows a significant increase in the upper part of the core, probably indicating an increase in sulfur loading in the marsh in recent times. Sulfur speciation analyses (Table 2, Fig. 5) indicate that most of the sulfur is in the form of organic sulfur, probably due to iron limitation of sulfide fixation. Positive $\delta^{34}S$ values for the sulfur species (Table 2, Fig. 5) show that there is a relatively restricted supply of sulfate for reduction to sulfide, although one negative $\delta^{34}S$ value for disufide sulfur (pyrite) at U3 could indicate an increase in sulfate availability at the time of fixation (Bates et al., 1998).

Sediment collected in 1996 from site F1 (near the Hillsboro Canal) and from site $U3_{new}$ ("new" U3--not the same as the site from 1994, see Fig. 1) has total sulfur content slightly lower than in the sediment collected in 1994 (Table 2, Fig. 6). Because the core lengths were shorter in 1996 (only the top 15 cm of sediment), it is not possible to tell if there is a decrease with depth as there was in the sediment collected in 1994. Organic sulfur is the dominant species (Table 2, Fig. 7) near the top of the sediment at F1 and U3, however, disulfides increase with depth. As in the sediment samples collected in 1994, the $\delta^{34}S$ values are positive (Table 2, Fig. 7), indicating a limited supply of sulfate.

Organic sulfur is the dominant sulfur species in another short core (top 15 cm) collected in WCA 2A in 1995 (Table 2, Fig. 8), however the results are available only on a percentage wet weight basis. More positive $\delta^{34}S$ values for disulfide sulfur and organic sulfur are found in the near-surface sediment (top 3 cm) (Table 1, Fig. 8) near the canal (F1) than far from the canal ($U3_{new}$). This may be the result of higher rates of sulfate reduction near the canal.

Everglades Agricultural Area. Agricultural soil at the U.S. Department of Agriculture (USDA) Research Center at Canal Point and at the University of Florida Agricultural Research Center was analyzed for total sulfur $\delta^{34}S$ values. These values fall in a range from 12.63 to 19.37, with higher values in the top 5 cm of the three cores sampled (Table 3, Fig. 9). Total sulfur was determined only on a dry weight basis, and appears to increase with depth in the two meter core (Table 3).

Lake Okeechobee. Total sulfur as a percent of dry weight was obtained for two cores from Lake Okeechobee, one from the center of the lake and the other from South Bay at the southern tip of the lake (Table 4, Fig. 10). Total sulfur content is higher at the periphery of the lake than at the center, and both cores show a general decrease in sulfur content with depth.

Taylor Slough. Total sulfur contents (Table 5, Fig. 11) are higher in the upper part of sediment collected at the head of Taylor Slough (Fig. 1) than in sediment collected in the middle part of the Slough (Fig. 1). This could be the result of the proximity of the head of the slough to agricultural fields and canal drainage (the head of the Slough also has higher total phosphorus levels in the sediment (Orem et al., 1999), possibly from agricultural runoff. Organic sulfur is the dominant sulfur species at both sites (Table 5, Fig. 12). Sulfur species $\delta^{34}S$ values are positive at both sites (Table 5, Fig. 12), indicating freshwater levels of sulfate. The $\delta^{34}S$ values of sulfate sulfur are quite high (approaching 30 per mil) near the top of the core at the head of the slough. This could be the result of a very restricted source of sulfate (not likely considering that the sulfur content is relatively high near the top of the core) or to high $\delta^{34}S$ values in the source sulfate.

Table 1. Sulfur species concentrations and δ34S values in sediment from WCA 1A (Loxahatchee National Wildlife Refuge), sites 1 and 7, April 1995.

WCA 1A, Site 1, 4-21-95 (26 28.782'N 80 26.565'W)

Core Segment	Av. Depth (cm)	Sulfate % Wet Wt.	AVS % Wet Wt.	DS % Wet Wt.	OS % Wet Wt.	Sulfate δ34S	AVS δ34S	DS δ34S	OS δ34S
0-5 cm	2.5	0.009	0.008	0.020	0.084	17.89	21.40	14.87	13.36
5-10	7.5		0.004	0.010	0.055	14.55	22.86	17.80	17.71
10-15	12.5	0.002	0.004	0.005	0.033	14.40	21.52	12.29	15.78
15-20	17.5	0.032	0.003	0.005	0.024	15.53		14.26	16.17
25-30	27.5	0.011	0.003	0.005	0.018		15.26	14.13	15.48
35-45	40.0	0.015	0.006	0.004	0.012		17.11	15.03	15.74

WCA 1A, Site 7, 4-21-95 (26 28.873'N 80 24.931'W)

Core Segment	Av. Depth (cm)	Sulfate % Wet Wt.	AVS % Wet Wt.	DS % Wet Wt.	OS % Wet Wt.	Sulfate δ34S	AVS δ34S	DS δ34S	OS δ34S
0-5cm	2.5	0.010	0.007	0.003	0.023	16.32	22.44	15.43	15.32
5-10	7.5	0.012	0.009	0.004	0.017	15.19	21.25	12.12	16.10
10-15	12.5	0.008	0.003	0.002	0.008	14.21	27.34	17.45	16.57
15-20	17.5	0.009	0.003	0.002	0.015	15.25	19.58	18.80	15.83
25-30	27.5	0.006	0.003	0.002	0.011	14.19	19.93	10.56	15.40
40-50	45.0	0.003	0.001	0.002	0.007	14.83		5.19	16.51

Figure 3

Sulfur Species in Loxahatchee Sediment: Percent Wet Weight and δ34S Values

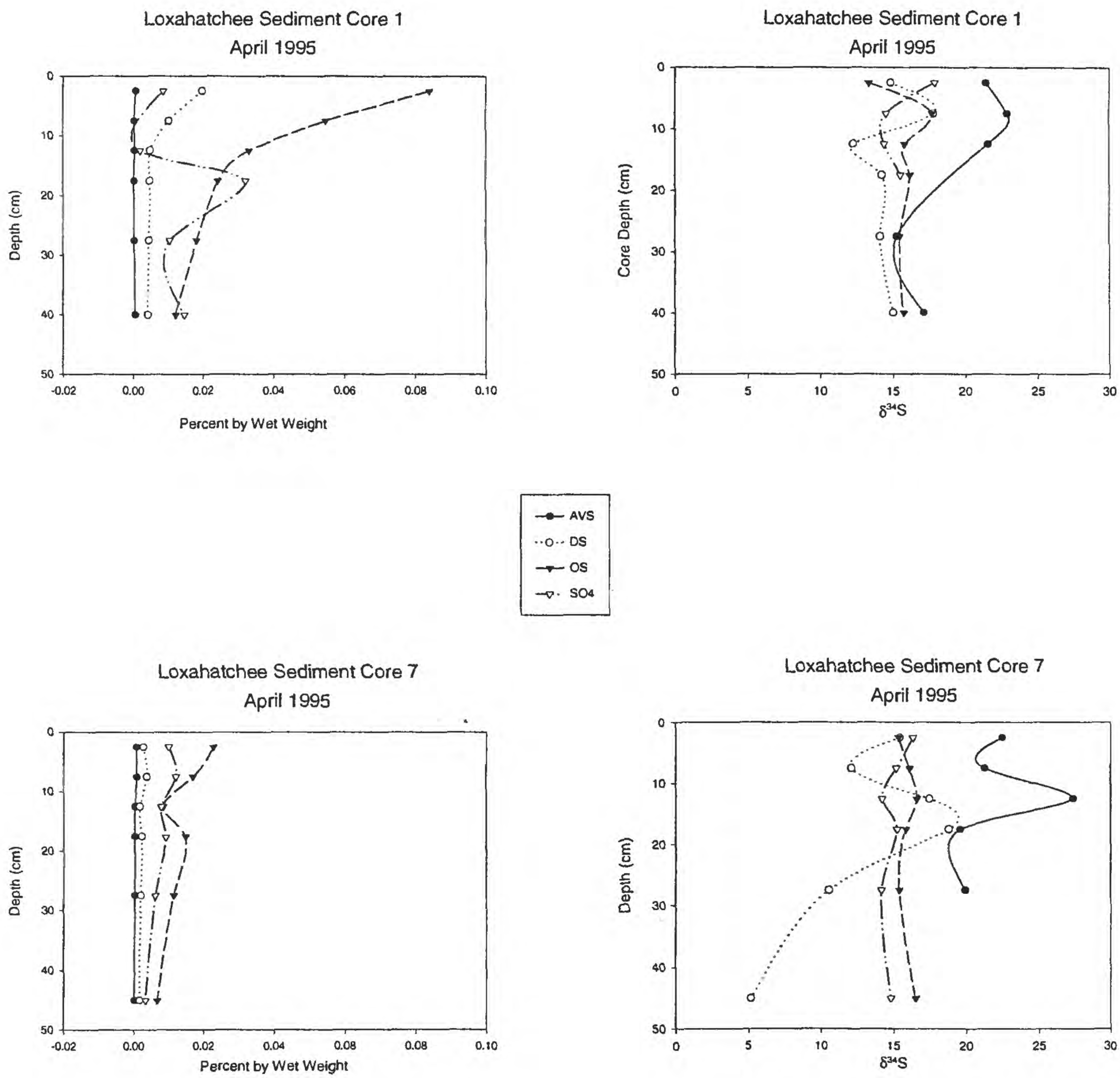
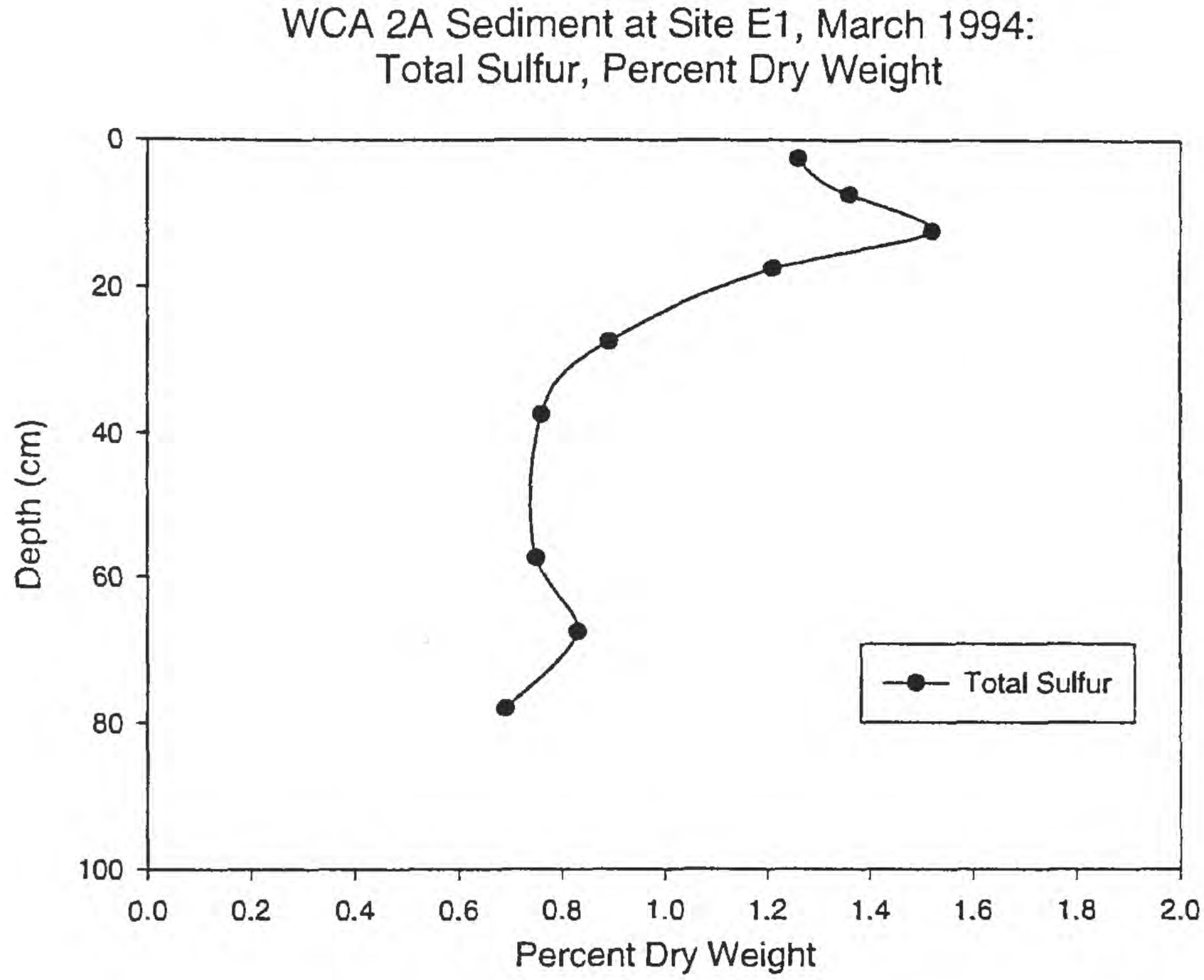


Table 2. Sulfur species concentrations and δ34S values in sediment from WCA 2A, sites E1, U3, and U3 (new).

