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Sulfur in the South Florida Ecosystem: Distribution, Sources, Biogeochemistry, Impacts, and Management for Restoration

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Sulfur in the South Florida Ecosystem: Distribution, Sources, Biogeochemistry, Impacts, and Management for Restoration

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Sulfur is broadly recognized as a water quality issue of significance for the freshwater Florida Everglades. Roughly 60% of the remnant Everglades has surface water sulfate concentrations above 1 mg l^{-1}, a restoration performance measure based on present sulfate levels in unenriched areas. Highly enriched marshes in the northern Everglades have average sulfate levels of 60 mg l^{-1}. Sulfate loading to the Everglades is principally a result of land and water management in South Florida. The highest concentrations of sulfate (average 60–70 mg l^{-1}) in the ecosystem are in canal water in the Everglades Agricultural Area (EAA). Potential sulfur sources in the watershed are many, but geochemical data and a preliminary sulfur mass balance for the EAA are consistent with sulfur presently used in agricultural, and sulfur released by oxidation of organic EAA soils (including legacy agricultural applications and natural sulfur) as the primary sources of sulfate enrichment in the EAA canals. Sulfate loading to the Everglades increases microbial sulfate reduction in soils, leading to more reducing conditions, greater cycling of nutrients in soils, production of toxic sulfide, and

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enhanced methylmercury (MeHg) production and bioaccumulation. Wetlands are zones of naturally high MeHg production, but the combination of high atmospheric mercury deposition rates in South Florida and elevated sulfate loading leads to increased MeHg production and MeHg risk to Everglades wildlife and human consumers. Sulfate from the EAA drainage canals penetrates deep into the Everglades Water Conservation Areas, and may extend into Everglades National Park. Present plans to restore sheet flow and to deliver more water to the Everglades may increase overall sulfur loads to the ecosystem, and move sulfate-enriched water further south. However, water management practices that minimize soil drying and rewetting cycles can mitigate sulfate release during soil oxidation. A comprehensive Everglades restoration strategy should include reduction of sulfur loads as a goal because of the many detrimental impacts of sulfate on the ecosystem. Monitoring data show that the ecosystem response to changes in sulfate levels is rapid, and strategies for reducing sulfate loading may be effective in the near term. A multifaceted approach employing best management practices for sulfur in agriculture, agricultural practices that minimize soil oxidation, and changes to stormwater treatment areas that increase sulfate retention could help achieve reduced sulfate loads to the Everglades, with resulting benefits.

KEYWORDS: Everglades, methylmercury, sulfate, sulfur, water quality

1. INTRODUCTION

The south Florida wetlands ecosystem is an environment of great size (28,000 km^2) and contains a variety of habitats, including freshwater marshes (the Everglades) and cypress swamps, and brackish water mangrove forests along the coast (Davis and Ogden, 1994). This diverse environment is interconnected by the flow of freshwater from one part of the ecosystem to another (Figure 1), and provides a habitat for an abundance of wildlife. The waterlogged conditions allow for the accumulation of organic soils (peat) in most of the greater Everglades.

