

Tracing Sources of Sulfur in the Florida Everglades

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ABSTRACT

We examined concentrations and sulfur isotopic ratios ($^{34}\text{S}/^{32}\text{S}$, expressed as $\delta^{34}\text{S}$ in parts per thousand [‰] units) of sulfate in surface water, ground water, and rain water from sites throughout the northern Everglades to establish the sources of sulfur to the ecosystem. The geochemistry of sulfur is of particular interest in the Everglades because of its link, through processes mediated by sulfate-reducing bacteria, to the production of toxic methylmercury in this wetland ecosystem. Methylmercury, a neurotoxin that is bioaccumulated, has been found in high concentrations in freshwater fish from the Everglades, and poses a potential threat to fish-eating wildlife and to human health through fish consumption. Results show that surface water in large portions of the Everglades is heavily contaminated with sulfate, with the highest concentrations observed in canals and marsh areas receiving canal discharge. Spatial patterns in the range of concentrations and $\delta^{34}\text{S}$ values of sulfate in surface water indicate that the major source of sulfate in sulfur-contaminated marshes is water from canals draining the Everglades Agricultural Area. Shallow ground water underlying the Everglades and rain water samples had much lower sulfate concentrations and $\delta^{34}\text{S}$ values distinct from those found in surface water. The $\delta^{34}\text{S}$ results implicate agricultural fertilizer as a major contributor to the sulfate contaminating the Everglades, but ground water under the Everglades Agricultural Area (EAA) may also be a contributing source. The contamination of the northern Everglades with sulfate from canal discharge may be a key factor in controlling the distribution and extent of methylmercury production in the Everglades.

THE EVERGLADES REGION of southern Florida is the subject of multidisciplinary investigations to determine the effects of agricultural and water management practices on the geochemistry of the ecosystem. Understanding the biogeochemistry of sulfur (S) in this environment is important because sulfate-reducing bacteria are a primary agent for the production of toxic methylmercury in wetlands (Compeau and Bartha, 1985; Gilmour et al., 1992, 1998; Hurley et al., 1998; Lambou et al., 1991). We recently demonstrated that total sulfur content in sediments in the Everglades has increased above historical levels in recent times (Bates et al., 1998). A corresponding increase in phosphorus loading from agricultural runoff has also been observed (Craft and Richardson, 1993; DeBusk et al., 1994; Koch and Reddy, 1992; Zielinski et al., 2000).

The predevelopment northern Everglades were oligotrophic, freshwater wetlands with very low phosphorus and nitrogen contents (Lodge, 1994). Sulfate concentrations in surface water of the predevelopment Everglades were also likely to have been very low, similar to sulfate concentrations in the more pristine areas of the wetlands today, including Everglades National Park ($\leq 1 \text{ mg L}^{-1}$ or 0.01 mmol L^{-1} ; Orem et al., 1997). The increase in

phosphorus loading to the ecosystem during the last half century has been shown to be the result of extensive use of phosphorus fertilizer in the Everglades Agricultural Area or EAA (Zielinski et al., 2000), which is located to the north (upstream) of the Everglades. The phosphorus fertilizer is mobilized from the agricultural soils during rain events, transported to canals traversing the EAA, and eventually discharged into the Everglades from the canals (Davis, 1994). Nitrogen fertilizer is not used for sugarcane production in the EAA (Bottcher and Izuno, 1994), and nitrate concentrations are usually very low ($<0.016 \text{ mmol L}^{-1}$ [$<1 \text{ mg L}^{-1}$]) in surface waters and sediment pore waters (McCormick et al., 2000; McPherson et al., 2000; Orem and Bates, unpublished data, 2000). Agricultural S (largely in the form of elemental S) is used as a soil amendment in the EAA to enhance the uptake of phosphorus by crop plants (Bottcher and Izuno, 1994). Oxidation of the agricultural S in the aerobic soils of the EAA produces sulfate, which is highly soluble in water and washes off the fields into canals during rain events. This sulfate may then be delivered to the Everglades in the same manner as phosphorus. Other potential contributors of S to the Everglades are ground water discharge, rain water, sea water aerosol, and surface water from Lake Okeechobee.

In this project, we examined spatial and temporal trends in sulfate concentrations and stable isotopic ratios of S ($^{34}\text{S}/^{32}\text{S}$, expressed as $\delta^{34}\text{S}$ in parts per thousand [‰] units) in the northern Everglades (Fig. 1). We also determined sulfate concentrations and $\delta^{34}\text{S}$ values in the known potential major sources of sulfur to the wetlands. We found regional differences in the range of concentrations and $\delta^{34}\text{S}$ values of sulfate that indicate sulfur contamination to the northern Everglades probably originates from canals draining the EAA.

Sulfur Contamination in the Everglades

There is widespread sulfur contamination of surface water and sediments in the northern Everglades. Marsh areas adjacent to canal discharge have surface water sulfate concentrations that frequently exceed 0.5 mmol L^{-1} ($0.5 \text{ mmol L}^{-1} \cong 48 \text{ mg L}^{-1}$ for sulfate). In contrast, pristine sites in marsh areas far removed from agricultural runoff typically have sulfate concentrations in surface water of $0.005 \text{ mmol L}^{-1}$ or less. The sources that are potential contributors of sulfur (primarily in the form of sulfate) to the ecosystem include sulfur used in agriculture, ground water, rain water, sea water aerosol, sulfur recycling from sediments, and water channeled from Lake Okeechobee through canals traversing the EAA. Canal water is released into the Water Conserva-

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Abbreviations: EAA, Everglades Agricultural Area; ENR, Everglades Nutrient Removal Area; MeHg, methylmercury; WCA, Water Conservation Area.

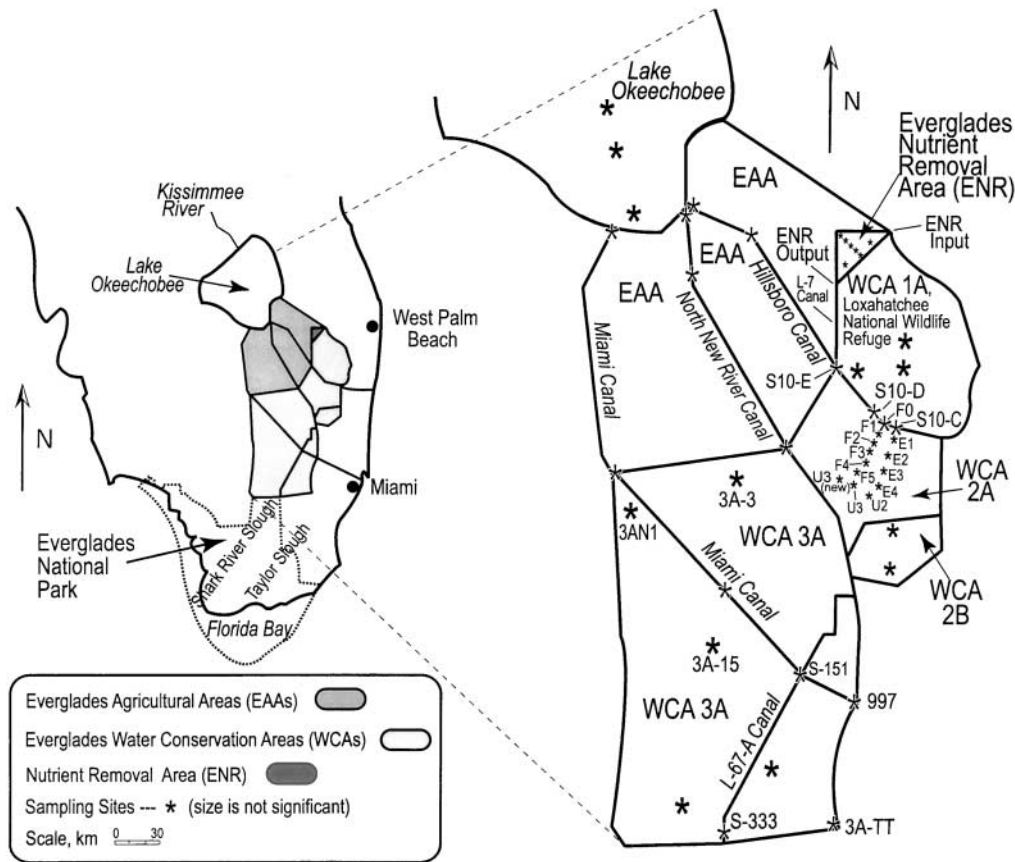


Fig. 1. Study areas in the northern Everglades of southern Florida. Surface water flow in the Everglades is generally from north to southwest (from Lake Okeechobee to Florida Bay).

tion Areas (WCAs) at pumping stations and spillways (Fig. 1). The canal water consists of both irrigation drainage from the EAA, water from Lake Okeechobee, and possibly ground water that discharges to canals in the EAA and WCAs.