Core Segment	Average Depth (cm)	Sulfate % Dry Wt.	AVS % Dry Wt.	DS % Dry Wt.	OS % Dry W	TS % Dry Wt.	Sulfate δ34S	AVS δ34S	DS δ34S	OS δ34S
WCA 2A, Site E1, 3-1-94			(26 21.090'N	80 21.200'W)						
0-5	2.5	0.160	0.020	0.220	0.870	1.26	15.72	14.19	13.62	14.08
5-10	7.5	0.050	0.010	0.220	1.090	1.36	14.78	13.69	12.06	12.21
10-15	12.5	0.140	0.010	0.270	1.090	1.52	14.21	14.00	10.78	12.05
15-20	17.5	0.150	0.010	0.250	0.800	1.21	14.51	15.82	10.76	14.08
25-30	27.5	0.120	0.010	0.150	0.610	0.89	14.35	16.08	11.44	15.31
35-40	37.5	0.090	0.010	0.130	0.540	0.76	15.72	20.24	15.97	16.89
55-60	57.5	0.030	0.000	0.150	0.570	0.75	22.57	21.01	18.78	15.01
65-70	67.5	0.180	0.000	0.170	0.480	0.83	17.14	21.28	11.16	16.10
76-80	78	0.100	0.000	0.120	0.470	0.69	14.31	19.60	6.97	13.82
WCA 2A, Site U3, 3-1-94				(26 17.270'N	80 24.680'W)					
0-5	2.5	0.310	0.010	0.440	0.800	1.57	18.17	9.31	6.84	8.19
5-10	7.5	0.390	0.010	0.390	0.940	1.74	15.46	21.86	-1.09	12.52
10-15	12.5	0.260	0.010	0.370	0.760	1.40	18.51	19.76	15.24	16.93
20-25	22.5	0.160	0.000	0.420	0.760	1.34	19.57	23.61	19.93	16.15
30-35	32.5	0.090	0.000	0.220	0.610	0.92	22.21		22.21	15.61
50-55	52.5	0.000	0.000	0.100	0.550	0.65			17.02	14.53
63-73	68	0.060	0.000	0.080	0.470	0.61			13.28	15.55
WCA-2A, Site F1, 3-27-95				(26 21.580'N	80 22.230'W)					
0-3 cm	1.5	0.004	0.005	0.006	0.032		18.127	7.78	7.943	10.61
3-6	4.5	0.018	0.004	0.016	0.047		15.196	10.70	9.69	10.42
6-9	7.5	0.015	0.005	0.020	0.112		16.663	17.34	14.23	9.90
12-16	14	0.016	0.005	0.024	0.105		19.788	16.07	14.19	10.43
WCA 2A, Site U3 (new), 3-27-95				(26 17.250'N	80 24.680'W)					
0-3 cm	1.5	0.008	0.001	0.006	0.002		14.70	17.80	7.93	8.35
3-6	4.5	0.020	0.002	0.014	0.020		17.78	15.70	6.64	6.80
6-9	7.5		0.002	0.011				16.34	6.52	
9-12	10.5	0.027	0.003	0.019	0.067		18.02	16.77	9.92	13.11
12-15	14	0.021	0.002	0.018	0.065		17.67	17.95	12.53	15.21
WCA 2A, Site F1, 4-26-96				(26 21.580'N	80 22.230'W)					
0-5	2.5	0.130	0.010	0.160	0.570	0.87	17.79	18.32	11.9	10.998
5-10	7.5	0.090	0.010	0.200	0.610	0.91	20.18	18.98	13.94	13.726
10-15	12.5	0.000	0.070	0.980	0.000	1.04		19.73	15.691	17.873
WCA 2A, Site U3 (new), 4-25-96				(26 17.250'N	80 24.680'W)					
0-5	2.5	0.080	0.001	0.470	0.630	1.18	19.934	16.577	8.776	16.338
5-10	7.5	0.110	0.025	0.750	0.000	0.89		18.097	10.813	15.262
10-15	12.5	0.000	0.019	0.700	0.000	0.72		19.044	16.186	11.861

Total Sulfur in WCA 2A Sediment at Sites E1 and U3, March 1994: Percent Dry Weight



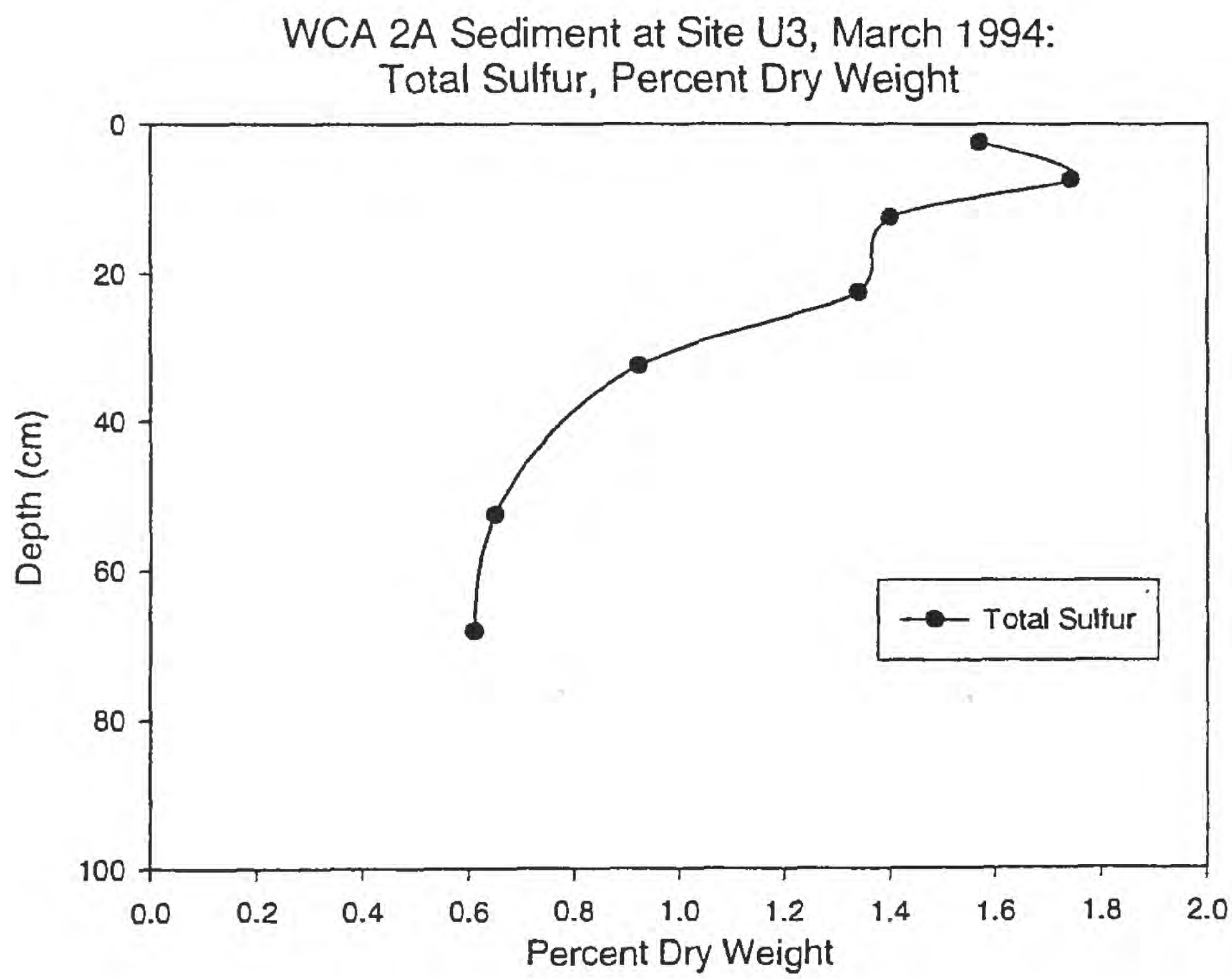
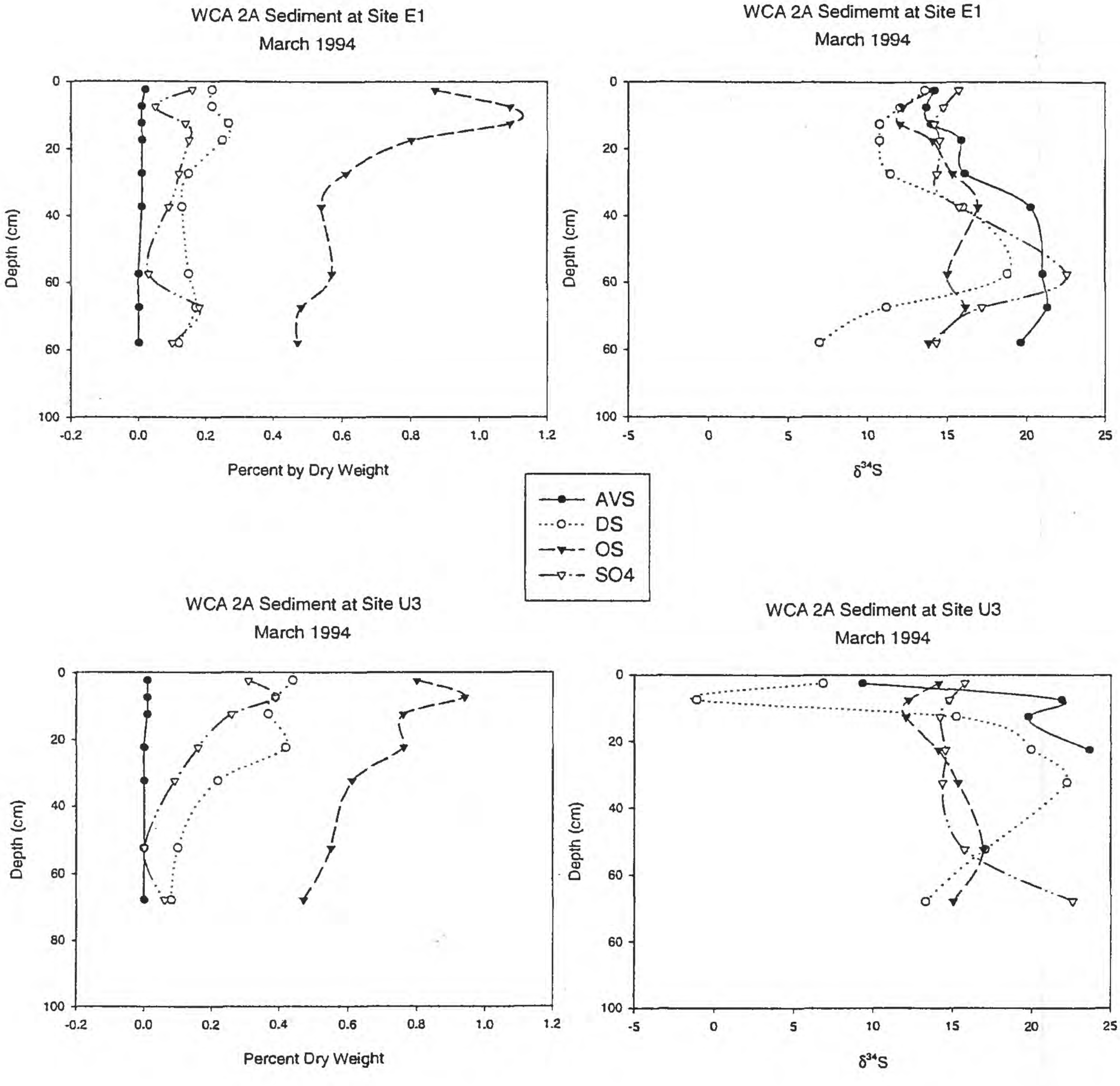
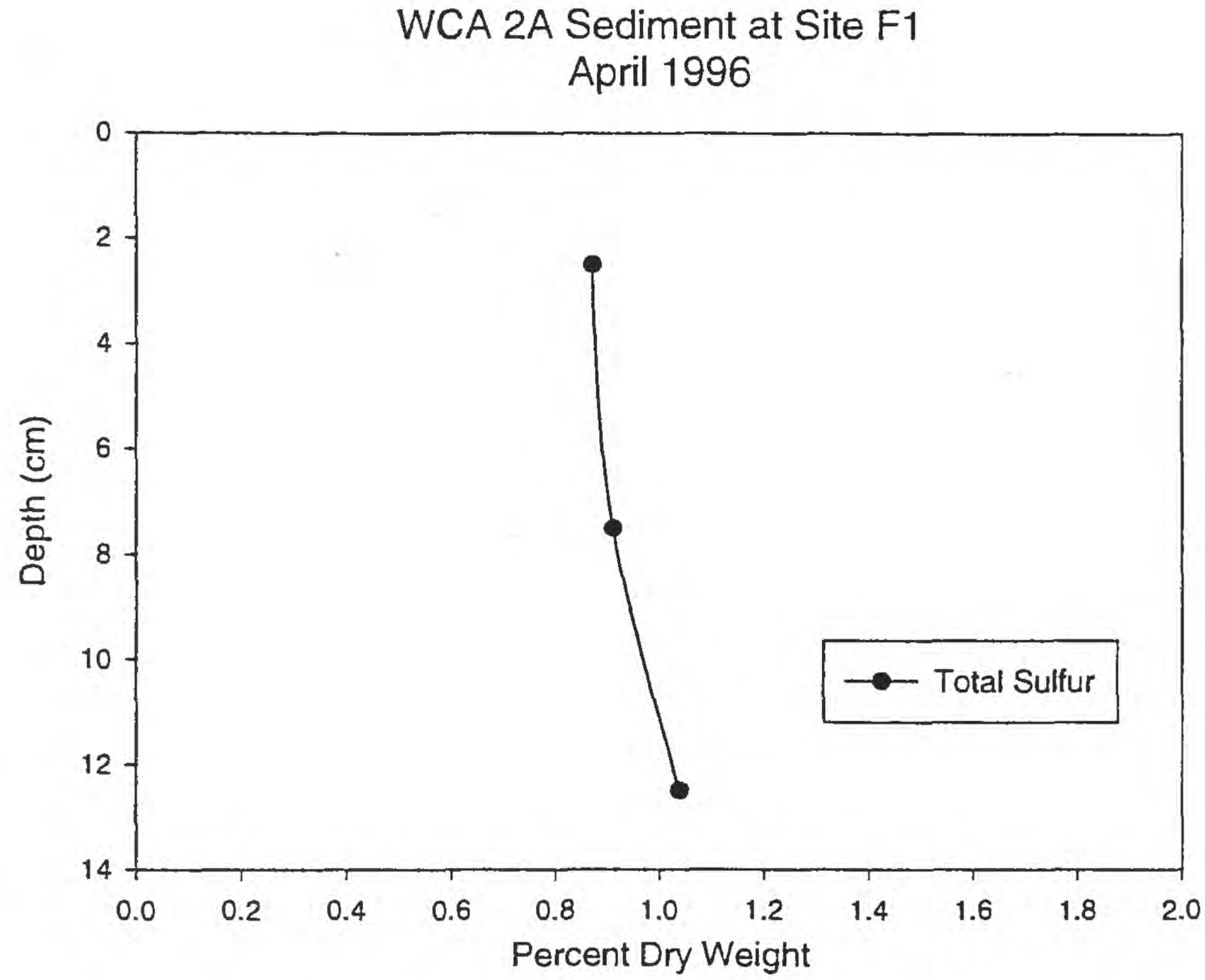