The Everglades are impacted by the combined effects of urbanization, agriculture, and nearly 100 years of water management entailing construction of canals, levees, and impoundments. Critical problems include (a) water quantity, driven by the competing needs of agriculture, urban areas, and wetlands; (b) changes in the natural hydrologic flow of the region through the construction of canals, levees, and highways; (c) water quality, due to contaminants of anthropogenic origin; and (d) significant declines and continued threats to native flora and fauna from issues of water quantity, water
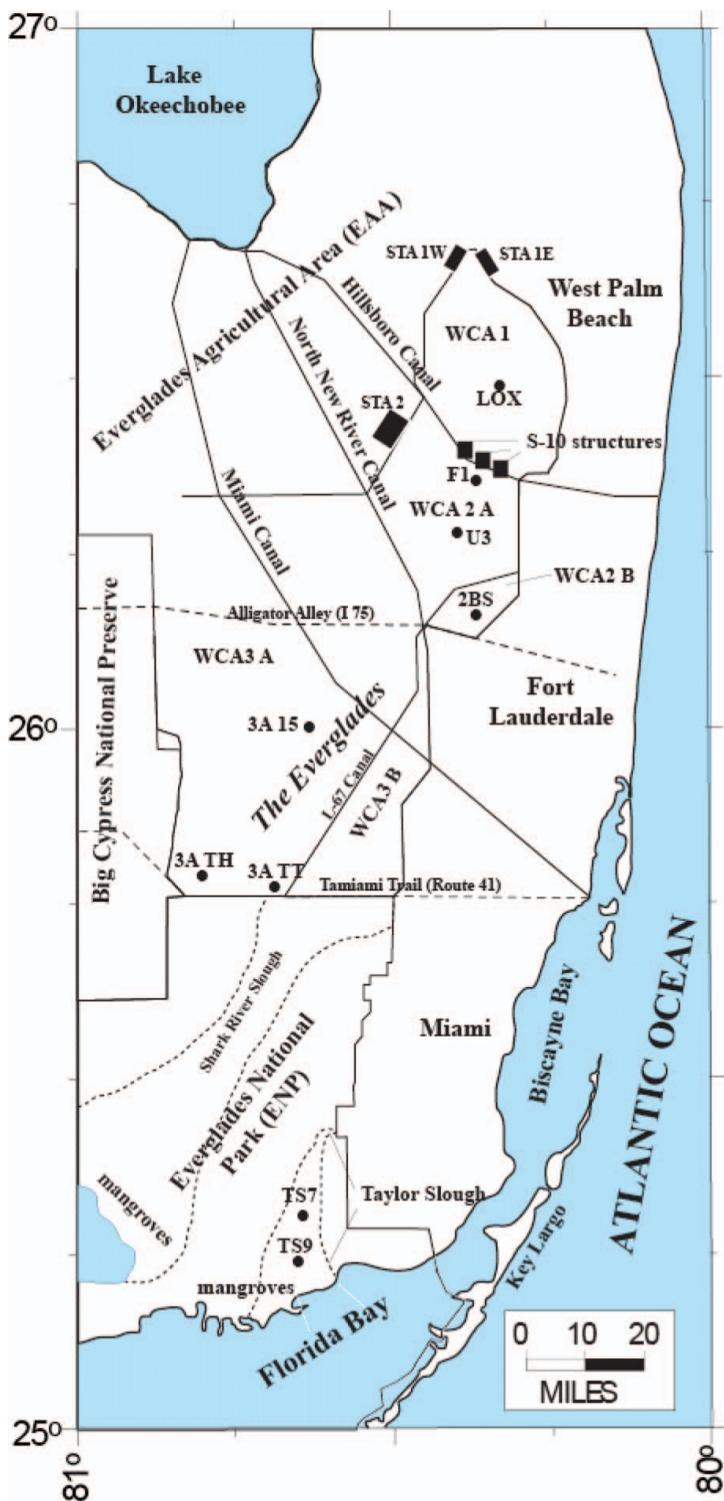
FIGURE 1. Map of the Everglades and its environs, showing major locations mentioned in the text and the principal ACME sampling sites. (This figure is available in color online).

quality, and invasive species (Light and Dineen, 1994; Sklar et al., 2002). To address these problems, a restoration plan for the Everglades was developed involving State and Federal resources, and known since 2000 as the Comprehensive Everglades Restoration Plan (CERP). The principal goal of CERP is to restore the quantity, quality, timing and distribution of water to the Everglades (South Florida Water Management District and Florida Department of Environmental Protection, 2000). This includes restoring natural sheet flow and increasing water delivery to wetlands in the south, including Everglades National Park (ENP), that presently receive insufficient freshwater to sustain natural habitats.

Although restoration efforts are proceeding, water quality remains a daunting challenge (Perry, 2008). Water quality in the Everglades has historically focused on phosphorus contamination from sources in the Everglades Agricultural Area or EAA (Davis, 1994; Koch and Reddy, 1992). Total phosphorus levels in surface water were up to 150 μg l^{-1} in the northern Everglades in the 1970s, compared to 4–10 μg l^{-1} prior to human development of the region (McCormick et al., 2002). Excess phosphorus has caused eutrophication of parts of the historically oligotrophic Everglades, and is linked to changes in macrophyte distributions, and impacts on other aquatic organisms in the northern Everglades (McCormick et al., 1996, 2002). Restoration efforts, including best management practices (BMPs) for phosphorus use in the EAA, and the construction of stormwater treatment areas (STAs) have reduced phosphorus in water discharged to the Everglades to present levels of 30–50 μg l^{-1} (Reddy et al., 2006).