The environmental and public health significance of sulfur contamination in these wetlands is primarily in the linkage between sulfur cycling and toxic methylmercury (MeHg) production in anoxic wetland sediments (Fig. 2). Laboratory and field studies show that rates of MeHg production increase as sulfate concentration increases from the very low levels typical of freshwater wetlands (Compeau and Bartha, 1985). This trend results from stimulation by sulfate (SO_4^{2-}) of the bacterially mediated reduction of sulfate to sulfide (S^{2-}) under anoxic conditions when a supply of labile organic matter (the reducing agent) is available (Fig. 2). As sulfate concentrations increase to levels approaching those of estuaries, however, mercury methylation declines (Gilmour et al., 1992, 1998). This decline is thought to result from an excessive buildup of sulfide in porewater, as changes in the porewater speciation of mercury limit the availability of mercury to sulfate-reducing bacteria for methylation (Benoit et al., 1998; Hayes et al., 1998).

**Sulfur Cycling in Wetlands:
Isotopic Fractionation**

Fractionation of sulfur isotopes occurs during bacterial reduction of sulfate to sulfide under anoxic condi-

tions. In wetlands, this occurs primarily in the sediment (Fig. 2). The sulfide produced is depleted in ^{34}S relative to sulfate (Goldhaber and Kaplan, 1974), and the residual sulfate enriched in ^{34}S (Nakai and Jensen, 1964). The $\delta^{34}S$ values of the residual sulfate can become large when the sulfate reservoir is small relative to the extent of reduction. Oxidation of sulfide to sulfate generally does not further fractionate the sulfur isotopes, hence decreasing the $\delta^{34}S$ value of sulfate in the reservoir.

Redox reactions involving sulfur also fractionate oxygen isotopes, changing the $^{18}O/^{16}O$ ratio (expressed as $\delta^{18}O$) of sulfate. Bacterial reduction of sulfate will enrich the remaining sulfate in ^{18}O (Holt and Kumar, 1991). The oxidation of reduced sulfur to sulfate in an aqueous medium occurs mainly by the acquisition by chemical reaction of oxygen from ambient water molecules (Holt and Kumar, 1991; Stempvort and Krouse, 1994), with little subsequent uptake of oxygen by exchange. This reaction causes the $\delta^{18}O$ of sulfate to tend toward that of the ambient water. A comparison of the $\delta^{18}O$ values of sulfate with those of water can, therefore, reveal if a portion of the sulfate was derived from sulfide oxidation.

Hydrologic Conditions in the Everglades

The natural flow of surface water and ground water through the Everglades wetlands is generally toward the southwest, following the gentle topographic gradient

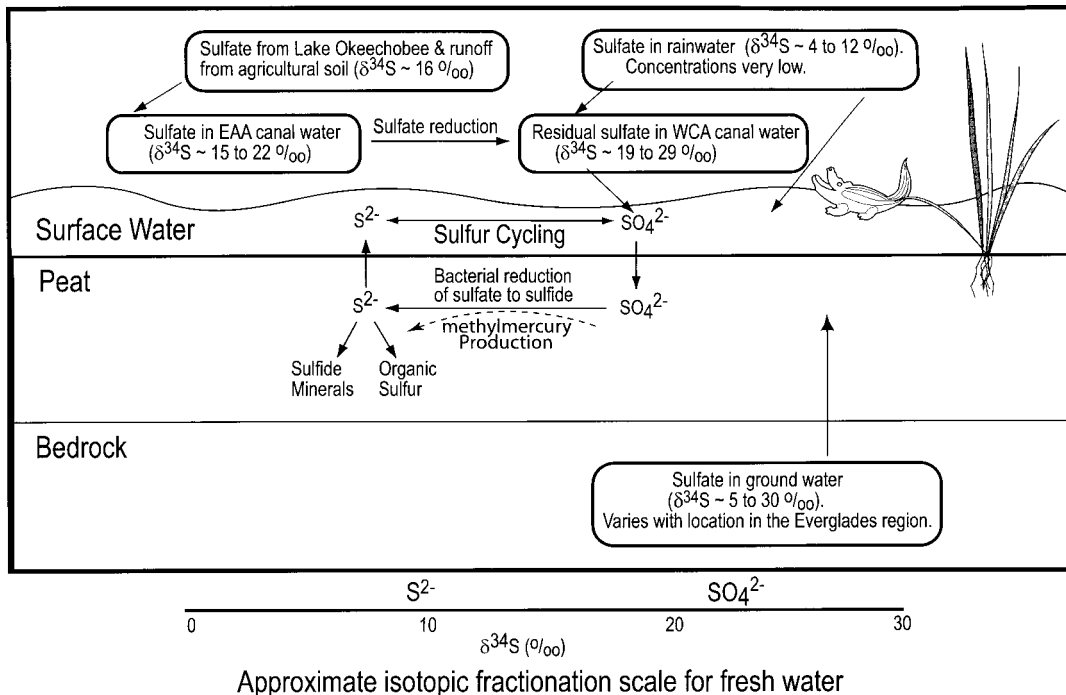


Fig. 2. Sources of sulfate to marshes of the northern Everglades.

along the main axis of the Everglades toward Florida Bay. An exception to this pattern exists in the vicinity of the EAA. For example, ground water flow in the Everglades Nutrient Removal Area or ENR (a constructed wetland on old agricultural land between WCA 1 and the EAA; Fig. 1) is in a northwest direction, toward the EAA (Harvey et al., 2000), the result of drainage and subsidence in the EAA over the past century.

Surface waters in the northern Everglades interact with the unconfined, Surficial Aquifer System (SAS) (Sonntag, 1987; Gleason and Stone, 1994). The SAS consists of sand and limestone bedrock (containing moving ground water) overlain by peat (containing stagnant porewater) and surface water. The SAS immediately beneath the north-central part of the Everglades contains both fresh and saltwater (Howie, 1987). A calcium-bicarbonate water is usually present in the top 9 m of the aquifer, and relict sea water is present in the bottom half of the aquifer (beneath 30 m) (Howie, 1987; Harvey et al., 2000). Between 9 and 30 m is a mixing zone for the two water types. In areas with persistent ground water discharge the mixing zone extends all the way to the wetland surface (Harvey et al., 2000).

Area-averaged rates of ground water flow are relatively low in most areas of the Everglades, less than 0.01 m d^{-1} in the horizontal direction. The low rates mainly reflect the low (topographic) driving force for flow rather than the hydraulic conductivity of the aquifer, which is moderately high to high in the upper portion of the surficial aquifer system (Harvey et al., 2000). Direct discharge of ground water in WCA 2A is relatively small on an area-averaged basis, and only about 3% of surface water pumpage from canals into WCA 2A (Harvey, unpublished results, 2000). Ground water

flow rates are much higher in the vicinity of levees, due to ponding of water at different elevations on either side. Surface-water recharge occurs on the upgradient side of levees, and ground water discharge occurs on the downgradient side. Rates of vertical ground water flow near levees typically range between 0.5 and 4 cm d^{-1} . Far away from levees vertical fluxes are typically less than 0.2 cm d^{-1} (Harvey et al., 2000).

Rainfall normally varies during the year between the wet season (June–October) and the dry season (November–May). Conditions tended to be dry during the last two years of this study.

MATERIALS AND METHODS

Study Area and Sampling Strategy

The study area (Fig. 1) included sites in the freshwater marshes of the Everglades, along the major canals traversing the EAA, in Lake Okeechobee and the Kissimmee River discharging into the lake from the north, and on former agricultural land in the ENR. Samples collected for analysis included (i) surface water from rivers, canals, Lake Okeechobee, and marshes; (ii) ground water from WCA 2A and the ENR; (iii) rain water; (iv) porewater from sediments; (v) peat; and (vi) agricultural sulfur.

From 1995 through 1999, we collected surface water from the Hillsboro, North New River, and Miami Canals in the EAA; from the ENR; from WCA 1A, 2A, 2B, 3A; and from the canals bordering or within these areas. Heavily nutrient-contaminated WCA 2A was intensely investigated because it receives direct discharge from the Hillsboro Canal that drains the EAA. Water was collected from two northeast–southwest trending transects in WCA 2A, the east (E sites) and west (F sites) transects (Fig. 1). From 1997 through 1999 rain water and ground water were collected in the ENR and WCA 2A, and surface water was collected from Lake Okeechobee

and from the Kissimmee River near its point of discharge into the lake.