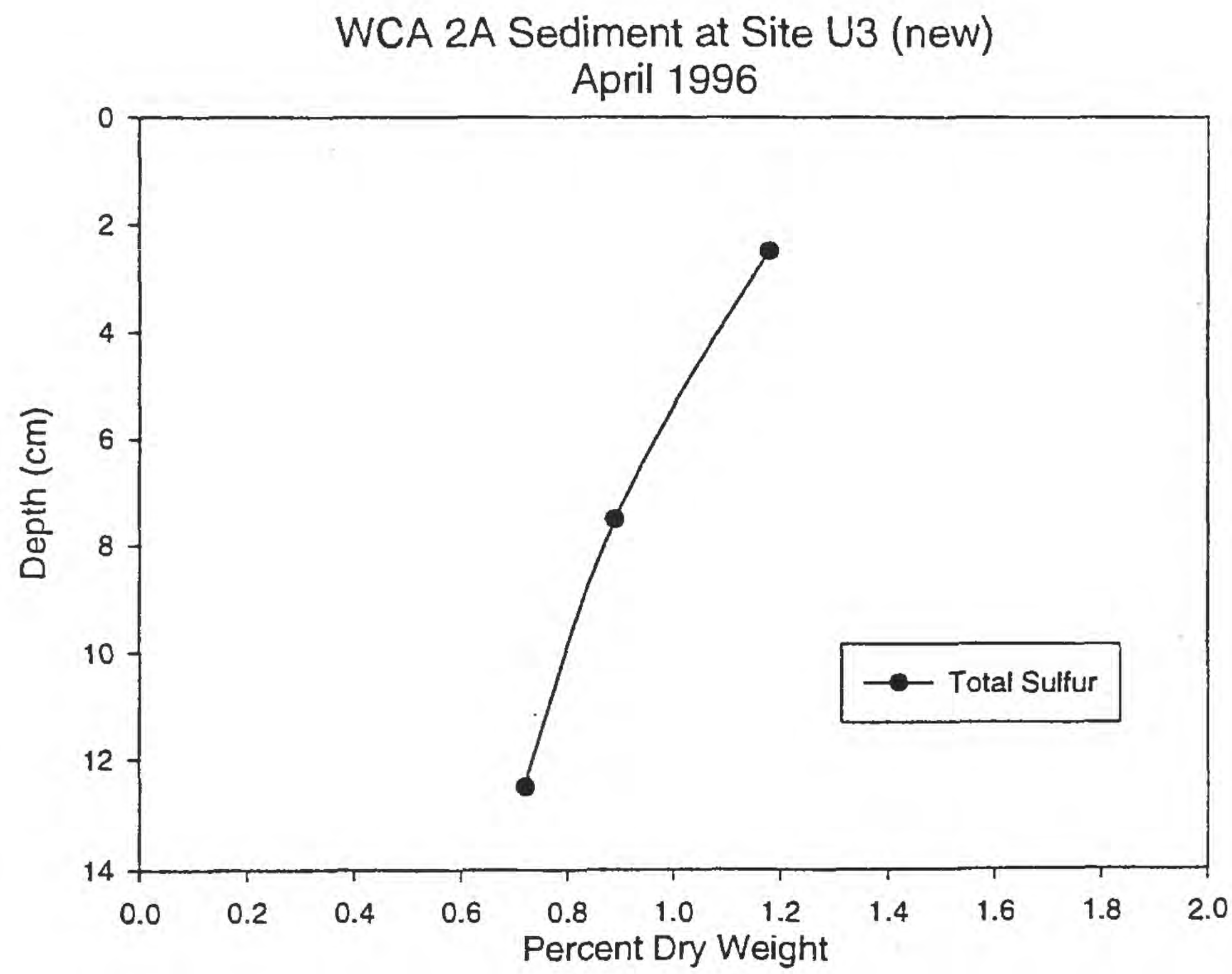
Figure 5

Sulfur Species in WCA 2A Sediment at Sites E1 and U3
March 1994: Percent Dry Weight and δ34S



Total Sulfur in WCA 2A Sediment at Sites F1 and U3 (new): Percent Dry Weight





Sulfur Species in WCA 2A Sediment at Sites F1 and U3, April 1996: Percent Dry Weight and δ34S Values

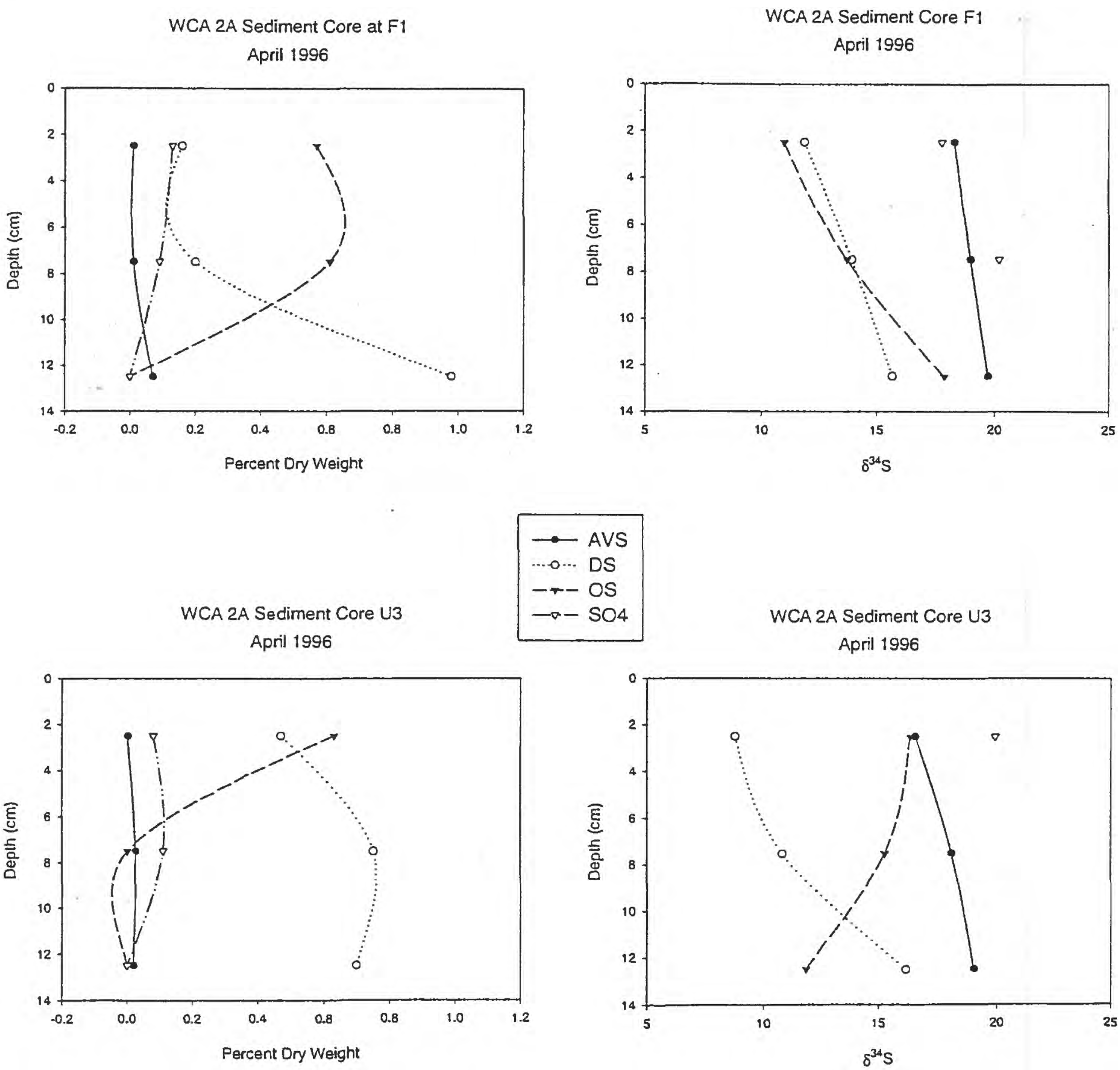


Figure 8

Sulfur Species in WCA 2A Sediment at Sites F1 and U3 (new), March 1995: Percent Wet Weight and δ34S

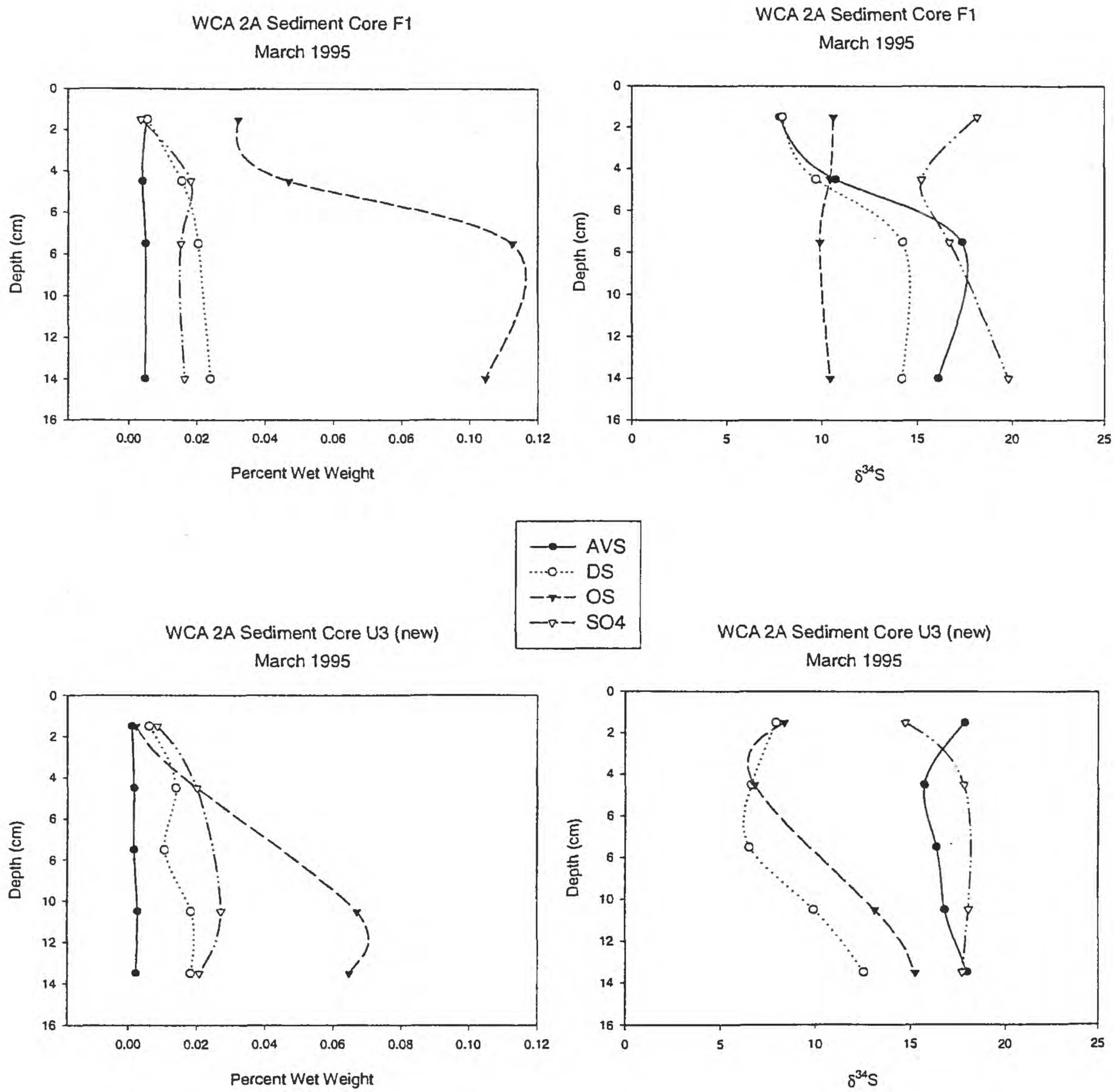
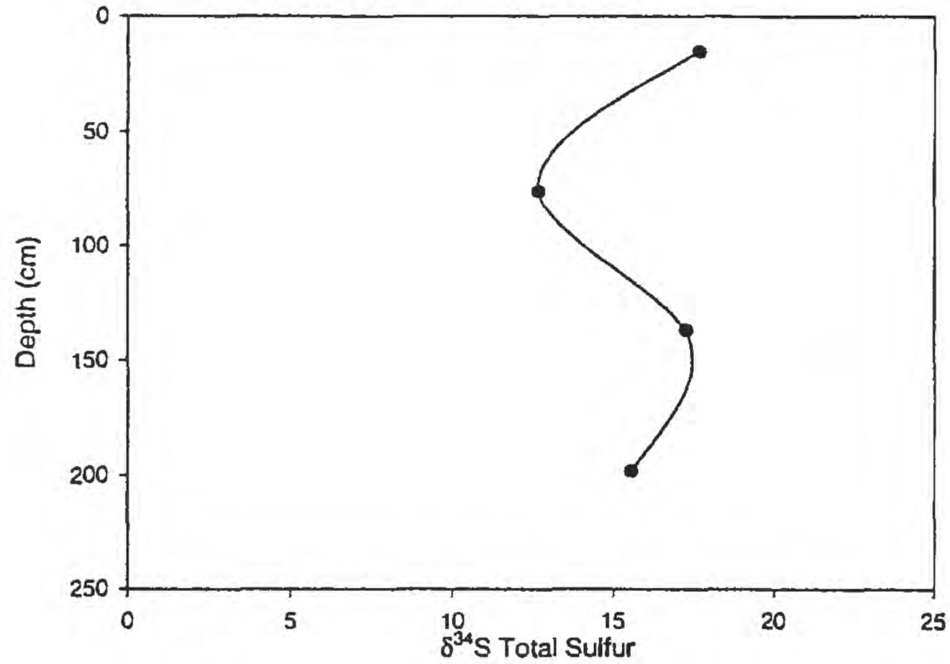


Table 3. Total sulfur contents (percent dry weight) and δ34S values in the Everglades Agricultural Area at the Department of Agriculture Research Center at Canal Point (A1) and The University of Florida Research Station at Belleglade (G1 and G2).