Phosphorus contamination, however, is not the only water quality issue of concern in the Everglades (Bates et al., 2002; Pfeuffer and Rand, 2004; Scheidt and Kalla, 2007). Sulfur has emerged as another critical water quality issue (Orem, 2004). Sulfur enters the Everglades primarily as highly water-soluble sulfate. Most freshwater wetlands have low levels of sulfate (Gorham et al., 1985; Wetzel, 1975), and unenriched areas of the Everglades have very low sulfate levels, ranging from 1 to <0.1 mg l^{-1} (Gilmour et al., 2007b; Scheidt and Kalla, 2007). Parts of the northern Everglades, however, have average sulfate levels of 60 mg l^{-1}, far in excess of background levels and 1,000 times more than levels of phosphorus entering the ecosystem (Gilmour et al., 2007b; Table 1). Sulfate is not toxic or chemically reactive, but plays a key role in wetland biogeochemistry as a metabolic terminal electron acceptor in microbial sulfate reduction (MSR). The major endproduct of MSR is sulfide, a toxic and highly reactive chemical species, potentially harmful to aquatic fauna and flora. MSR also plays a major role in the transformation of inorganic mercury to a more toxic and bioaccumulative form, methylmercury (MeHg). MeHg is a major environmental issue for piscivorous wildlife in the Everglades, and for human health from consumption of MeHg-contaminated Everglades fish (Axelrad et al., 2007, 2008).

In this paper, we review the distribution, sources, biogeochemistry, and impacts of sulfur on the Everglades. We summarize the wealth of surface

TABLE 1. North to south gradient in water quality in the Everglades derived from ACME data sets (1995–2000)

	Northern Everglades (Enriched Site)	Southern Everglades (Unenriched Site)
Surface Water		
Phosphate	50 μg l^{-1}	<10 μg l^{-1}
Sulfate	60 mg l^{-1}	<1 mg l^{-1}
Porewater		
Redox	−250 mv	−30 mv
Phosphate	2,000 μg l^{-1}	30 μg l^{-1}
Sulfide	1,000–15,000 μg l^{-1}	<1 μg l^{-1}
Soil		
AR[1] Organic Carbon	3,000 mg Cm^{-2} day^{-1}	150 mg Cm^{-2} day^{-1}
Total Phosphorus	2,000 μg g^{-1} (dry wt.)	400 μg g^{-1} (dry wt.)
AR[1] Total Phosphorus	10 mg P m^{-2} day^{-1}	0.05 mg P m^{-2} day^{-1}
AR[1] Total Sulfur	11 mg S m^{-2} day^{-1}	1.4 mg S m^{-2} day^{-1}

[1]AR = Accumulation Rate (soil accumulation rate × dry bulk density × soil elemental content).

water sulfate data collected for the ecosystem over the last 15–20 years, and examine the potential effects of Everglades restoration on sulfur distributions and impacts on the ecosystem. We conclude with observations on possible approaches for reducing sulfate loads to the Everglades and minimizing the impacts of sulfur.

2 DISTRIBUTIONS OF SULFATE IN SURFACE WATER

Large areas of the Everglades have elevated surface water sulfate concentrations (Figure 2), including, Water Conservation Areas (WCAs) 2A and 2B, most of the northern third of WCA-3A, and locations adjacent to canals in WCA-1, WCA-3, ENP, and Big Cypress National Preserve (BCNP). Surface water sulfate data summarized here were collected by the South Florida Water Management District (SFWMD), the U.S. Geological Survey (USGS) Aquatic Cycling of Mercury in the Everglades (ACME) project, and the U.S. Environmental Protection Agency (USEPA) Regional Environmental Monitoring and Assessment Program (REMAP).