Sampling

Surface Water

Surface water for sulfate content and sulfur isotope ($\delta^{34}\text{S}$) analyses was collected from about midway between the water surface and the sediment in clean, dry 500-mL Nalgene¹ bottles (Nalge Nunc Int., Rochester, NY). Sample bottles were topped off and contained no 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. Water samples for $\delta^{18}\text{O}$ analysis (Epstein and Mayeda, 1953) were collected at the same sites at the same time in 65-mL glass bottles with airtight caps. These bottles were always filled to capacity and did not contain any air.

Ground Water

A detailed description of ground water sampling methods is given elsewhere (Harvey et al., 2000). Briefly, sampling wells were purged before obtaining samples using a peristaltic pump and sampling apparatus consisting of cleaned Teflon and silicone tubing. Samples were collected in 500-mL Nalgene bottles, prepared as described for surface water samples.

Rain Water

Rain water collection methods are described in detail elsewhere (Harvey et al., 2000). Rain water was collected into a 2-L HDPE bottle held in a PVC pipe holder. A funnel loaded with acrylic fiber filter material and a delivery tube were mounted above the collection bottle. The entire apparatus was mounted on a pole or fence post. Rain water was delivered to the bottom of the collection bottle, under a 1/4-inch layer of mineral oil, added to prevent evaporation and contamination of the rain water. After at least 1 L of rain water was collected, the water under the mineral oil was siphoned into clean, 500-mL Nalgene bottles.

Sediments and Sediment Pore Water

Marsh sediments were collected by piston coring, using methods described previously (Orem et al., 1997). The cores were extruded and sectioned into 2-, 5-, or 10-cm subsections with depth. Core sections were stored in zip-lock type bags.

Separate peat cores were collected for porewater analyses. Sediment porewater was obtained by in situ squeezing of a piston core, as described by Orem et al. (1997). Filtered porewater (0.4 μm) was collected for sulfide analysis at various depths downcore by squeezing into airtight plastic syringes through lateral ports in the coring cylinder.

Agricultural Sulfur

Samples of agricultural sulfur were obtained from 1997 to 1999 from fertilizer distributors or farm stores in Okeechobee, Belle Glade, and Clewiston, FL.

Analytical Methods

Sulfate in Water

Water samples (surface water, ground water, and rain water) were filtered through 0.4- μm Nuclepore filters (Whatman,

Maidstone, England) before analysis in order to remove particulates, and the volume of the filtrate was measured to the nearest milliliter. The samples were then transferred to Erlenmeyer flasks, and the contents acidified to pH 4 with concentrated HCl. Samples were then heated on a hot plate, and barium chloride (10%) was added after boiling began. After volume reduction to about 100 mL, the samples were filtered through 0.4- μm Nuclepore filters to collect the precipitated barium sulfate (BaSO_4). The mass of recovered BaSO_4 was determined after drying the filters to a constant weight in a desiccator. Sulfate concentrations were calculated from the mass of sulfate recovered and the measured volume of the water sample.

Water samples were also analyzed for sulfate by ion chromatography (IC) using a chromatographic system with Waters (Milford, MA) 515 HPLC pump and 432 conductivity detector, Alltech (Deerfield, IL) 335 suppressor module and Allsep anion column (100 \times 4.6 mm; 7- μm particle size), and a carbonate-bicarbonate mobile phase. The percent difference between results by IC and gravimetric analysis of the same sample was $\pm 5\%$ for sulfate concentrations $> 0.5 \text{ mmol L}^{-1}$ (48 mg/L), and $\pm 10\%$ for sulfate concentrations between 0.5 mmol L^{-1} and 0.025 mmol L^{-1} (2.4 mg L^{-1}). For sulfate contents $\leq 0.025 \text{ mmol L}^{-1}$ ($\leq 2.5 \text{ mg L}^{-1}$), agreement between the two methods was $\pm 0.01 \text{ mmol L}^{-1}$ ($\pm 1 \text{ mg L}^{-1}$).

Sulfate Isotopic Ratio Determinations

The recovered BaSO_4 from water samples (described above) was converted to SO_2 by combustion on a vacuum line and isolated for stable isotope analysis using vacuum line methods. The $^{34}\text{S}/^{32}\text{S}$ of SO_2 was determined using a Finnigan MAT 251 isotope ratio mass spectrometer (Thermo Finnigan, Bremen, Germany), and the results reported in delta notation ($\delta^{34}\text{S}$) as parts per thousand (‰) deviation from Canyon Diablo Triolite (CDT) reference standard (Thode et al., 1961). The analytical uncertainty is estimated to be $\pm 0.2\text{‰}$ based on duplicate runs. Samples with low BaSO_4 and SO_2 yields were concentrated for analysis on the mass spectrometer using liquid nitrogen. Three sulfur standards (NBS-123, NZ-1, and Maine Light) were analyzed to calibrate the calculation of $\delta^{34}\text{S}$ values.

The $\delta^{18}\text{O}$ values of the oxygen in sulfate from water samples were determined from the BaSO_4 precipitates using methods described in Pickthorn and O'Neil (1985) and Wasserman et al. (1992). The $\delta^{18}\text{O}$ data are reported as parts per thousand (‰) relative to Standard Mean Ocean Water (SMOW), with an analytical uncertainty of $\pm 0.4\text{‰}$.

Sulfide and Salinity Measurements

Sulfide concentrations in surface water and porewater were determined in the field using sulfide-selective electrode analysis as described in Orem et al. (1997). Sulfides in the water samples were stabilized within several minutes of collection in sulfide antioxidant buffer (SAOB) solution. Sulfide analysis took place within several hours.

The salinity (grams of dissolved salts per kilogram of water in units of parts per thousand) of surface water and ground water was determined in the laboratory using a Thermo Orion (Beverly, MA) Model 115 conductivity-salinity meter and cell with an integral temperature sensor for temperature compensation. The uncertainty in the measurements is ± 1 part per thousand.

Analyses of Sediment

Sediments were analyzed for total sulfur using methods described elsewhere (Bates et al., 1998).

¹ Trade names are used in this report for full disclosure of the methodologies used. No endorsement of any product by the U.S. Geological Survey is implied.

The total phosphorus contents of sediments from cores collected in 1994 at sites E1 and U3 were determined spectrophotometrically as phosphate (based on methods described by Aspila et al. [1976]) after oxidation of the samples in a muffle furnace at 550°C for 3 h.

Sedimentation rates were determined using ²¹⁰Pb analysis and the continuous rate of supply (CRS) model of Binford (1990). Sulfur accumulation rates were calculated using sediment total S data, sedimentation rates, and sediment dry bulk density.

Analysis of Sulfur in Agricultural Chemicals

Sulfur in agricultural chemicals was oxidized to sulfate by fusion with Eschka's mixture (magnesium oxide and calcium carbonate). After fusion for 2 h at 800°C, the fusion mixture was slowly cooled and suspended in boiling distilled-deionized water for 30 min. The suspension was filtered to remove solid residue, and the recovered solution was then treated as described above for water samples to precipitate BaSO₄. The precipitated BaSO₄ was weighed to determine the mass of sulfur in the sample and analyzed for isotopic composition (δ³⁴S) as described above.

RESULTS AND DISCUSSION

Distribution of Sulfur in the Northern Everglades

Average sulfate concentrations of surface water from the northern Everglades tend to decrease along a north-south gradient, from the EAA into the wetland areas (Fig. 3). Many other surface water chemical parameters (e.g., phosphate concentration, conductivity, chloride, and many metals) also show a similar north-south gradient in concentration (McCormick et al., 2000). Sulfate concentrations are highest in the EAA canals, with average sulfate concentrations at least 0.5 mmol L⁻¹ in canal water in the EAA and in marsh water (WCA 2A) adjacent to canal discharge areas (Fig. 3). Average sulfate