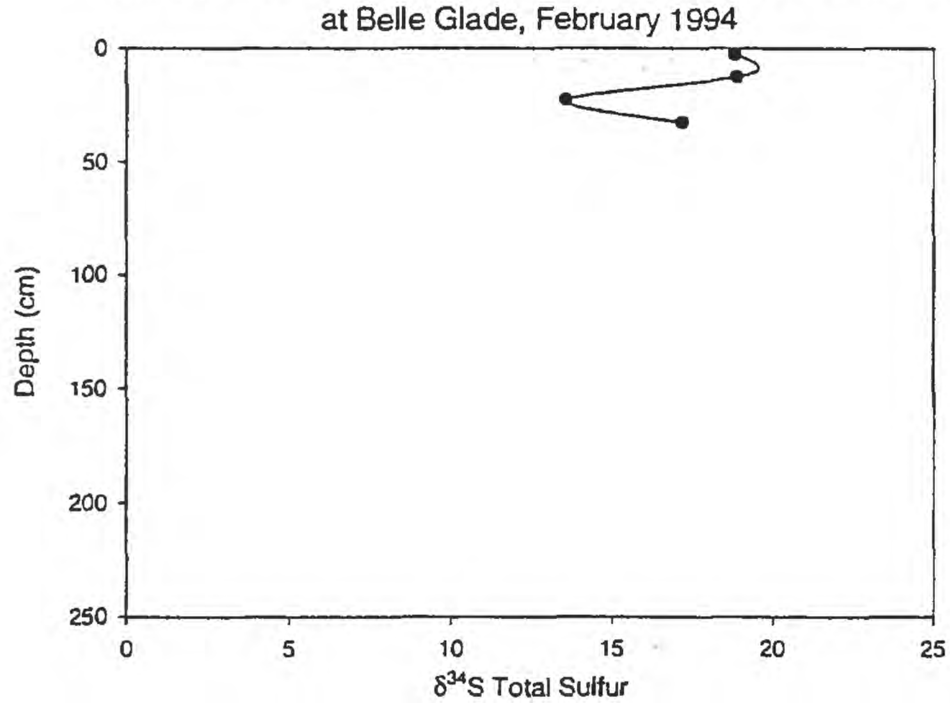
Core Segment	Average Depth (cm)	Sulfate % Dry Wt.	AVS % Dry Wt.	DS % Dry Wt.	OS ö Dry W	TS % Dry Wt.	Sulfate δ34S	AVS δ34S	DS δ34S	OS δ34S	TS δ34S
EAA, Site A1, 2-28-94				(Lat and long coordinates unknown)							
0-1 ft.	15.24 cm					0.10					17.63
2-3 ft.	76.20 cm					0.88					12.63
4-5 ft.	137.2 cm					2.02					17.23
6-7 ft.	198.1 cm					2.27					15.55
EAA, Site G1, 2-28-94				(Lat and long coordinates unknown)							
0-5 cm						0.50					18.75
10-15 cm						0.53					18.82
20-25 cm						0.60					13.51
30-35 cm						0.48					17.12
EAA, Site G2, 2-28-94				(Lat and long coordinates unknown)							
0-5 cm						0.56					19.37
20-25 cm						0.44					18.82
40-45 cm						0.57					19.23

Figure 9

Total Sulfur δ34S Values at the U.S. Department of Agricultural Research Center at Canal Point, February 1994



Total Sulfur δ34S Values at the University of Florida Cane Field at Belle Glade, February 1994



Total Sulfur δ34S Values at the University of Florida Unused Field, February 1994

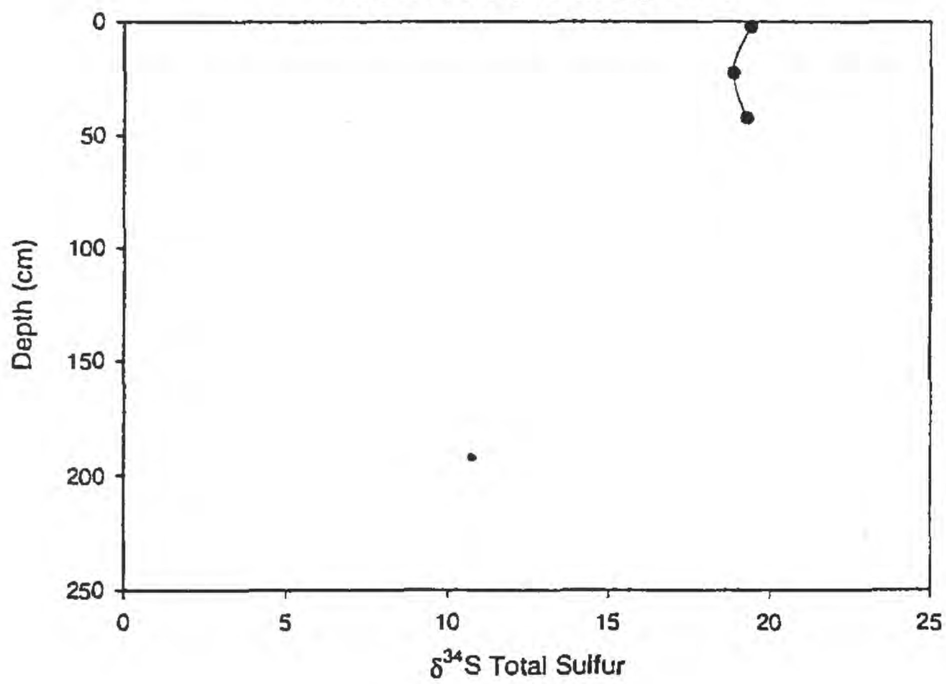


Table 4. Total sulfur contents (percent dry weight) for sediment cores from the center and the periphery of Lake Okeechobee.

Core Segment	Average Depth (cm)	TS % Dry Wt.
Lake Okeechobee, Center Core		(26 57.783'N 80 49.931'W)
0-2	1	0.25
2-4	3	0.28
4-6	5	0.33
6-8	7	0.35
8-10	9	0.24
10-12	11	0.28
12-14	13	0.27
14-16	15	0.22
16-18	17	0.25
18-20	19	0.13
20-22	21	0.13
22-24	23	0.17
24-26	25	0.20
26-28	27	0.20
28-30	29	0.20
30-32	31	0.19
32-34	33	0.14
34-36	35	0.08
Lake Okeechobee, Periphery		(26 44.179'N 80 45.595'W)
0-2	1	0.60
2-4	3	1.00
4-6	5	1.01
6-8	7	0.97
8-10	9	0.90
10-12	11	0.91
12-14	13	1.11
14-16	15	0.85
16-18	17	0.84
18-20	19	0.79
20-22	21	0.65
22-24	23	0.63
24-26	25	0.65
26-28	27	0.80
28-30	29	0.73
30-32	31	0.73
32-34	33	0.83
34-36	35	0.84
36-38	37	0.76
38-42.5	40.25	0.69

Figure 10. Total Sulfur Content in Lake Okeechobee Cores: Percent Dry Weight

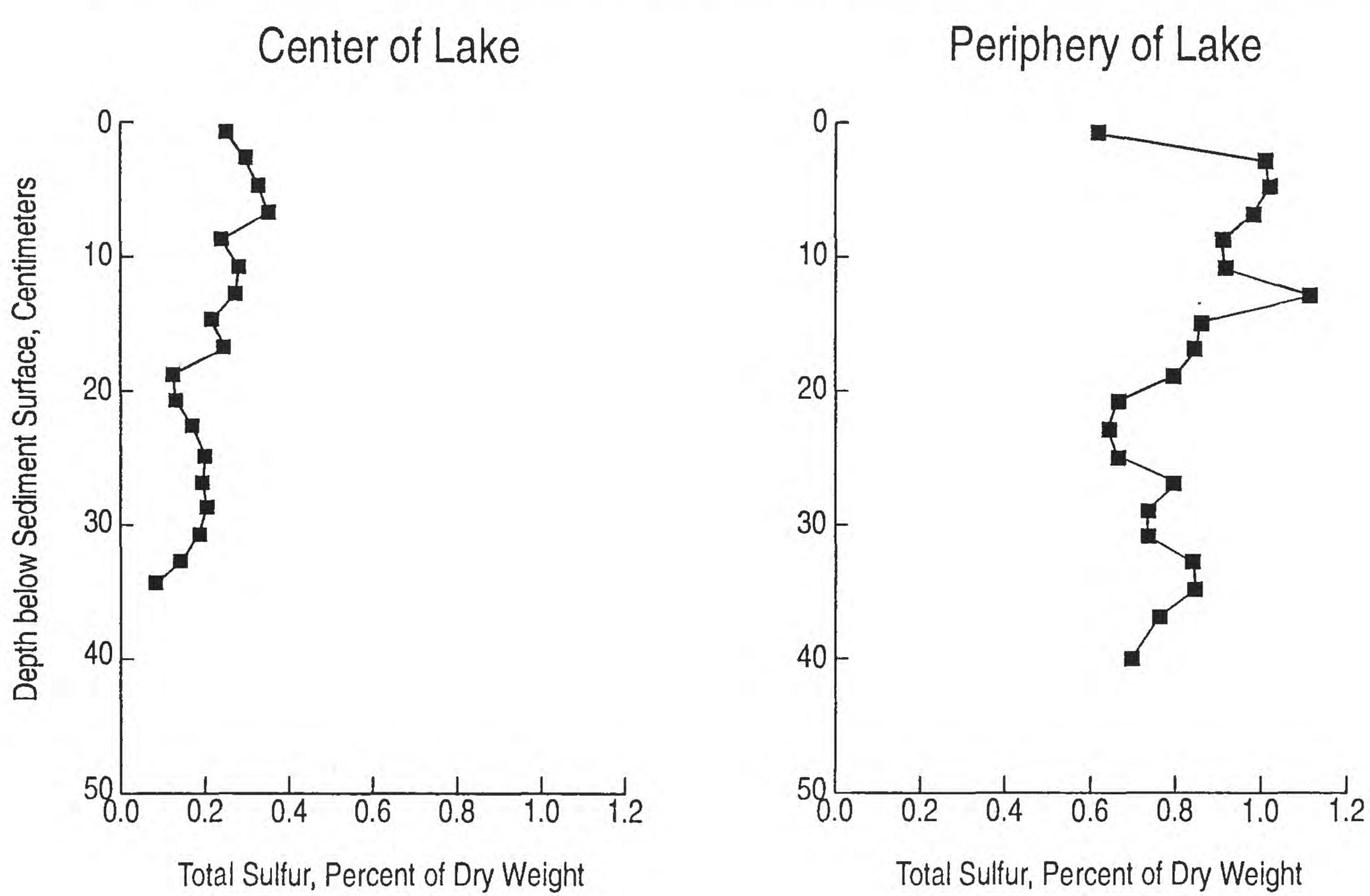


Table 5. Sulfur species contents (percent dry weight) and δ34S values in sediment collected at the head and mid-section of Taylor Slough, May 1996.

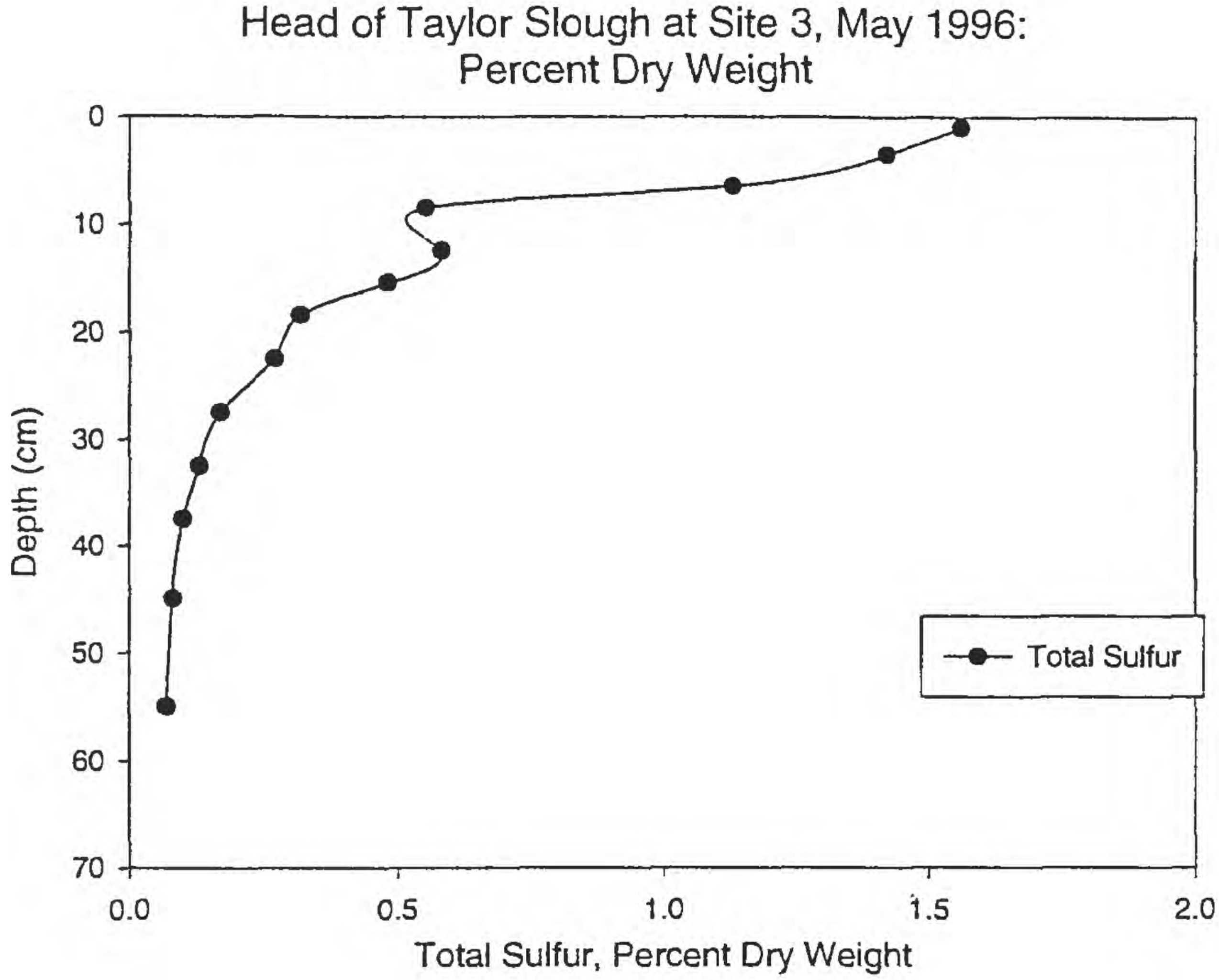
Head of Taylor Slough, Core 19, 5-22-96 (25 24.306'N 80 36.377'W)

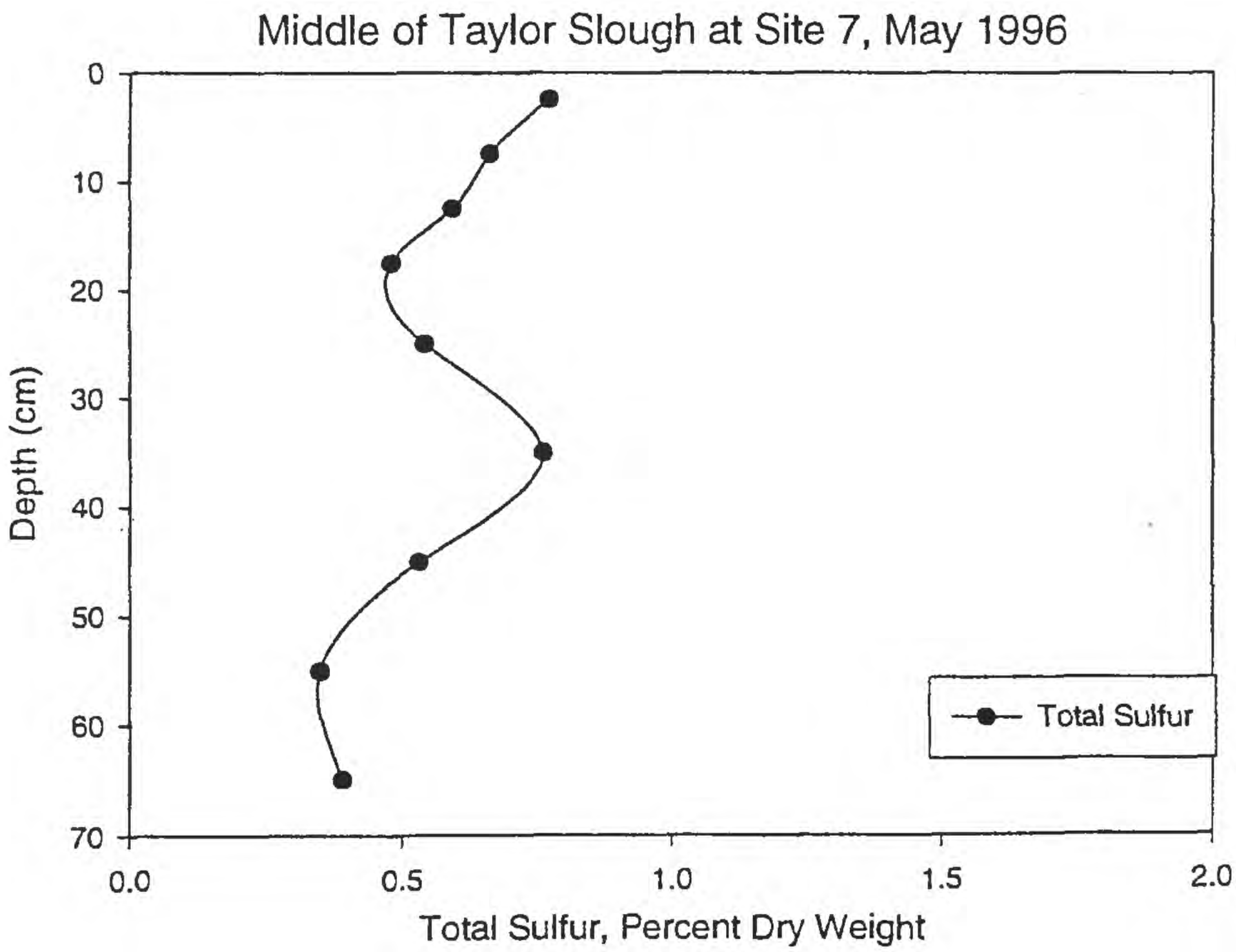
Core Segment	Average Depth (cm)	Sulfate % Dry Wt.	AVS % Dry Wt.	DS % Dry Wt.	OS % Dry Wt.	Sulfate δ34S	AVS δ34S	DS δ34S	OS δ34S
0-2 cm	1.0	0.190	0.045	0.660	0.670	28.85	24.28	22.31	22.63
2-5	3.5	0.290	0.031	0.430	0.670	28.45	26.02	22.85	22.85
5-8	6.5	0.380	0.009	0.140	0.610	29.19	25.55	22.47	23.13
8-11	8.5	0.070	0.006	0.070	0.400	23.92	n.d.	18.77	19.56
11-14	12.5	0.120	0.008	0.080	0.370	20.48	n.d.	17.09	18.42
14-17	15.5	0.180	0.005	0.070	0.230	20.94	n.d.	18.43	18.91
17-20	18.5	0.070	0.003	0.060	0.190	20.43	n.d.	20.20	18.99
20-25	22.5	0.040	0.004	0.060	0.170	20.43	n.d.	19.18	18.82
25-30	27.5	0.020	0.001	0.030	0.110	19.92	n.d.	23.04	18.38
30-35	32.5	0.010	0.001	0.040	0.070	19.56	n.d.	20.16	18.03
35-40	37.5	0.020	0.001	0.040	0.040	18.80	n.d.	21.91	17.79
40-50	45.0	0.010	0.000	0.040	0.030	n.d.	n.d	17.35	17.35
50-60	55.0	0.020	0.003	0.020	0.020	n.d.	14.51	20.96	14.16

Mid Taylor Slough, Core 5, 5-17-96 (25 17.231'N 80 38.780'W)

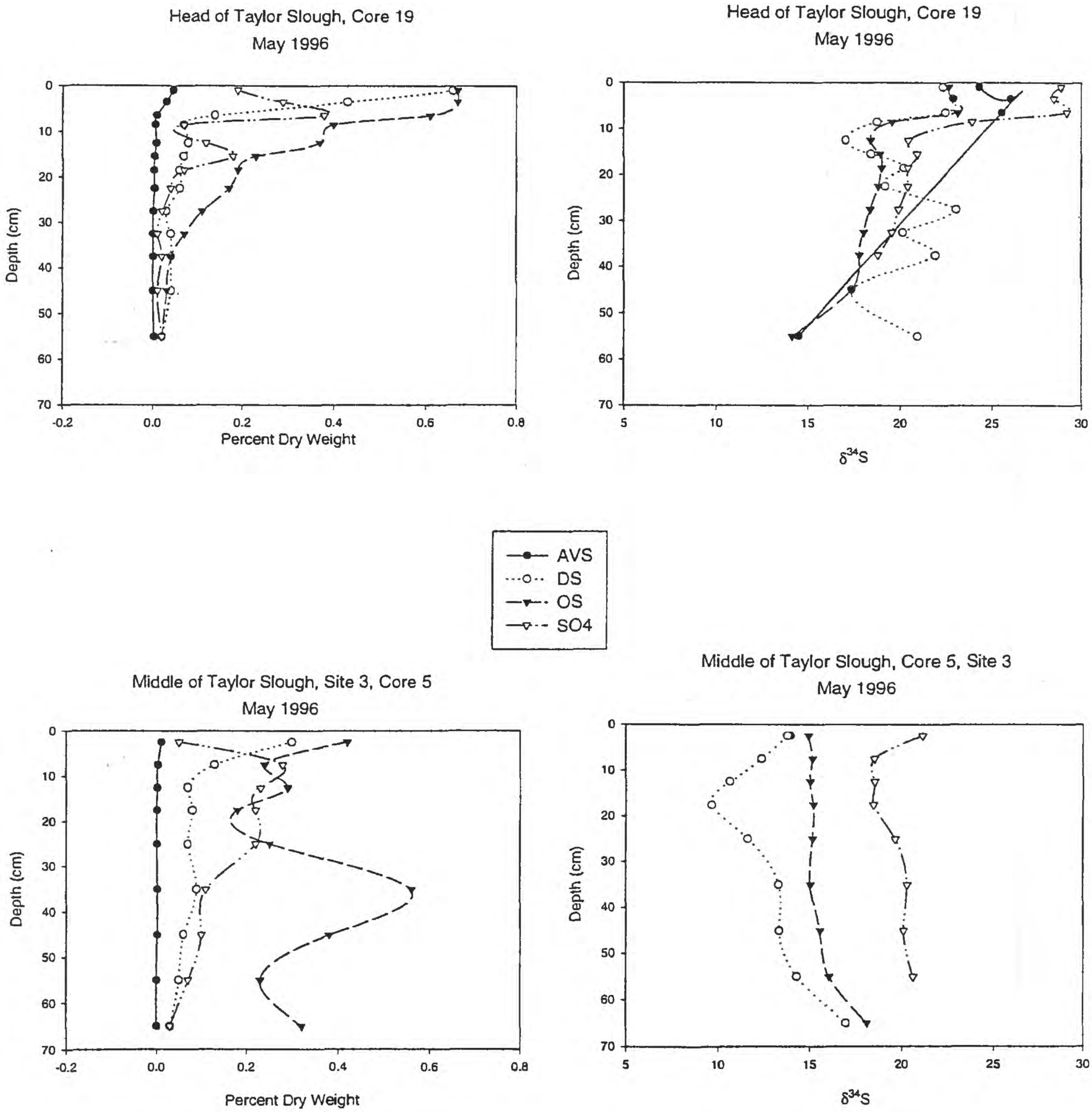
Core Segment	Average Depth (cm)	Sulfate % Dry Wt.	AVS % Dry Wt.	DS % Dry Wt.	OS % Dry Wt.	Sulfate δ34S	AVS δ34S	DS δ34S	OS δ34S
0-5 cm	2.5	0.050	0.011	0.300	0.770	21.13	13.96	13.77	14.93
5-10	7.5	0.280	0.004	0.130	0.660	18.51		12.38	15.14
10-15	12.5	0.230	0.001	0.070	0.590	18.52		10.62	15.01
15-20	17.5	0.220	0.001	0.080	0.480	18.45		9.64	15.18
20-30	25.0	0.220	0.001	0.070	0.540	19.63		11.61	15.14
30-40	35.0	0.110	0.002	0.090	0.760	20.29		13.30	15.02
40-50	45.0	0.100	0.002	0.060	0.530	20.08		13.32	15.54
50-60	55.0	0.070	0.000	0.050	0.350	20.62		14.30	16.03
60-70	65.0	0.030	0.000	0.030	0.390	n.d.		16.97	18.10

Total Sulfur Contents in Sediment from Taylor Slough, May 1996: Percent Dry Weight





Sulfur Species in Taylor Slough Sediment at Sites 3 and 7, May 1996: Percent Dry Weight and δ34S



Dissolved Sulfate Concentrations and Isotopic Compositions

Surface waters were collected in the EAA, the ENR, WCA 1A, 2A, 2B, and 3A, Lake Okeechobee, and Taylor Slough (Figs. 1 and 2). Groundwater and rainwater were collected in WCA 2A and in the ENR. The concentrations and sulfur isotopic ratio data were determined for samples from each area (Tables 6, 7, 8; Figs. 13 and 14).

Surface Water. Regional patterns in sulfate concentration and $\delta^{34}S$ values obtained from March 1995 through July 1998 are shown in (Fig. 13a-g). Surface waters collected from the canals in the EAA tend to have higher sulfate concentrations with lower $\delta^{34}S$ values compared to water samples from the Hillsboro Canal where it is adjacent to WCA 2A. Sulfate concentrations of water from the Kissimmee River and Lake Okeechobee (Fig. 13a) are low compared to water collected from the EAA canals. Surface water in WCA 2A, which receives discharge from the Hillsboro Canal through the S-10 spillways, tends to be somewhat lower in sulfate concentration with higher $\delta^{34}S$ values than water collected from the canal. These changes are probably due to progressive reduction of sulfate and to dilution with rainwater or groundwater. Surface waters from WCA 3A and 2B have relatively low sulfate content. WCA 2B receives water from the southern part of WCA 2A but not directly from the canals, and WCA 3A is a very large area, most of which is far from canal discharge sites. The Loxahatchee National Wildlife Refuge (WCA 1A), with little direct input of water from the Hillsboro Canal, also has very low sulfate content although the $\delta^{34}S$ values are in the same range as the canals in the EAA. In contrast, the $\delta^{34}S$ values of water from WCAs 3A and 2B are in the same range as water from WCA 2A, suggesting that similar sulfate processing is occurring in these areas.

Table 6. Sulfate concentrations and δ34S values in surface water, samples grouped by area.

Month/Year of Collection	Sampling Location	Lat	Long	SO4 mg/l	SO4 meq/l	SO4 δ34S
	Water Conservation Area 2A:					
3/95	F0	26 22.520'N	80 21.860'W	93.99	1.96	20.47
3/95	F0	26 22.520'N	80 21.860'W	81.30	1.69	20.53
3/95	F1	26 21.580'N	80 22.230'W	61.94	1.29	23.04
3/95	E1	26 21.090'N	80 21.200'W	23.77	0.50	21.35
3/95	E2	26 20.520'N	80 21.160'W	37.09	0.77	22.58
3/95	F2			30.85	0.64	24.05
3/95	E4	26 18.550'N	80 21.430'W	44.29	0.92	22.27
3/95	F3	26 19.790'N	80 23.290'W	55.19	1.15	21.71
3/95	F4	26 19.000'N	80 23.120'W	67.79	1.41	20.75
3/95	F5			58.61	1.22	24.48
3/95	U1	26 14.450'N	80 21.390'W	58.34	1.22	23.48
3/95	U2	26 15.750'N	80 23.050'W	57.32	1.19	23.40
3/95	U3	26 17.250'N	80 24.680'W	41.86	0.87	20.70
4/95	F1	26 21.580'N	80 22.230'W	25.13	0.52	25.50
4/95	E1	26 21.090'N	80 21.200'W	9.19	0.19	17.49
4/95	F4	26 19.000'N	80 23.120'W	59.51	1.24	23.79
4/95	F4	26 19.000'N	80 23.120'W	54.53	1.14	23.44
4/95	F4	26 19.000'N	80 23.120'W	53.99	1.12	n.d.
4/95	F4	26 19.000'N	80 23.120'W	60.59	1.26	n.d.
4/95	U3	26 17.250'N	80 24.680'W	47.01	0.98	22.83
7/95	F0	26 22.520'N	80 21.860'W	77.42	1.61	20.69
7/95	F1, 1 of 2	26 21.580'N	80 22.230'W	59.41	1.24	25.39
7/95	F1, 2 of 2	26 21.580'N	80 22.230'W	57.65	1.20	n.d.
7/95	F4	26 19.000'N	80 23.120'W	36.15	0.75	21.57
7/95	E1	26 21.090'N	80 21.200'W	43.21	0.90	25.91
7/95	E4	26 18.550'N	80 21.430'W	24.04	0.50	22.13
7/95	U3	26 17.250'N	80 24.680'W	52.31	1.09	21.00
12/95	U1	26 14.450'N	80 21.390'W	37.53	0.78	25.02
12/95	U3	26 17.250'N	80 24.680'W	50.87	1.06	23.83
12/95	E1	26 21.090'N	80 21.200'W	42.97	0.90	24.90
12/95	E4	26 18.550'N	80 21.430'W	37.49	0.78	23.85

Table 6. Sulfate concentrations and $\delta^{34}S$ values in surface water, samples grouped by area.