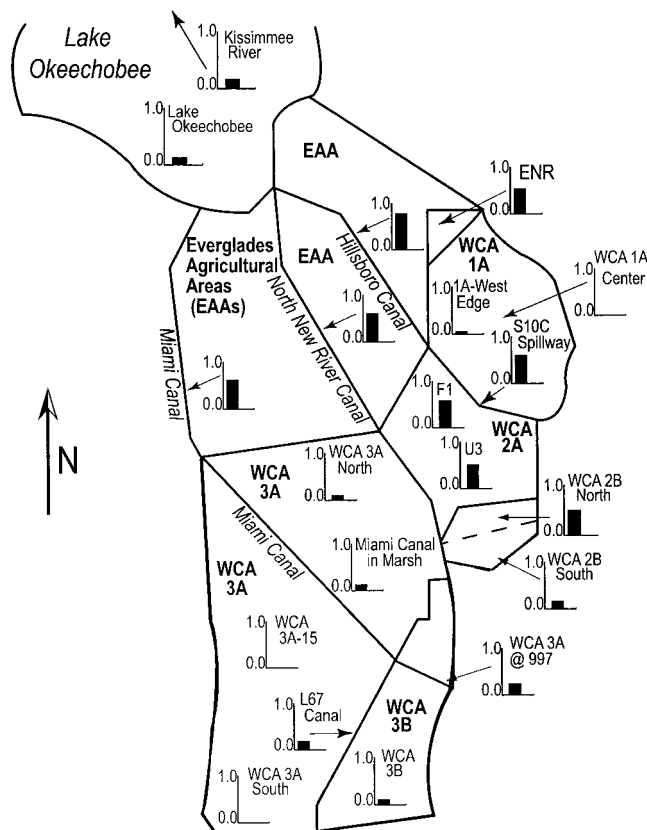


Fig. 3. Distribution of average sulfate concentrations (mmol L⁻¹) in surface waters of the northern Everglades.

concentrations are more than twofold higher in EAA canals compared with Lake Okeechobee. Marsh areas that are remote or protected from direct canal discharge have sulfate concentrations averaging less than 0.1 mmol L⁻¹, and the lowest concentrations of sulfate (≤0.005

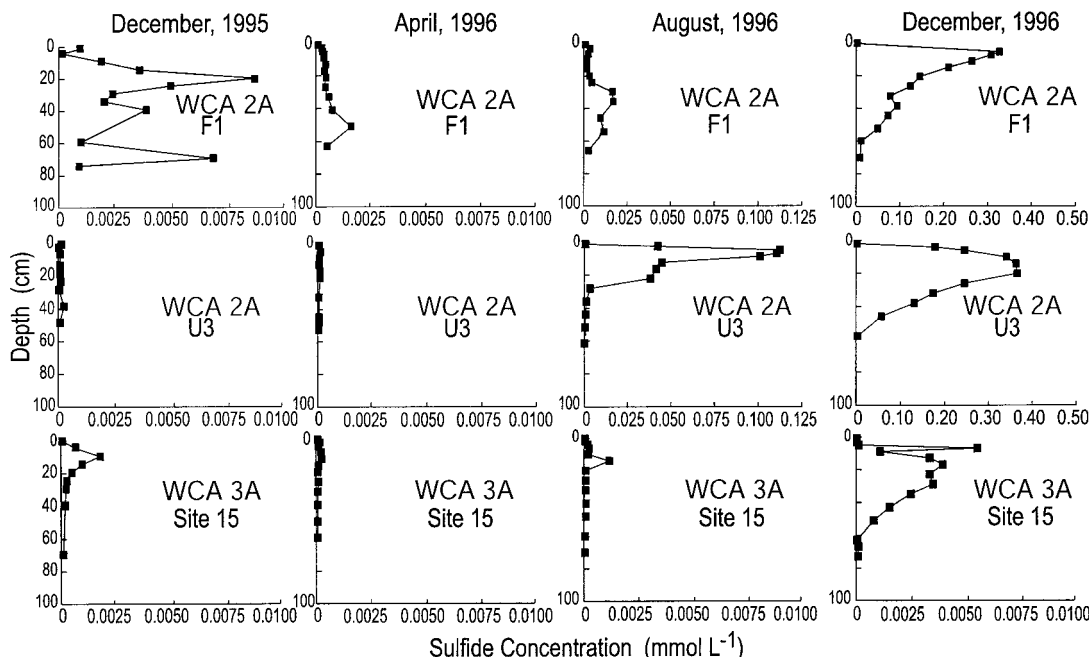


Fig. 4. Comparison of sulfide concentrations (mmol L⁻¹) in sediment porewater from Water Conservation Area (WCA) 2A and WCA 3A, December 1995 through December 1996. Note the changes in scale: data for August and December 1996, F1 and U3.

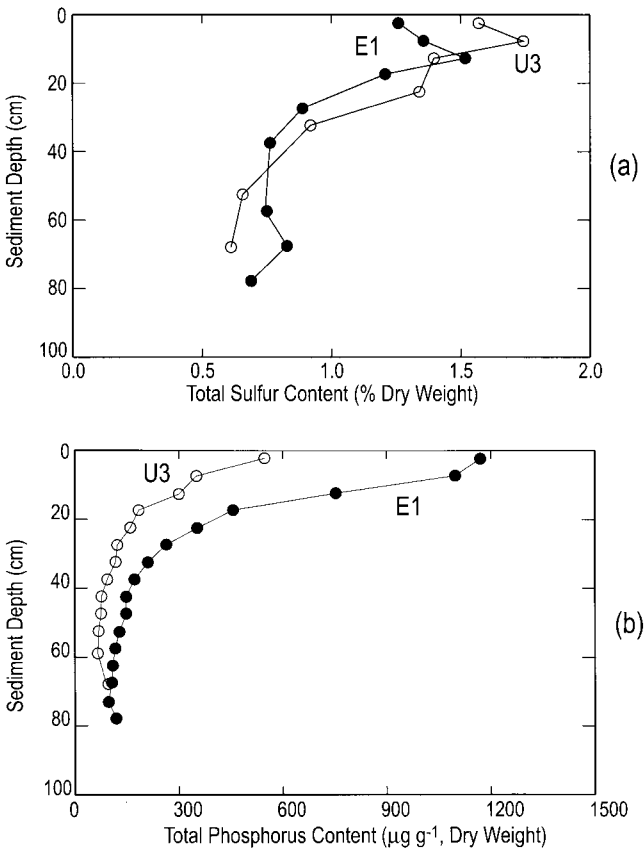


Fig. 5. (a) Comparison of total sulfur (% dry weight) and (b) total phosphorus ($\mu\text{g g}^{-1}$ dry weight) depth profiles in sediment from Water Conservation Area (WCA) 2A at Sites E1 and U3, 1994. Sulfur profile adapted from data in Bates et al. (1998).

mmol L^{-1}) are in the center of WCA 1A and the southernmost parts of WCA 3A.

The present worldwide average concentration of sulfate in freshwaters is approximately 0.12 mmol L^{-1} (11.4 mg L^{-1}) (Bernier and Bernier, 1987), with a normal range from 0.05 mmol L^{-1} to 0.32 mmol L^{-1} . This worldwide average may be elevated over historical levels due to the effects of acid precipitation. Thus, average concentrations of sulfate in large areas of the northern Everglades, especially in EAA canals, and WCA 2A are anomalously high for freshwaters.

Other indicators of sulfur enrichment show spatial patterns similar to that for sulfate in the Everglades. Sulfide concentrations (Orem et al., 1997) in sediment pore water (Fig. 4) are significantly higher at sites in WCA 2A compared with WCA 3A (note the changes in scale in Fig. 4). Seasonal changes are probably due to a combination of changes in sulfate content, hydroperiod, and redox conditions. Total sulfur (Fig. 5a) and total phosphorus (Fig. 5b) in sediment at sites E1 and U3 in WCA 2A display concentration profiles similar to each other with depth, suggesting a coincident enrichment of both elements in recent times. Sediment accumulation rates for sulfur in the upper 10 cm of sediment from sites throughout the Everglades range from 9.0×10^{-3} to $0.38 \times 10^{-3} \text{ g m}^{-2} \text{ d}^{-1}$, calculated from sedimentation rates (^{210}Pb), dry bulk density, and total sulfur

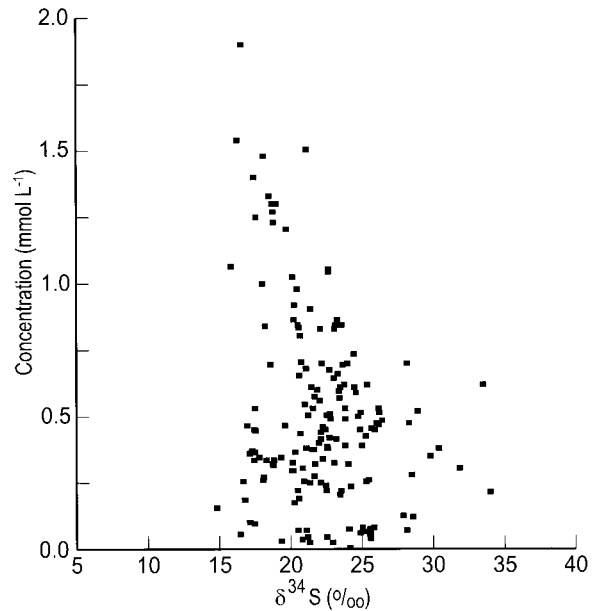


Fig. 6. Concentrations of sulfate (mmol L^{-1}) versus $\delta^{34}\text{S}$ values in surface water collected in the northern Everglades from 1995–1999.

concentration as described by Orem et al. (1997). The average sulfur accumulation rate ($\text{g m}^{-2} \text{ d}^{-1}$) for pristine sites is $1.6 \times 10^{-3} \text{ g m}^{-2} \text{ d}^{-1}$, compared with $4.5 \times 10^{-3} \text{ g m}^{-2} \text{ d}^{-1}$ at sites near canal discharge with high surface water sulfate concentrations. Thus, areas in the freshwater Everglades that receive excess sulfur from canal discharge are accumulating (on average) nearly threefold as much sulfur as pristine freshwater sites.