Month/Year of Collection	Sampling Location	Lat	Long	SO4 mg/l	SO4 meq/l	SO4 δ34S
12/95	F0	26 22.520'N	80 21.860'W	31.41	0.65	20.14
12/95	F1	26 21.580'N	80 22.230'W	49.55	1.03	26.22
12/95	F1	26 21.580'N	80 22.230'W	50.80	1.06	26.20
12/95	F4	26 19.000'N	80 23.120'W	46.98	0.98	23.85
3/96	F1	26 21.580'N	80 22.230'W	39.79	0.83	22.15
3/96	F4	26 19.000'N	80 23.120'W	33.82	0.70	29.81
3/96	U3	26 17.250'N	80 24.680'W	5.95	0.12	24.87
6/96	E0	26 22.280'N	80 21.090'W	32.41	0.68	22.27
6/96	F1	26 21.580'N	80 22.230'W	48.27	1.01	21.23
6/96	E1	26 21.090'N	80 21.200'W	48.37	1.01	22.57
6/96	U1	26 14.450'N	80 21.390'W	36.36	0.76	22.60
6/96	U3	26 17.250'N	80 24.680'W	43.43	0.90	22.45
12/96	F1	26 21.580'N	80 22.230'W	64.65	1.35	22.74
12/96	U3	26 17.250'N	80 24.680'W	67.08	1.40	28.18
12/96	E0	26 22.280'N	80 21.090'W	36.14	0.75	21.53
3/97	U3	26 17.250'N	80 24.680'W	3.91	0.08	25.63
3/97	F1	26 21.580'N	80 22.230'W	50.85	1.06	17.52
6/97	F4	26 19.000'N	80 23.120'W	59.55	1.24	33.48
6/97	U3	26 17.250'N	80 24.680'W	42.48	0.88	22.14
7/97	U3	26 17.250'N	80 24.680'W	100.21	2.09	22.66
7/97	F1	26 21.580'N	80 22.230'W	50.81	1.06	21.58
8/97	E1	26 21.090'N	80 21.200'W	81.09	1.69	23.60
9/97	F1	26 21.580'N	80 22.230W	67.17	1.40	24.02
9/97	U3	26 17.250'N	80 24.680'W	66.59	1.39	23.68
9/97	F4	26 19.000'N	80 23.120'W	79.88	1.66	23.09
1/98	F1	26 21.580'N	80 22.230'W	63.16	1.32	23.33
1/98	U3	26 17.250'N	80 24.680'W	82.87	1.73	23.28
6/98	U3	26 17.250'N	80 24.680'W	52.27	1.09	23.28
6/98	U1	26 14.450'N	80 21.390'W	38.24	0.80	22.00
6/98	E4	26 18.550'N	80 21.430'W	40.55	0.84	22.75
6/98	F4	26 19.000'N	80 23.120'W	36.18	0.75	21.66
6/98	F1	26 21.580'N	80 22.230'W	32.94	0.69	19.34
6/98	E1	26 21.090'N	80 21.200'W	53.93	1.12	22.05

Table 6. Sulfate concentrations and $\delta^{34}S$ values in surface water, samples grouped by area.

Month/Year of Collection	Sampling Location	Lat	Long	SO4 mg/l	SO4 meq/l	SO4 δ34S
	Hillsboro Canal Samples:					
3/95	S10E			96.06	2.00	18.03
3/95	S10D			117.94	2.46	18.79
3/95	S10D			121.99	2.54	18.80
3/95	S10C			83.10	1.73	20.25
3/95	S10C			80.01	1.67	20.60
7/95	S10C			65.32	1.36	21.11
7/95	S10D			88.14	1.84	20.26
7/95	S10E			98.19	2.05	20.14
12/95	S10E			36.29	0.76	21.11
6/96	S10E			48.99	1.02	22.79
7/97	Hillsoro Canal between EAA & WCA 2A	26 28.362'N	80 26.839'W	87.08	1.81	21.41
9/97	S10C, head			67.28	1.40	22.21
9/97	S10C, tail			58.43	1.22	21.47
6/98	S10C, Head			25.85	0.54	18.11
6/98	S10C, Tail			24.76	0.52	18.08
	Loxahatchee Wildlife Refuge:					
4/95	C2 (Site 7)	26 28.873'N	80 24.931'W	4.23	0.09	21.19
4/95	C2 (Site 7)	26 28.873'N	80 24.931'W	2.96	0.06	19.36
4/95	C2 (Site 7)	26 28.873'N	80 24.931'W	2.42	0.05	n.d.
4/95	C3			5.40	0.11	16.46
4/95	C4			14.79	0.31	14.82
1/98	Loxahatchee Flume	26 28.87'N	80 24.93'W	0.00	0.00	n.d.

Table 6. Sulfate concentrations and δ34S values in surface water, samples grouped by area.

Month/Year of Collection	Sampling Location	Lat	Long	SO4 mg/l	SO4 meq/l	SO4 δ34S
	L67 Canal:					
3/95	L67 @ S151	26 00.900'N	80 30.342'W	28.18	0.59	20.12
3/95	L67 @ S333	25 46.116'N	80 40.380'W	21.23	0.44	23.55
7/95	L67 @ S333	25 46.116'N	80 40.380'W	18.30	0.38	20.59
7/95	L67 @ S151	26 00.900'N	80 30.342'W	16.61	0.35	20.28
7/95	Miami Canal @ L67 (S151)	26 00.900'N	80 30.342'W	7.62	0.16	25.06
12/95	L67			24.48	0.51	25.33
6/96	L67 @ 151	26 00.900'N	80 30.342'W	6.49	0.14	20.52
12/96	L67			22.59	0.47	24.23
	Miami Canal:					
7/95	Miami Canal @ L67 (S-151)	26 00.900'N	80 30.342'W	7.62	0.16	25.06
8/97	Miami Canal # 1	26 41.783'N	80 48.376'W	147.89	3.08	16.27
8/97	Miami Canal # 2	26 37.434'N	80 49.994'W	62.71	1.31	20.61
8/97	Miami Canal # 3	26 19.915'N	80 46.479'W	66.74	1.39	18.61
1/98	Miami Canal off 27	26 41.783'N	80 48.376'W	102.16	2.13	15.84
1/98	Miami Canal at 6 miles	26 37.434'N	80 49.994'W	134.51	2.80	17.42
1/98	Miami Canal at 12mi @ pump station	26 19.915'N	80 46.479'W	20.98	0.44	22.53
1/98	Miami Canal @ Rt 75	26 08.769'N	80 37.983'W	6.71	0.14	21.13
	Water Conservation Area 2B:					
12/95	WCA2B North	26 12.000'N	80 22.500'W	47.82	1.00	24.74
12/95	WCA2B South	26 09.580'N	80 22.680'W	6.07	0.13	25.31
12/95	WCA 2B			4.13	0.09	22.54
12/96	WCA 2B South	26 09.580'N	80 22.680'W	11.36	0.24	28.59
3/96	WCA 2B South	26 09.580'N	80 22.680'W	20.85	0.43	33.99
6/96	WCA 2B			6.97	0.15	25.59
3/97	WCA 2B South	26 09.580'N	80 22.680'W	21.32	0.44	20.52
8/97	WCA 2B South	26 09.580'N	80 22.680'W	7.04	0.15	24.10
1/98	WCA 2B South	26 09.580'N	80 22.680'W	26.77	0.56	28.51

Table 6. Sulfate concentrations and $\delta^{34}S$ values in surface water, samples grouped by area.

Month/Year of Collection	Sampling Location	Lat	Long	SO4 mg/l	SO4 meq/l	SO4 δ34S
	Water Conservation Area 3A:					
12/95	WCA 3A @ hydro 15	25 58.455'N	80 40.127'W	0.00	n.d.	n.d.
3/96	WCA 3A			2.58	0.05	22.93
3/96	S9			6.78	0.14	28.15
6/96	S9			5.40	0.11	25.59
6/96	WCA 3A			0.60	0.01	24.17
12/98	3A-TT	25 45.720'N	80 30.460'W	0.18	0.00	n.d.
12/96	3A-15	25 58.455'N	80 40.127'W	1.30	0.03	n.d.
12/96	3A-3	26 16.164'N	80 36.816'W	11.88	0.25	27.90
3/97	3A-15	25 58.455'N	80 40.127'W	0.81	0.02	n.d.
7/97	3A @ rt. 997	25 56.736'N	80 26.601'W	26.17	0.55	21.66
8/97	3A-15	25 58.455'N	80 40.127'W	1.98	0.04	n.d.
1/98	3A-15	25 58.455'N	80 40.127'W	0.49	0.01	n.d.
4/98	Skinner Island	25 51.615'N	80 43.926'W	0.00	0.00	n.d.
4/98	Head Edge East, 3ANI	26 11.200'N	80 44.351'W	2.49	0.05	20.62
4/98	Nuthouse Head	25 53.345'N	80 33.750'W	11.33	0.24	25.00
4/98	Marsh West, 3AN1	26 11.209'N	80 44.405'W	4.90	0.10	19.69
4/98	Nut House Marsh	25 53.365'N	80 33.674'W	10.97	0.23	24.60
4/98	Skinner Island, marsh east	25 5136.88	80 4355.57	0.00	0.00	n.d.
4/98	Skinner near trail	25 5029.77	80 4418.34	0.17	0.00	n.d.
	Nutrient Removal Area:					
12/95	ENR 102 (SW)	26 3848.307	80 2451.467	32.21	0.67	18.31
12/95	ENR G253E			34.82	0.73	20.34
12/95	ENR G250			32.31	0.67	17.43
3/97	ENR 102	26 3848.307	80 2451.467	101.37	2.11	22.66
3/97	ENR 303	26 36.660'N	80 26.364'W	80.88	1.69	23.17
6/96	ENR 103	26 38.244'N	80 25.362'W	57.48	1.20	21.88
6/96	ENR 303	26 36.660'N	80 26.364'W	31.18	0.65	23.06
12/96	ENR P12	26 3811.276	80 2442.926	29.32	0.61	31.84
12/96	ENR, P5	26 3827.925	80 2640.854	40.73	0.85	25.30
12/96	ENR, G'water, 11A	26 3750.892	80 2600.504	50.05	1.04	28.93
12/96	ENR, G'water, 11A	26 3750.892	80 2600.504	45.69	0.95	28.32
9/97	ENR 012 (Project outflow)			70.53	1.47	24.46

Table 6. Sulfate concentrations and δ34S values in surface water, samples grouped by area.

Month/Year of Collection	Sampling Location	Lat	Long	SO4 mg/l	SO4 meq/l	SO4 δ34S
9/97	ENRG259 (head of seepage C.)			36.28	0.76	30.41
9/97	ENR 002 (project inflow)			144.35	3.01	21.13
9/97	ENR 011 (seepage Canal return)			45.70	0.95	26.04
9/97	ENR 103 SW (1)	26 38.244'N	80 25.362'W	45.31	0.94	26.18
9/97	ENR 103 SW (2)	26 38.244'N	80 25.362'W	46.59	0.97	26.44
6/98	ENR 004			30.14	0.63	18.80
6/98	ENR 011			56.84	1.18	24.60
6/98	ENR G259			49.55	1.03	24.95
6/98	ENR 012			30.69	0.64	18.77
6/98	ENR 002			24.72	0.51	16.69
6/98	M103	26 38.244'N	80 25.362'W	32.27	0.67	18.83
6/98	M102	26 3848.307	80 2451.467	33.18	0.69	17.79
6/98	M203	26 3835.054	80 2601.548	29.18	0.61	20.85
6/98	M204	26 3902.993	80 2524.223	28.54	0.59	20.18
6/98	M303	26 36.660'N	80 26.364'W	30.79	0.64	21.71
6/98	M401	26 3746.312	80 2624.110	24.37	0.51	20.94
	Everglades Agricultural Area:					
8/96	Canal surface water			124.86	2.60	19.01
12/96	EAA Site 1	26 36.593'N	80 42.617'W	34.97	0.73	17.27
12/96	EAA Site 4	26 38.745'N	80 34.890'W	34.96	0.73	17.51
12/96	EAA Site 2	26 42.093'N	80 42.418'W	34.98	0.73	17.35
12/96	EAA Site 3	26 41.865'N	80 41.469'W	35.59	0.74	17.31
3/97	EAA Site 1	26 36.593'N	80 42.617'W	42.81	0.89	17.54
3/97	EAA Site 2	26 42.093'N	80 42.418'W	44.70	0.93	16.96
3/97	EAA Site 3	26 41.865'N	80 41.469'W	34.57	0.72	17.14
3/97	EAA Site 4	26 38.745'N	80 34.890'W	43.38	0.90	17.48
3/97	Canal Site 1	26 36.593'N	80 42.617'W	124.87	2.60	18.72
7/97	Canal Site 2	26 42.093'N	80 42.418'W	119.85	2.50	17.58
7/97	Canal Site 3	26 41.865'N	80 41.469'W	182.24	3.80	16.58
7/97	Canal Site 4	26 38.745'N	80 34.890'W	142.00	2.96	18.13
7/97	Hillsoro Canal, betw'n EAA & WCA 2A	26 28.362'N	80 26.839'W	87.08	1.81	21.41
7/97	N. New River Canal, betw'n EAA and 2A	26 20.143'N	80 32.333'W	44.66	0.93	19.61
1/98	N. New River Canal at Golf Course	26 42.091'N	80 42.915'W	80.68	1.68	18.23
1/98	N. New River Canal	26 36.575'N	80 42.679'W	115.71	2.41	19.72

Table 6. Sulfate concentrations and δ34S values in surface water, samples grouped by area.

Month/Year of Collection	Sampling Location	Lat	Long	SO4 mg/l	SO4 meq/l	SO4 δ34S
1/98	W. Canal St., S	26 41.837'N	80 41.474'W	127.56	2.66	18.49
1/98	Hillsboro Canal @ Rt. 880	26 38.739'N	80 34.883'W	79.77	1.66	22.10
7/98	Miami Canal, 6 mi.	26 37.434'N	80 49.994'W	22.95	0.48	16.37
7/98	Miami Canal, 12 mi.	26 19.915'N	80 460479'W	23.76	0.50	16.48
7/98	North New River Canal @ Rt 27 & 827	26 36.586'N	80 42.667'W	25.43	0.53	17.33
7/98	N. New River Canal @ Golf Course	26 42.091'N	80 42.915'W	26.80	0.56	17.01
7/98	N. New River Canal near Holey Land	26 20.118'N	80 32.310'W	31.96	0.67	18.16
7/98	Hillsboro Canal, Junkyard	26 41.837'N	80 41.474'W	29.88	0.62	17.27
7/98	Hillsboro Canal, @ Rts. 827 & 880	26 38.748'N	80 34.891'W	28.65	0.60	17.08
7/98	Hillsboro Canal, @ Rt. 827	26 28.363'N	80 26.809'W	40.70	0.85	18.90
5/99	#1, Below bridge, Palm Beach & Ocean Canal	26 41.059'N	80 23.422'W	38.57	0.80	17.26
5/99	#2, 880 & ENR, Ocean Canal along 880 before bric	26 41.077'N	80 23.490'W	38.86	0.81	17.45
5/99	#3, Along 880 @ ~ 9 mi bend, Senter Rd.	26 40.690'N	80 32.126'W	36.67	0.76	17.52
5/99	#4, Hillsboro C., near 880-827 intersection	26 38.748'N	80 34.891'W	70.58	1.47	15.01
5/99	#5, Off platform end of dirt road (827)	26 28.406'N	80 26.813'W	65.66	1.37	n.d.
5/99	#6, Junkyard off W. Canal Street	26 41.837'N	80 41.474'W	71.16	1.48	n.d.
5/99	#7,Golf Course near pump station	26 42.091'N	80 42.915'W	57.95	1.21	15.10
5/99	#8, N. New River Canal @ Rts. 327-27	26 36.608'N	80 42.606'W	66.27	1.38	18.68
5/99	#9, Rt 27 at Holy Land Wildlife Refuge	26 20.132'N	80 32.316'W	53.09	1.11	19.45
5/99	#10, Miami Canal off Rt. 27	26 41.783'N	80 48.376'W	132.90	2.77	14.61
5/99	#11, Miami Canal at 6 mi bridge	26 37.434'N	80 49.994'W	74.01	1.54	18.88
5/99	#12, Bridge at pump St. about 21 mi.	26 19.957'N	80 46.389'W	49.46	1.03	17.60
	Lake Okeechobee and Tributary Rivers and Creeks:					
7/97	Kissimee River	27 08.930'N	80 52.273'W	9.42	0.20	17.15
7/98	Lake O., Site 1, Mid-point, Surface	26 51.042'N	80 52.372'W	24.82	0.52	16.89
7/98	Lake O., Site 1, Mid-depth	26 51.042'N	80 52.372'W	26.60	0.55	17.01
7/98	Lake O., Site 1, Bottom	26 51.042'N	80 52.372'W	23.66	0.49	16.57
7/98	Lake O., Site 2, Center, Surface	26 57.783'N	80 49.931'W	23.93	0.50	16.80
7/98	Lake O., site 2, Mid-depth	26 57.783'N	80 49.931'W	26.17	0.55	16.73
7/98	Lake O., Site 2, Bottom (11')	26 57.783'N	80 49.931'W	24.43	0.51	16.56
7/98	Lake O., Site 3, South Bay, Surface	26 44.179'N	80 45.595'W	23.73	0.49	16.70
7/98	Lake O., Site 3, Bottom, (3.5')	26 44.179'N	80 45.595'W	24.72	0.51	16.54
7/98	Kissimmee River	27 08.930'N	80 52.273'W	22.75	0.47	17.01

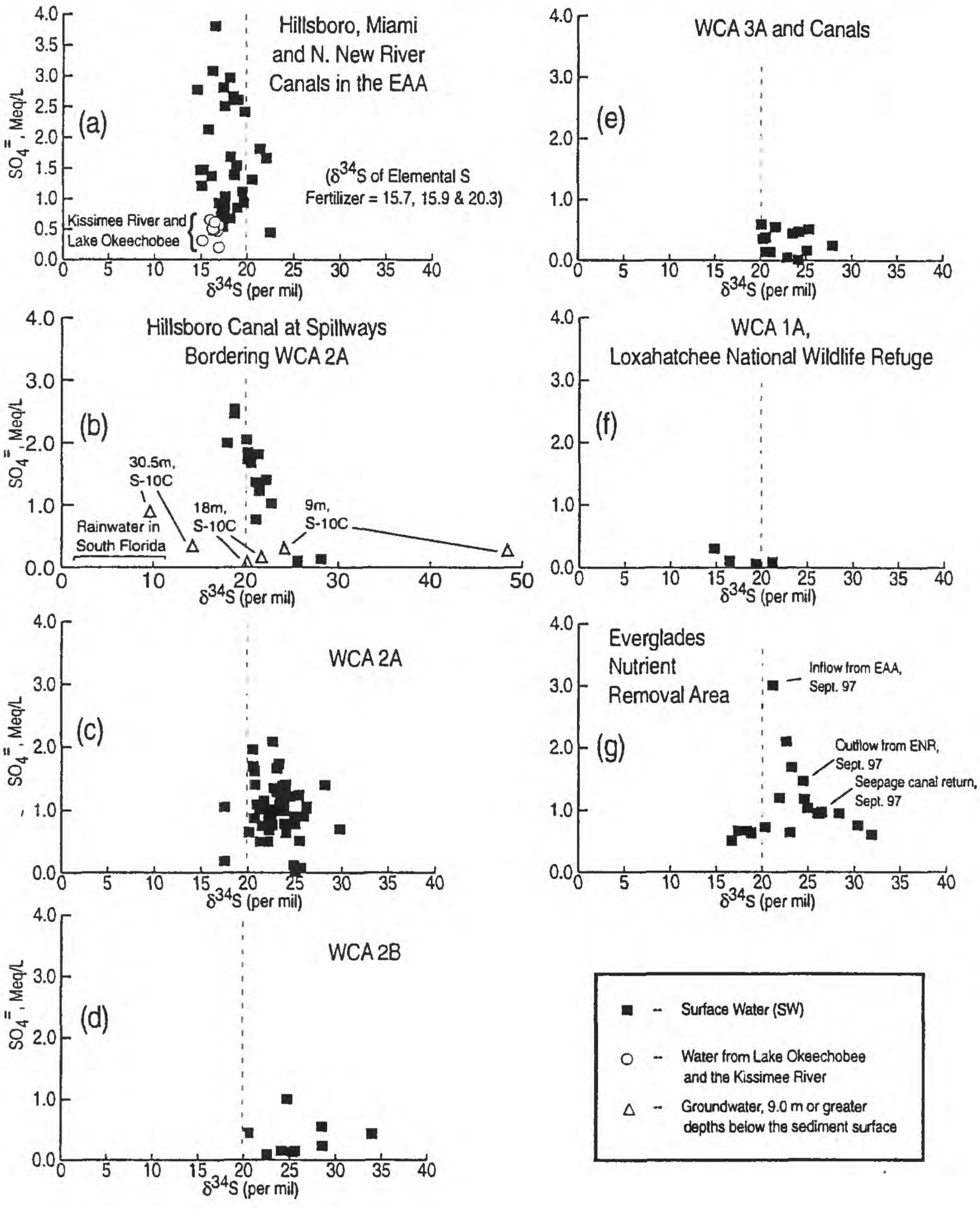
Table 6. Sulfate concentrations and δ34S values in surface water, samples grouped by area.

Month/Year of Collection	Sampling Location	Lat	Long	SO4 mg/l	SO4 meq/l	SO4 δ34S
7/98	Fisheating Creek	26 57.788'N	81 07.223'W	11.79	0.25	22.79
7/98	Taylor Creek	27 12.596'N	80 47.866'W	32.13	0.67	17.06
5/99	Taylor Creek	27 12.596'N	80 47.866'W	30.21	0.63	16.75
5/99	Kissimmee River off 78	27 08.930'N	80 52.273'W	14.65	0.31	15.17
5/99	Fisheating Creek, off 78	26 57.788'N	81 07.223'W	10.62	0.22	24.01
5/99	L Ok., center	26 57.783'N	80 49.931'W	30.28	0.63	16.06
5/99	L Ok., Mid-point	26 51.042'N	80 52.372'W	29.25	0.61	16.47
5/99	L Ok., South Bay	26 44.179'N	80 45.595'W	30.99	0.65	15.99
	Taylor Slough, North:					
5/96	Taylor Slough, near pump station (TS1)	25 25.010'N	80 35.668'W	3.24	0.07	n.d.
5/96	Taylor Slough, center (TS7)	25 17.231'N	80 38.780'W	0.00	0.00	n.d.
5/96	Taylor Slough, center (TS7)	25 17.231'N	80 38.780'W	0.33	0.01	n.d.
5/96	Head of Taylor Slough, near bridge (TS2)	25 24.306'N	80 36.377'W	6.64	0.14	29.95
5/96	Taylor Slough, mid-west (TS7W)	25 17.419'N	80 40.496'W	0.00	0.00	n.d.
5/96	Taylor Slough, mid-east (TS7E)	25 17.258'N	80 38.235'W	0.18	0.00	n.d.
5/96	Taylor Slough, Delta, western edge (TS11)	25 12.786'N	80 44.170'W	58.96	1.23	26.95
7/98	TS4	25 20.310'N	80 38.670'W	0.00	0.00	n.d.
7/98	TS5	25 20.030'N	80 37.040'W	0.65	0.01	n.d.
7/98	TS7	25 17.231'N	80 38.780'W	0.00	0.00	n.d.
7/99	TS7	25 17.231'N	80 38.780'W	0.00	0.00	n.d.
7/99	TS9	25 14.230'N	80 40.936'W	0.08	0.00	n.d.
	Taylor Slough, South:					
5/96	1.5 mi. north of Madiera Bay (TC2)	25 12.709'N	80 38.889'W	129.64	2.70	23.03
5/96	Mangrove swamp, behind spider alley (TC1)	25 11.773'N	80 38.216'W	1065.75	22.20	20.60
5/96	Taylor Creek, Sklar (TC1A)	25 11.863'N	80 38.598'W	1895.63	39.49	20.77
5/96	Taylor Creek, North (TC3)	25 12.722'N	80 38.877'W	1445.81	30.12	20.98

Table 6. Sulfate concentrations and $\delta^{34}S$ values in surface water, samples grouped by area.

Month/Year of Collection	Sampling Location	Lat	Long	SO4 mg/l	SO4 meq/l	SO4 $\delta^{34}S$
	Florida Bay:					
5/96	Pass Key, Forida Bay	25 08.866'N	80 34.471'W	1760.96	36.69	20.48
5/96	Whip Ray Key, Florida Bay	25 04.309'N	80 44.312'W	2832.73	59.02	20.24
5/96	Bob Allen Bank, Florida Bay	25 01.378'N	80 39.371'W	2753.68	57.37	20.37
5/96	Russel Key, Florida Bay	25 0.3841'N	80 37.511'W	2409.00	50.19	20.39
1/1/98	Russel Key, Florida Bay	25 0.3841'N	80 37.511'W	1698.29	35.38	20.22
1/1/98	Pass Key, Forida Bay	25 08.866'N	80 34.471'W	1414.87	29.48	20.34
1/1/98	Bob Allen Bank, Florida Bay	25 01.378'N	80 39.371'W	2186.46	45.55	20.20
4/98	Eagle Key Pond 3			2336.22	48.67	19.92

Figure 13. Sulfatê in Water in the Northern Everglades, 1995-1999



In the Taylor Slough of the southern Everglades (Fig. 2) sulfate concentrations are low and $\delta^{34}S$ values are high in the northern part of the Slough (Table 6). The mangrove swamps of the southern part of Taylor Slough have very high sulfate concentrations, reflecting marine influence from Florida Bay. Interestingly, Taylor Creek, in the mangrove swamps, had high sulfate concentrations in 1996 and relatively low sulfate concentrations in 1998 and 1999, probably reflecting differences in freshwater discharge.

Bay waters near small islands (keys) in Florida Bay have sulfate concentrations near seawater levels (56 meq/L) and $\delta^{34}S$ values at the seawater value (~20 per mil) (Table 6; Fig 2). Sulfate concentrations slightly greater than that of seawater are probably caused by evaporation of the shallow waters of the Bay, while sulfate concentrations lower than that of seawater are caused by dilution with water from Taylor Slough. Proximity to the coastline determines the amount of dilution (Pass Key>Russell Key>Bob Allen Key>Whipray Basin).

Rainwater. Rainwater could cause dilution trends in surface water, but certainly not trends of increase in $\delta^{34}S$ values. Analysis of rainwater collected in the ENR from January through March 1998 gives a $\delta^{34}S$ value of 10.7 per mil (Table 7); rainwater samples collected from the same site in approximately two month intervals from March through September 1998 show a range of $\delta^{34}S$ values from 2.1 to 3.2 per mil. Rainwater collected in WCA 2A in July 1998 had a $\delta^{34}S$ value 5.9 per mil. These values are much lower than $\delta^{34}S$ values for sulfate from surface water that we have analyzed in any part of the northern Everglades. The rainwater that we collected had sulfate concentrations (0.04 to 0.09 meq/L), that are low in comparison to sulfate concentrations in surface water and quite similar to sulfate concentrations

Table 7. Sulfate concentrations and δ34S values in rainwater, 1998.

Month/Year of Collection	Sampling Location	SO4 mg/l	SO4 meq/l	SO4 δ34S
3/98	ENR at G253	3.38	0.07	10.742
6/98	ENR at G253	4.27	0.09	3.158
7/98	ENR at G253A	1.73	0.04	2.721
7/98	WCA 2A at S10-C	1.71	0.04	5.892
9/98	ENR at G253A	3.06	0.06	2.059
9/98	WCA 2A at S10-C	0.65	0.01	n.d.

found in rainwater from the northern Everglades region in the early to mid 1970's (Waller and Earl, 1975).

Groundwater. Surface and groundwater were collected in WCA 2A (Table 8; Fig. 14a, b) and at the head and tail of the S-10C spillway (Table 8; Fig. 13b) on the Hillsboro Canal in September, 1997. The sulfate concentration and $\delta^{34}S$ values from all of the surface water samples collected at this time fall in range typical of surface water in WCA 2A (Figs. 13c and 14a). Groundwater beneath WCA 2A (Fig. 14b) is generally much lower in sulfate concentration compared to surface water (particularly at 4.5 m depth, and is variable with respect to $\delta^{34}S$ values. Groundwater collected at S-10C at 30.5 m depth (Fig. 14b) and at F1 at 9 m depth (Fig. 14b) have sulfate concentrations as high or higher than surface water. However, their $\delta^{34}S$ values are significantly different from surface water; this is also true of groundwater collected at 9 m depth at all sites. All of these results suggest that groundwater was not the major source of sulfate to surface water in WCA 2A at the time of collection, although there does appear to be a greater potential for at least some groundwater influence near the Hillsboro Canal (sites E1, F1, and S-10C; see figure 1) than at sites away from the canal (Harvey et al., 1998).

Groundwater collected in WCA 2A (Fig. 14c) and at S-10C (Fig. 13b) in June 1998 displays a similar pattern, with sulfate concentrations low in comparison to sulfate concentrations in surface water except for a very high sulfate concentration for groundwater at 9 m at site F1 in WCA 2A. The $\delta^{34}S$ values for groundwater in June 1998 have a greater range of values in comparison to the $\delta^{34}S$ values obtained from samples collected in September 1997 (five of the groundwater samples collected at that time are not included in figure 14c because they had sulfate concentrations insufficient for isotopic analysis). The very high $\delta^{34}S$ values in three of the water samples (40 per mil or greater) are probably due to nearly complete reduction of a limited sulfate reservoir in groundwater at these sites, possibly the result of drought conditions during this season (summer of 1998). The $\delta^{34}S$ values in groundwater collected at this time are all very different than those obtained in surface water (Fig. 14a).

Groundwater hydrology in the ENR appears to be more complex, and definite conclusions cannot be drawn concerning its influence on surface water. Groundwater was collected at five sites along a transect across the ENR (see figure 1), parallel to the direction of groundwater flow (south-east to north-west). In September 1997, the near-surface groundwaters (at or above 8 m depth) at these sites fall in the same [SO4--]--$\delta^{34}S$ field as the surface water samples in the ENR (Figs. 14d,e,f). In June 1998, the concentrations of sulfate in groundwater at these same sites (Fig. 14f) were not much changed compared to 1997, but the $\delta^{34}S$values of sulfate tended to be higher. Groundwater collected at greater depths at these sites tends to have higher sulfate concentrations, similar to values found in water from the EAA canals. Groundwater taken at 58 m at the northernmost site on the transect in the ENR

(Fig. 1) had sulfate concentrations of 31.99 meq/L (1997) and 33.58 meq/L (1998) with $\delta^{34}S$ values of 24.68 and 25.11 per mil, respectively (not shown in figures 14e or 14f).