Sulfate Concentrations and $\delta^{34}\text{S}$ Values in Surface Water

Surface Water of the Northern Everglades

A wide dispersal of values in the $[\text{SO}_4^{2-}]$ - $\delta^{34}\text{S}$ field is seen when the concentrations of sulfate in all of the surface water collected for this study from 1995 through 1999 are plotted versus the corresponding $\delta^{34}\text{S}$ values (Fig. 6). There is a wider range of $\delta^{34}\text{S}$ values at low sulfate concentrations compared with the range of $\delta^{34}\text{S}$ values at higher concentrations of sulfate. When the same data are broken down by area (Fig. 7a–g), regional patterns emerge. Surface waters collected from canals in the EAA (Fig. 7a) range to higher sulfate concentrations and lower $\delta^{34}\text{S}$ values (average value of about 17.8) compared with other areas of the ecosystem. Sulfate concentrations in surface water from the Kissimmee River and Lake Okeechobee (Fig. 7a) are low compared with water collected from the EAA canals. Surface water in WCA 2A (Fig. 7c), which receives discharge from the Hillsboro Canal through the S10 spillways, tends to be somewhat lower in sulfate concentration with higher $\delta^{34}\text{S}$ values than water collected from the canal at the spillways (Fig. 7b). Surface waters from WCA 2B and 3A (Fig. 7d,e) have relatively low sulfate contents and mean $\delta^{34}\text{S}$ values of about 26 and 24‰, respectively. The Loxahatchee National Wildlife Refuge (WCA 1A; Fig. 7f), with little direct input of water from the Hills-

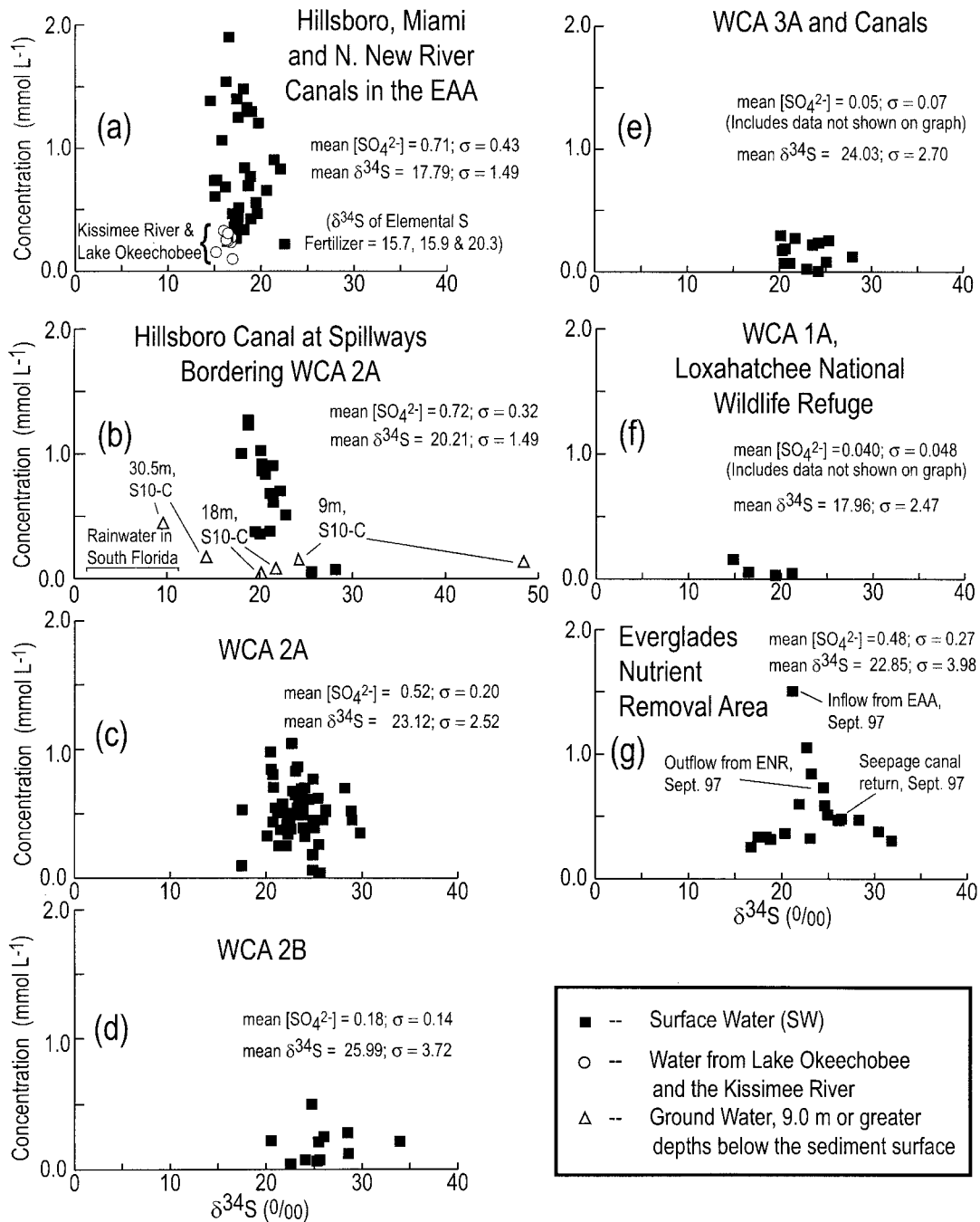


Fig. 7. Sulfate in surface water, 1995–1999: Sulfate concentrations versus δ³⁴S values in the Everglades Agricultural Area (EAA) canals, the Everglades Nutrient Removal Area (ENR), and the Water Conservation Areas (WCAs) in the northern Everglades.

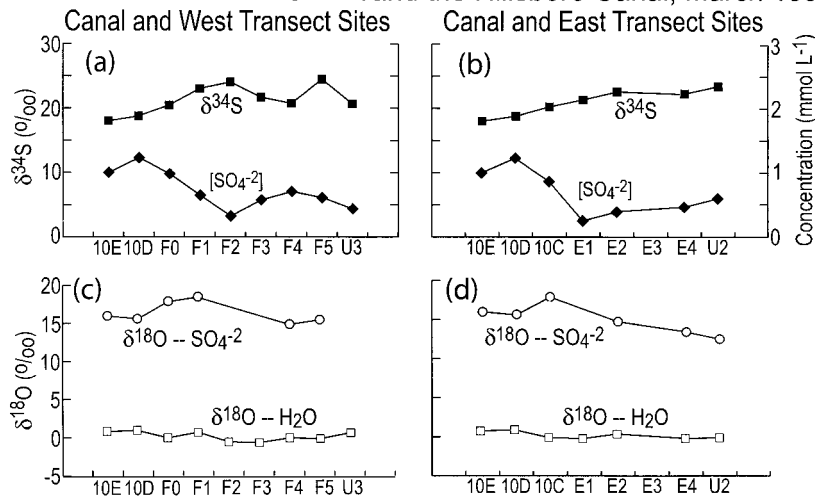
boro Canal, has a very low sulfate content although the δ³⁴S values are in the same range as the canals in the EAA (the mean [SO₄²⁻] value seen in Fig. 7f includes data not included in the figure because there was not enough sample for isotopic analysis).

A positional relationship is seen between sulfate concentration and δ³⁴S values at the sampling sites along the Hillsboro Canal and in WCA 2A for surface water samples collected in March and July 1995 (Fig. 8). There appears to be a tendency for sulfate concentration to decrease and δ³⁴S values to increase with distance along the Hillsboro Canal (from north to south) and out into

the sampling transects in WCA 2A. This trend reverses at the far ends of the sampling transects.