Table 8. Sulfate concentrations and $\delta 34S$ values in groundwater, samples grouped by area. Data from surface water taken at the same time at the same collection sites is included.

Month/Year of Collection	Sampling Location	SO4 mg/l	SO4 meq/l	SO4 $\delta 34S$
	Hillsboro Canal:			
9/97	S-10C, head	67.28	1.40	22.21
9/97	S-10C, tail	58.43	1.22	21.47
9/97	S-10C, WA	42.79	0.89	9.63
9/97	S-10C, WB	7.79	0.16	21.71
9/97	S10C,WC	14.94	0.31	24.25
6/98	S10C, Head	25.85	0.54	18.11
6/98	S10C, Tail	24.76	0.52	18.08
6/98	S10C-WA	15.61	0.33	14.33
6/98	S10C-WB	4.30	0.09	20.27
6/98	S10C-WC	13.51	0.28	48.50
	WCA 2A:			
6/97	F4, GW 4	2.47	0.05	21.95
6/97	F4, Surface	59.55	1.24	33.48
6/97	F4, GW 3	1.29	0.03	8.13
6/97	U3, Gw 3	0.99	0.02	6.38
6/97	U3, Surface	42.48	0.88	22.14
8/97	E1, GW4	2.45	0.05	21.35
8/97	E1, GW3	17.82	0.37	16.78
8/97	E1, Surface	81.09	1.69	23.60
9/97	WCA-2A, F1, SW	67.17	1.40	24.02
9/97	WCA-2A, F1, GW4	1.08	0.02	25.05
9/97	WCA-2A, F1, GW3	187.26	3.90	11.80
9/97	WCA-2A, U3, SW	66.59	1.39	23.68
9/97	WCA-2A, U3, GW4	0.67	0.01	31.46
9/97	WCA-2A, U3, GW3	3.36	0.07	0.94
9/97	WCA-2A, F4, SW	79.88	1.66	23.09
9/97	WCA-2A, F4, GW4	0.92	0.02	19.60

Table 8. Sulfate concentrations and δ34S values in groundwater, samples grouped by area. Data from surface water taken at the same time at the same collection sites is included.

Month/Year of Collection	Sampling Location	SO4 mg/l	SO4 meq/l	SO4 δ34S
6/98	WCA2A, U3, GW3	2.00	0.04	0.09
6/98	WCA2A, U3, GW4	0.34	0.01	n.d.
6/98	WCA2A, U3, Surface Water	40.01	0.83	23.21
6/98	WCA2A, U1, GW3	0.16	0.00	n.d.
6/98	WCA2A, U1, GW4	3.03	0.06	43.96
6/98	WCA2A, U1, Surface Water	38.24	0.80	22.00
6/98	WCA2A, E4, GW3	3.61	0.08	45.85
6/98	WCA2A, E4, GW4	15.87	0.33	15.51
6/98	WCA2A, E4, Surface Water	40.55	0.84	22.75
6/98	WCA2A, F4, GW3	1.62	0.03	8.58
6/98	WCA2A, F4, GW4	0.34	0.01	n.d.
6/98	WCA2A, F4, Surface Water	36.18	0.75	21.66
6/98	WCA2A, F1, GW3	185.24	3.86	12.60
6/98	WCA2A, F1, GW4	0.00	0.00	n.d.
6/98	WCA2A, F1, Surface Water	32.94	0.69	19.34
6/98	WCA2A, E1, GW3	4.40	0.09	39.88
6/98	WCA2A, E1, GW4	0.25	0.01	n.d.
6/98	WCA2A, E1, Surface Water	53.93	1.12	22.05
	Nutrient Removal Area:			
12/96	12-5-96, ENR, G'water, 11A	50.05	1.04	28.93
12/96	12-5-96, ENR, G'water, 11A	45.69	0.95	28.32
9/97	ENR 102	62.05	1.29	28.67
9/97	ENRG259	36.28	0.76	30.41
9/97	ENR 002	144.35	3.01	21.13
9/97	ENR 011	45.70	0.95	26.04
9/97	ENR 103 SW (1)	45.31	0.94	26.18
9/97	ENR 103 SW (2)	46.59	0.97	26.44
9/97	MP3-A	1535.51	31.99	24.68
9/97	MP3-B	79.11	1.65	19.65
9/97	MP3-C	39.59	0.82	23.78
9/97	MP3-D	61.64	1.28	27.79
9/97	MP1-A	40.28	0.84	27.77
9/97	MP1-B	54.41	1.13	27.22

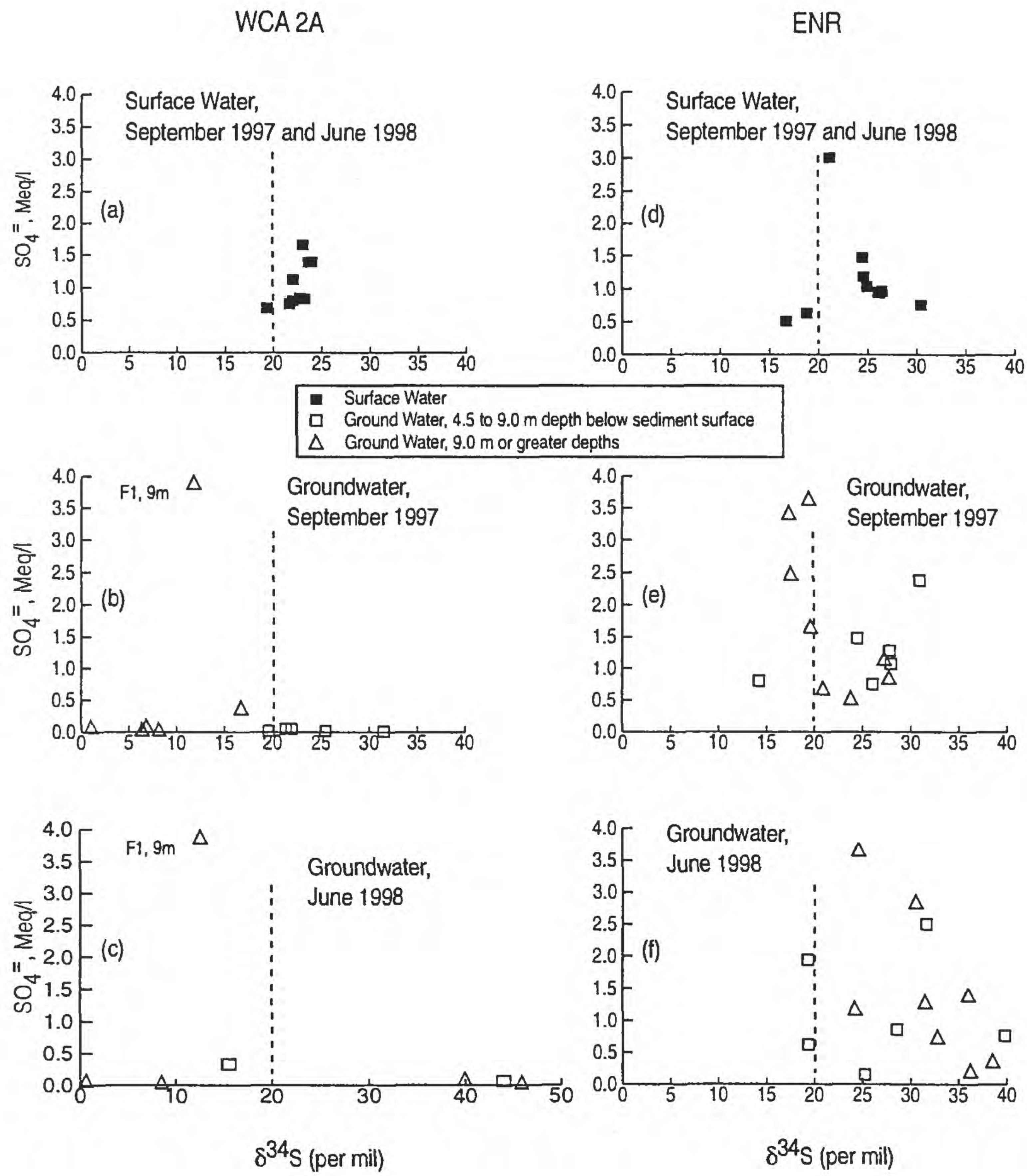
Table 8. Sulfate concentrations and δ34S values in groundwater, samples grouped by area. Data from surface water taken at the same time at the same collection sites is included.

Month/Year of Collection	Sampling Location	SO4 mg/l	SO4 meq/l	SO4 δ34S
9/97	MP1-C	35.89	0.75	26.06
9/97	MP1-D	26.67	0.56	22.19
9/97	MP2-A (1)	118.41	2.47	17.51
9/97	MP2-A (2)	70.53	1.47	24.46
9/97	MP2-B	164.23	3.42	17.36
9/97	M203P	38.38	0.80	14.21
9/97	M203PZ	114.10	2.38	30.94
9/97	M103P	174.09	3.63	19.41
9/97	M103PZ	51.16	1.07	27.94
6/98	ENR 004	30.14	0.63	18.80
6/98	ENR 011	56.84	1.18	24.60
6/98	ENR G259	49.55	1.03	24.95
6/98	ENR 012	30.69	0.64	18.77
6/98	ENR 002	24.72	0.51	16.69
6/98	MP1-A	34.88	0.73	32.78
6/98	MP1-B	16.97	0.35	38.53
6/98	MP1-C	6.99	0.15	25.25
6/98	MP1-D	9.77	0.20	36.22
6/98	MP2-A	92.93	1.94	19.35
6/98	MP2-B	175.53	3.66	24.69
6/98	MP2-C	61.75	1.29	31.53
6/98	MP2-D	n.d.	n.d.	n.d.
6/98	MP3-A	1611.30	33.57	25.11
6/98	MP3-B	56.45	1.18	24.27
6/98	MP3-C	66.47	1.38	36.13
6/98	MP3-D	41.13	0.86	28.58
6/98	MP3-TW	42.17	0.88	25.78
6/98	MP3-HW	55.91	1.16	20.46
6/98	MOP3-A	1857.70	38.70	15.52
6/98	MOP2-A	52.26	1.09	31.12
6/98	MOP2-B	16.91	0.35	40.69
6/98	MOP2-C	9.79	0.20	25.62
6/98	MOP1-A	69.00	1.44	18.23
6/98	MOP1-B	1.65	0.03	36.71
6/98	M103PZ	36.60	0.76	39.77
6/98	M103P	135.65	2.83	30.52

Table 8. Sulfate concentrations and δ34S values in groundwater, samples grouped by area. Data from surface water taken at the same time at the same collection sites is included.

Month/Year of Collection	Sampling Location	SO4 mg/l	SO4 meq/l	SO4 δ34S
6/98	M103 Surface Water	32.27	0.67	18.83
6/98	M102P	221.45	4.61	23.89
6/98	M102 Surface Water	33.18	0.69	17.79
6/98	M203PZ	119.90	2.50	31.64
6/98	M203P	29.62	0.62	19.32
6/98	M203 Surface Water	29.18	0.61	20.85
6/98	M204P	59.09	1.23	25.19
6/98	M204 Surface Water	28.54	0.59	20.18
6/98	M303P	67.02	1.40	28.83
6/98	M303 Surface Water	30.79	0.64	21.71
6/98	M401P	32.10	0.67	32.53
6/98	M401 Surface Water	24.37	0.51	20.94

Figure 14. Comparison of Sulfate Concentrations and $\delta^{34}S$ Values in Surface and Ground Water in WCA 2A and the ENR



Summary

The results of analysis of solid phase sediment samples from the Everglades indicate that there has been an increase in sulfur input to the Everglades in recent times. This is particularly evident in sediment from WCA 2A that receives direct runoff from the Hillsboro Canal. Concentrations of sulfur species show that organic sulfur is usually the dominant species in the core sediments, probably because sulfide fixation is limited by reactive iron availability. The organic sulfur is likely produced by reaction of sulfide with the organic matter-rich sediment. Positive $\delta^{34}S$ values for almost all sulfur species in all sediment samples indicate that there is a relatively restricted supply of sulfate. Variations in the $\delta^{34}S$ values with depth in the sediment are the result of changes in the amount of sulfate available, variations in the rate of reduction of sulfate to sulfide, and/or to changes in the $\delta^{34}S$ values of the source sulfate.

We conclude from our data that much of the dissolved sulfate in the northern Everglades is coming from the EAA by way of the canals that drain the agricultural lands. The origin of this sulfate could be sulfur from fertilizer used in the EAA, rainwater, Lake Okeechobee water, groundwater, or a combination of these sources. The sulfate concentration in rainwater is far too low to account for the concentration of sulfate found in the canals in the EAA. Lake Okeechobee is certainly the origin of much of the water in the EAA canals (Bottcher and Izuno, 1994). During seasons of normal rainfall, the sulfate concentration was low in surface water collected from Lake Okeechobee and from the Kissimmee River as it enters the lake (Fig. 1; Fig. 2a) in comparison to the sulfate concentrations in water collected from the canals in the EAA (Fig. 2a). In contrast, during the Spring-Summer 1998 drought season, sulfate concentrations in canal water in the EAA plummeted to values only a little higher than in the Lake. It is likely that during a dry season the water in the canals is dominated by discharge from the lake with limited contributions from rainfall runoff from EAA fields (Bottcher and Izuno, 1994). Sulfate concentrations during periods of drought therefore largely reflect Lake Okeechobee discharge. Three separate batches of elemental sulfur fertilizer (98% S^{O}), usually referred to as agricultural sulfur, were purchased in the EAA and analyzed for total sulfur $\delta^{34}S$ values. The values obtained were 15.7 (purchased in 1996), 20.3 (purchased in 1997), and 15.9 per mil (purchased in 1999). We found that sulfate extracted from agricultural soil had a $\delta^{34}S$ value of 15.6 per mil. These values are at least consistent with agricultural sulfur being a major contributor to sulfate content in the agricultural lands and the adjacent canals. However, concentrations of sulfate from groundwater (>9 m) beneath the ENR are as high as sulfate in the canals in the EAA, and some of the $\delta^{34}S$ values for sulfate in groundwater in the ENR are close to the values for sulfate in the EAA canals (15 to 22 per mil). If groundwater beneath the ENR (formerly a part of the EAA) is representative of groundwater beneath the EAA, then pumping or natural discharge of groundwater to the EAA canals cannot be excluded as contributors of sulfate to the canals that drain the EAA. An analysis of groundwater from within the EAA is planned for in the future.

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