The concentrations and δ³⁴S values of sulfate in surface water in any given area of the Everglades vary temporally to a great extent because of changes in rainfall, applications of agricultural sulfur, discharge of canal water, amounts of surface water evaporation, and sulfur cycling. Changes in these parameters will affect both sulfate concentrations and δ³⁴S values to a greater extent in water containing low concentrations of sulfate compared with water with high concentrations of sulfate. The wider variation in δ³⁴S values at lower sulfate con-

Surface Water from WCA 2A and the Hillsboro Canal, March 1995



Surface Water from WCA 2A and the Hillsboro Canal, July 1995

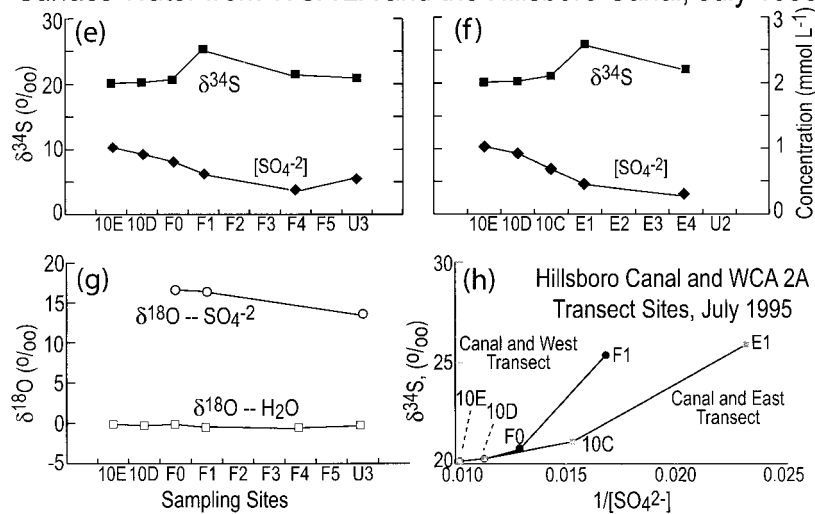


Fig. 8. (a-f) Trends in sulfate concentration and $\delta^{34}\text{S}$ values and in $\delta^{18}\text{O}$ values of sulfate and of water, March and July 1995. (h) $\delta^{34}\text{S}$ versus $1/[\text{SO}_4^{2-}]$ (as $1/\text{mg L}^{-1}$), July 1995. Surface water transects are in Water Conservation Area (WCA) 2A and along the Hillsboro Canal.

centrations compared with $\delta^{34}\text{S}$ values at higher sulfate concentrations seen in Fig. 6 reflects the wide range of sulfur sources (e.g., rainfall, sulfide oxidation, ground water, and canal discharge) affecting the sulfate pool at pristine sites. Furthermore, it is usually true that water containing high concentrations of sulfate is closer to a major source of sulfate than water containing low concentrations of sulfate. As sulfate concentration increases, the spread of $\delta^{34}\text{S}$ values diminishes, and a distinct trend line is apparent in the plot. The very highest sulfate concentrations approach a $\delta^{34}\text{S}$ value of about +16‰. When the data are broken down by region (Fig. 7), the highest sulfate concentrations and the narrowest range of $\delta^{34}\text{S}$ values are found in the canals in the EAA and the Hillsboro Canal adjacent to WCA 2A. The relatively low sulfate concentrations in Lake Okeechobee make the lake an unlikely source of most of the sulfate in the EAA canals. The relatively low sulfate contents in waters from WCA 2B and WCA 3A can perhaps be explained by the observations that 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 positional changes in sulfate content and $\delta^{34}\text{S}$ values seen in Fig. 8 could be due to progressive reduction of sulfate and to dilution with rain water or ground water. Progressive reduction of sulfate would result in a decrease in sulfate concentration and a corresponding increase in the $\delta^{34}\text{S}$ values of the residual sulfate. Such a trend is seen with distance along the Hillsboro Canal (from north to south, Sites 10E, 10D, and 10C; Fig. 8a,b,e,f). Plots of the $\delta^{34}\text{S}$ versus $1/[\text{SO}_4^{2-}]$ (Fig. 8h) are consistent with fractionation processes taking place in a complex open system where sulfur cycling effects are combined with mixing (from rain water, ground water, and flowing canal water), evaporation effects, and local changes in redox conditions. The reversal of the trend in sulfate content and $\delta^{34}\text{S}$ values seen at the far ends of the sampling transects in WCA 2A (Fig. 8) could be due to reoxidation of sulfides to sulfate in areas of the marsh far from the canal more prone to drying and

exposure to air. The sulfate $\delta^{18}\text{O}$ values, which tend toward the $\delta^{18}\text{O}$ of water at sites farthest from the canal in WCA 2A (Fig. 8c,d,g), are consistent with this explanation for the reversal in sulfate contents at sites far from the canal. The generally high sulfate $\delta^{18}\text{O}$ values (between 12.5 and 18.5‰) may be the result of a combination of processes including isotopic fractionation during reduction of sulfate and possible incorporation of atmospheric oxygen during abiotic, metal-catalyzed oxidation of reduced sulfur in aerobic soils (Stempvoort and Krouse, 1994) (the $\delta^{18}\text{O}$ of atmospheric oxygen is approximately 23‰; Horibe et al., 1973). Our sulfate $\delta^{18}\text{O}$ values are higher than the $\delta^{18}\text{O}$ values found in oceanic sulfate (from 9.5 to 10.1‰ [Lloyd, 1967]).

Surface Water in the Everglades Nutrient Removal Area

The ENR is a prototype for a planned series of constructed wetlands created from former agricultural land and designed to remove phosphorus from agricultural runoff before it reaches the Everglades (Lodge, 1994). The locations of inflow from the EAA to the ENR and outflow from the ENR into the L-7 Canal are shown in Fig. 1. A seepage canal is situated between the ENR and the EAA in order to prevent backflow into the EAA. Water from the seepage canal is shunted back into the ENR at a location near the ENR inflow.

The sulfate concentration and $\delta^{34}\text{S}$ data of surface water obtained from the ENR cover a wide range of values (Fig. 7g). Water from the ENR at the inflow, outflow, and seepage canal return sites were all collected on the same day in September 1997. Water flowing into the ENR from the EAA is similar in sulfate concentration to water collected from the canals in the EAA (Fig. 7a,g). Sulfate in the water from the ENR outflow and at the seepage canal return fall in the same $[\text{SO}_4^{2-}]$ - $\delta^{34}\text{S}$ field as most samples collected in WCA 2A. In fact, most other surface water samples collected in the ENR fall in this range, possibly because similar sulfur cycling processes are occurring in these areas.

Sulfate Concentrations and $\delta^{34}\text{S}$ Values in Rain Water

The rain water we collected had sulfate concentrations (0.020 to 0.045 mmol L⁻¹) that are low in comparison with sulfate concentrations in surface water, and quite similar to sulfate concentrations found in rain water from the northern Everglades region in the early to mid 1970s (Waller and Earle, 1975). Sulfate in rain water in north-central Florida has $\delta^{34}\text{S}$ values from 2.4 to 5.9‰ (Katz et al., 1995). Our own analysis of rain water collected in the ENR from January through March 1998 resulted in a $\delta^{34}\text{S}$ value of 10.7‰; rain water samples collected from the same site in approximately two-month intervals from March through September 1998 show a range of $\delta^{34}\text{S}$ values from 2.18 to 3.2‰. Rain water collected in WCA 2A in July 1998 had a $\delta^{34}\text{S}$ value of 5.9‰.

These values are much lower than $\delta^{34}\text{S}$ values for sulfate from surface water that we have analyzed in any

part of the northern Everglades. Thus, rain water could be responsible for dilution trends in surface water sulfate concentrations, but certainly not trends of increase in $\delta^{34}\text{S}$ values.

Sulfate Concentrations and $\delta^{34}\text{S}$ Values in Ground Water

Ground Water in WCA 2A and the S10-C Spillway

Surface and ground water were collected in WCA 2A (Fig. 7c and 9a-c) and at the S10-C spillway (Fig. 7b) on the Hillsboro Canal from May-September 1997 and in June 1998. The $\delta^{34}\text{S}$ values found in ground water in WCA 2A and at the S10-C spillway are quite variable (Fig. 7b and 9b,c), ranging from 0.9 to 48.5‰. Sulfate concentrations are ≤ 0.04 mmol L⁻¹ in shallow ground water (4.5 m depth) at all collection sites in WCA 2A, except for one sample collected at the E4 site in June 1998 with a sulfate concentration of 0.17 mmol L⁻¹. Sulfate concentrations in the deeper ground water (≥ 9.0 m) were ≤ 0.19 mmol L⁻¹, except for ground water collected at 30.5 m at the spillway (0.45 mmol L⁻¹ in Sept. 1997) and at 9 m at the F1 site (1.95 mmol L⁻¹ in Sept. 1997 and June 1998).

The sulfate concentration and $\delta^{34}\text{S}$ values from all of the surface water samples collected from May-September 1997 in WCA 2A and at the S10-C spillway fall in a range typical of surface water in WCA 2A (Fig. 7c and 9a). The salinity values for these samples, including the canal spillway at S10-C, are 0.5 or 0.6 parts per thousand at all sites. Ground water beneath WCA 2A (Fig. 9b) is generally much lower in sulfate concentration compared with surface water (particularly at a 4.5 m depth), somewhat higher in salinity (0.6 to 2.8 parts per thousand; average = 1.2 parts per thousand), and variable with respect to $\delta^{34}\text{S}$ values. Ground water collected at S10-C at 30.5 m depth (Fig. 7b) and at F1 at 9 m depth (Fig. 9b) have sulfate concentrations and salinities as high or higher than surface water. However, their $\delta^{34}\text{S}$ values are different from surface water, and the concentration of sulfate in the near-surface ground water at F1 (0.01 mmol L⁻¹ at 4.5 m depth) is very low compared with surface water. The ground water at 9- and 18-m depths at the S10-C spillway is much lower in sulfate concentration than the canal water in the EAA (Fig. 7a,b).

If near-surface ground water penetrates the canal at S10-C, its influence would be to dilute the sulfate contained in water coming from the EAA. Likewise, if the near-surface ground water in WCA 2A is mixing with the surface water, it would tend to dilute the sulfate in surface water. The salinity data are consistent with surface water at collection sites in WCA 2A having a common source from the Hillsboro Canal. These results suggest that near-surface ground water 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 deeper ground water influence near the Hillsboro Canal (sites E1, F1, and S-10C; see Fig. 1) than at sites away from the canal based on relatively high sulfate content in the deeper ground water.

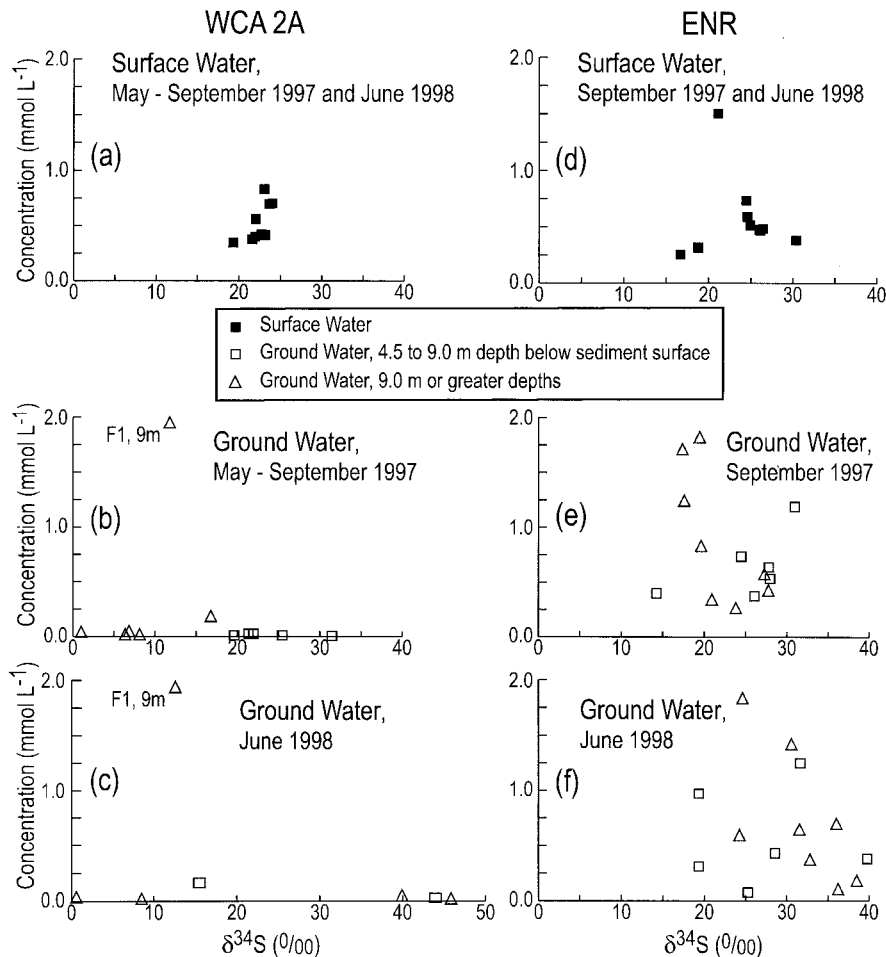


Fig. 9. Comparison of sulfate concentrations and $\delta^{34}\text{S}$ values in surface and ground water in Water Conservation Area (WCA) 2A and the Everglades Nutrient Removal Area (ENR) of the northern Everglades.

Ground water collected in WCA 2A (Fig. 9c) and at S10-C (Fig. 7b) in June 1998 displays a similar pattern, with sulfate concentrations low in comparison with sulfate concentrations in surface water except for a very high sulfate concentration for ground water at 9 m at site F1 in WCA 2A (the sulfate concentration of ground water at 4.5 m at site F1 was below the detection limit and therefore does not appear in Fig. 9c). The $\delta^{34}\text{S}$ values for ground water in June 1998 have a greater range of values in comparison with the $\delta^{34}\text{S}$ values obtained from samples collected in September 1997 (five of the ground water samples collected at that time are not included in Fig. 9c because they had sulfate concentrations insufficient for isotopic analysis). The $\delta^{34}\text{S}$ values in ground water collected at that time are all very different from those obtained in surface water (Fig. 9a). Salinity values are high in ground water below 9 m at sites F1 and E1 (2.4 and 1.1 parts per thousand, respectively) and are also slightly high in surface water at these two sites (0.9 and 0.7 parts per thousand). Salinities in surface water at all other sites in WCA 2A ranged from 0.2 to 0.6 parts per thousand.

The very high $\delta^{34}\text{S}$ values in three of the ground water samples (40‰ or greater) are probably due to nearly complete reduction of a limited sulfate reservoir in ground water at these sites. The salinity data suggest

some ground water influence on surface water at sites F1 and E1 in WCA 2A; however, the very low sulfate concentrations in the near-surface (4.5 m) ground water suggest that any upwelling ground water is likely to dilute sulfate in the surface water. Given also that the area-averaged discharge of ground water to WCA 2A has been calculated to be about 3% of the surface water pumpage into the area (Harvey, unpublished results, 2000), we conclude that ground water is not the major contributor of sulfate to WCA 2A.

Ground Water in the Everglades Nutrient Removal Area

Ground water was collected at five sites along a transect across the ENR (see Fig. 1), parallel to the direction of ground water flow (southeast to northwest). In September 1997, the near-surface ground water (at or above 8 m depth) at these sites falls in the same $[\text{SO}_4^{2-}]$ - $\delta^{34}\text{S}$ field as the surface water samples in the ENR (Fig. 9d-f), and the salinity values are similar to each other and to surface water (0.5–0.9 parts per thousand). In June 1998, the concentrations of sulfate in ground water at these same sites (Fig. 9f) were not much changed compared with 1997, but the $\delta^{34}\text{S}$ values of sulfate tended to be higher. Ground water collected at greater depths

at these sites tends to have higher sulfate concentrations, similar to values found in water from the EAA canals. The salinity values tend to be higher in ground water from 9 m and greater depths (0.4 to 10.9 parts per thousand; average = 2.7 parts per thousand). Ground water taken at 58 m at the northernmost site on the transect in the ENR (Fig. 1) had sulfate concentrations of 16.0 mmol L⁻¹ (1997) and 16.8 mmol L⁻¹ (1998) with $\delta^{34}\text{S}$ values of 24.7 and 25.1‰, respectively (not shown in Fig. 9e or 9f).

Based on the sulfate concentration and $\delta^{34}\text{S}$ results alone, we cannot draw definite conclusions concerning the influence of ground water on surface water in ENR. Ground water hydrology is more informative in this case. Direct ground water discharge occurs on the eastern side of ENR at a low rate, amounting to 3% of surface water pumped into ENR from EAA canals (the source of the canal water is agricultural runoff and water from Lake Okeechobee) (Choi and Harvey, 2000). Indirect ground water discharge occurs into ENR by way of the seepage canal, which collects ground water discharge on the western side of ENR and backpumps it to the headwater of ENR. The seepage canal recycles ground water flow equal to 22% of the surface water pumpage from EAA (Choi and Harvey, 2000). Much of the ground water collected by the seepage canal originated as ENR surface water that recharged vertically through peat into the ground water system. Also, there is geochemical evidence that some ground water is from deeper aquifer layers with higher salinity (Harvey et al., 2000). Thus, there is considerable evidence for interaction between ground and surface water in the ENR, with the dominant contribution of ground water discharge from shallow sources relatively low in sulfate, and a smaller contribution from deeper ground water that is higher in sulfate. Even with the contribution of deeper ground water, sulfate concentrations in the seepage canal were relatively low in comparison with surface water from EAA canals (Fig. 7g).

A conclusion that ENR receives sulfate predominantly from EAA canals is based on the following evidence. We know that ENR receives a significant component of surface inflow from EAA canals because the wetland was designed to remove nutrients from agricultural runoff. We also know that the sulfate content of the water entering from the EAA is high compared with the sulfate content at any other collection site in the ENR or seepage canal (Fig. 7g). We also know that the sulfate content at the outflow from the ENR exceeds the sulfate content at the seepage canal return (Fig. 7g). If direct ground water input to the ENR is 3% of the surface water inflow to the ENR, and if 21% of the water input to the seepage canal comes from ground water (much of which is downwelling surface water), we can conclude that the EAA is the most significant source of sulfate to the ENR.

Sources of Sulfate to the Everglades

Our sulfate concentration and isotopic results, as well as other evidence (sulfide in pore water, total sulfur and

phosphorus profiles in sediment, accumulation rates of sulfur in sediment), indicate that much of the sulfate in the northern Everglades is coming from the EAA by way of the canals that drain the agricultural lands. The remaining question is whether the origin of sulfur is fertilizer used in the EAA, or rain water, sea water aerosol, Lake Okeechobee water, ground water, cycling of sulfur in the soil, or a combination of these sources.

The sulfate concentration in rain water is far too low to account for the concentration of sulfate found in the canals in the EAA. Sea water aerosols containing sulfate undoubtedly add sulfate to the wetlands ($\delta^{34}\text{S}$ of sea water is from +19 to +21; Ault, 1959), either by dry deposition or as a component of rain water sulfate. The influence of sulfate in sea water aerosols is likely to be uniformly ubiquitous along a north-south gradient and unlikely to account for local concentrations of sulfate, although it could be a significant component of the total sulfate found in pristine areas of the wetlands.

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. 7a) in comparison with the sulfate concentrations in water collected from the canals in the EAA (Fig. 7a). In contrast, during the spring-summer 1998 drought, sulfate concentrations in canal water in the EAA dropped dramatically from their average concentrations, and were only a little higher than in the Lake. It is likely that during a drought period more of the water and sulfate in the canals comes from the lake, due to diminished runoff from agricultural lands in the EAA (Bottcher and Izuno, 1994).

Three separate batches of agricultural sulfur (98% S⁰) were purchased from farm stores and distributors in the EAA and analyzed for total sulfur $\delta^{34}\text{S}$ values. The values obtained were 15.7 (purchased in 1996), 20.3 (purchased in 1997), and 15.9‰ (purchased in 1999). We found that sulfate extracted from agricultural soil (sugarcane production) collected in the EAA had a $\delta^{34}\text{S}$ value of 15.6‰. Although we cannot state the origin of sulfur conclusively, these values are at least consistent with sulfur fertilizer being a major contributor to sulfate content in the agricultural lands and the adjacent canals.

Auger cores of soil collected in the EAA at the Department of Agriculture Research Center at Canal Point and at the University of Florida Research Station at Belle Glade were analyzed for total sulfur content and isotopic ratios. The $\delta^{34}\text{S}$ values found near the soil surface were between 17 and 20‰ (Bates et al., 2001). Total sulfur content in the top 30 cm was between 0.10 and 0.60% (dry weight). Below 122 cm (approximately 4 ft) total sulfur content was greater than 2.0% by dry weight (Bates et al., 2001). It is likely that most of the reduced sulfur (mostly organic sulfur) originally contained in the soil above 30 cm was oxidized to sulfate (by molecular oxygen, by oxygen in water molecules, and by oxygen in nitrogen compounds found naturally in the soil) and washed out of the soil (or deeper into the soil) after many years of cultivation and turnover

of the topsoil, hence the relatively low sulfur content near the soil surface. The remaining sulfur in EAA soil, therefore, must contain components of both residual and refractory sulfur native to the soil, and sulfur added for cultivation. The relative proportion of each, however, is unclear. In addition, the sulfur present in the EAA soil from agricultural additions probably reflects both recent additions and the legacy of past sulfur additions. Oxidation of EAA soil containing both background sulfur and added agricultural sulfur (recent and legacy sulfur additions) must be a major source of sulfate entering the canals in runoff from the agricultural fields.

Concentrations of sulfate from ground water (≥ 9 m) beneath the ENR are as high as sulfate in the canals in the EAA, and some of the $\delta^{34}\text{S}$ values for sulfate in ground water in the ENR are close to the values for sulfate in the EAA canals (15 to 22‰). If ground water beneath the ENR (formerly a part of the EAA) is representative of ground water beneath the EAA, then pumping or natural discharge of ground water to the EAA canals cannot be excluded as contributors of sulfate to the canals that drain the EAA (the extent to which ground water has been affected by agricultural practices is unknown at this time). Natural ground water discharge, however, does not appear to be an important source of sulfate to surface water in either ENR or WCA 2A, as discussed earlier

Environmental Significance of Sulfur Contamination to the Everglades

The contamination of the northern Everglades with excess sulfate from canal discharge may be a major factor contributing to the extent and distribution of methylmercury (MeHg) production found in the ecosystem (Compeau and Bartha, 1985; Gilmour et al., 1992, 1998; Hayes et al., 1998). Both sulfate and sulfide appear to play major roles in controlling MeHg production in wetland environments, with sulfate stimulating and sulfide inhibiting production of MeHg (Hayes et al., 1998; Benoit et al., 2001).

In the Everglades, the highest MeHg concentrations have been observed near the center of WCA 3A (Gilmour et al., 1998). Here, sulfate concentrations in surface water are above background (0.0075 to 0.020 mmol L^{-1}), and porewater sulfide concentrations are moderate (0.16×10^{-3} to 4.7×10^{-3} mmol L^{-1} ; Fig. 4) (Orem et al., 1997). We hypothesize that it is in the center of WCA 3A, at the downgrade edge of the sulfate plume, where the stimulating effects of sulfate and the inhibitory effects of sulfide achieve the optimal balance for MeHg production. Areas of the northern Everglades having high sulfate concentrations in the surface water (WCA 2A) have lower overall MeHg concentrations compared with the optimal area in the center of WCA 3A (Gilmour et al., 1998), probably due to the inhibitory effects of porewater sulfide levels up to 0.38 mmol L^{-1} (Orem et al., 1997). Pristine sites with sulfate concentrations at background levels in surface water (0.005 mmol L^{-1} or less) tend to exhibit relatively low MeHg concentrations (Stober et al., 1998; Gilmour et al., 1998), probably due to limitation of sulfate reduction (and MeHg

production) by sulfate availability. These pristine areas with low porewater sulfate (0.005 mmol L^{-1} or less) and sulfide ($< 3.1 \times 10^{-7}$ mmol L^{-1}) concentrations include much of Everglades National Park, the southernmost part of WCA 3A, and WCA 1 (Loxahatchee National Wildlife Refuge) (Orem et al., 1997).

Ongoing research includes the use of environmental chambers (mesocosms) placed at numerous key sites in the ecosystem to test the hypothesis that sulfur is a major control on MeHg production in the Everglades.

CONCLUSIONS

The results presented in this paper suggest that sulfate contamination in the Everglades ecosystem originates from canals draining the EAA. This conclusion is based on the observed pattern of high sulfate concentrations in the canals and in water conservation areas that receive direct discharge from the canals. The sulfate concentration and isotopic data appear to exclude rain water and ground water as major contributors of sulfate to wetlands of the northern Everglades that are highly contaminated with sulfur. Other evidence supporting this conclusion includes patterns of seasonally high dissolved sulfide content in sediment porewater at sites affected by canal discharge, the high rate of sulfur accumulation in the sediment at sites near canal discharge, and the decrease in total sulfur content with depth in the sediment in nutrient-affected areas (correlating with total phosphorus contents), suggesting that contamination is recent. The isotopic evidence implicates agricultural fertilizer as a major contributor to the sulfate load in the canals; however, ground water under the EAA, release of sulfur from oxidation of agricultural soils, and sulfate from agricultural uses north of Lake Okeechobee may also be contributing sources.

Sulfate is generally considered to be a relatively innocuous substance, and is used extensively in agricultural amendments and fertilizer. However, in situations where agricultural land abuts environmentally sensitive wetlands, sulfate input to the wetland combined with atmospheric or point sources of mercury can generate a potential environmental MeHg problem.

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