The SFWMD and ACME data derive from repeated sampling, mostly since 1995, at fixed sites in canals and marshes. The SFWMD data are from the DBHYDRO database (http://my.sfwmd.gov/dbhydroplsql/show_dbkey_info.main_menu). ACME data are from the USGS and the Smithsonian Environmental Research Center, and include data from a set of nine primary marsh sites distributed across WCAs 1, 2A, 2B, 3A, and ENP, additional marsh sites in the Everglades, BCNP, and STAs, and survey data from canals. The DBHYDRO and ACME data sets were compiled into a single database, which
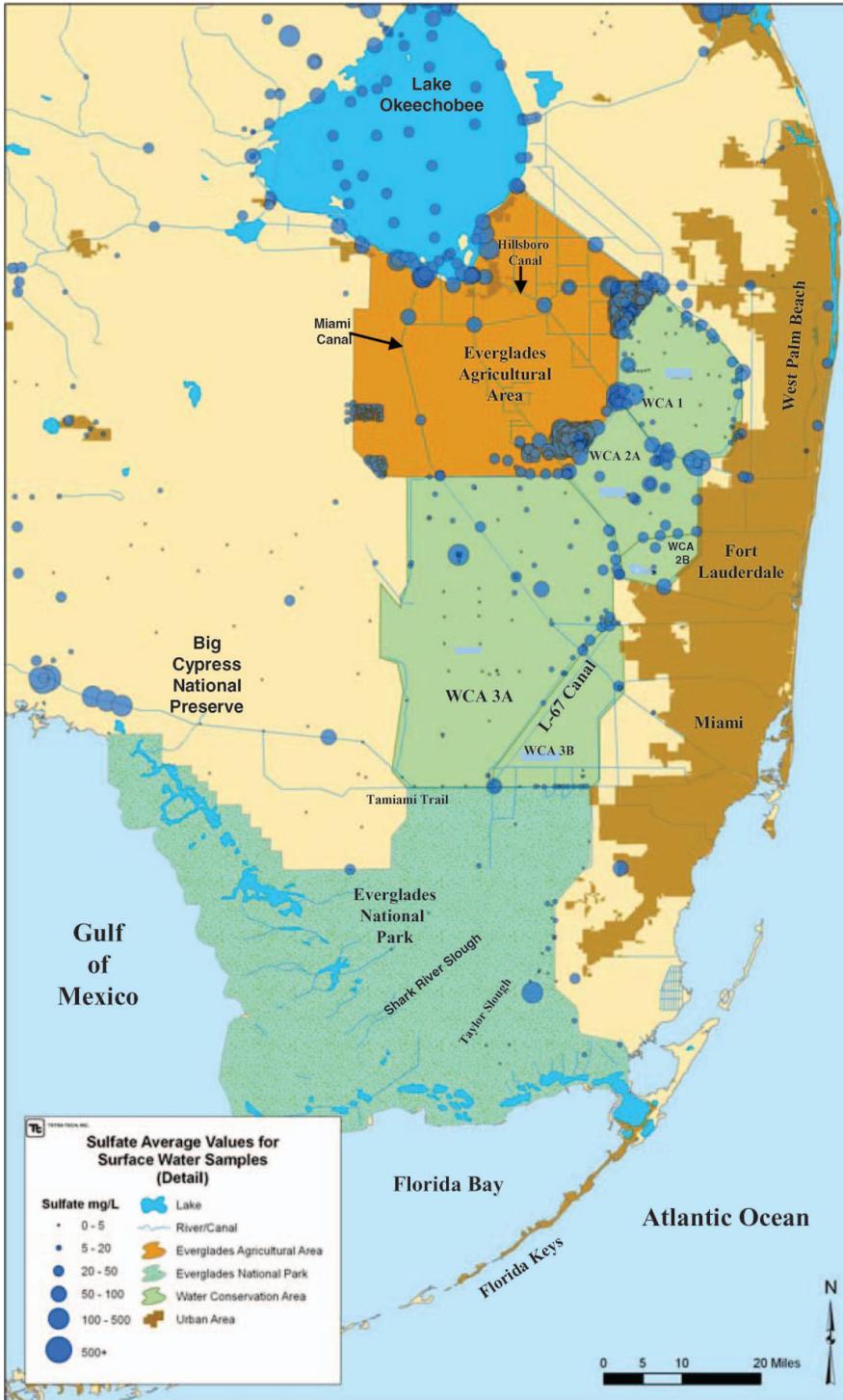
FIGURE 2. Map of average surface water sulfate concentrations (mg l^{-1}) for all sites sampled by SFWMD and ACME, 1993–2005. Map adapted from Gilmour et al. (2007b). (This figure is available in color online).

was used to map both spatial and temporal trends in these data (Gilmour et al., 2007b).

USEPA REMAP data come from randomized sampling at a large number of locations (marsh and canal sites) during dry- and wet-season sampling in 1995–1996, 1999, and 2005 (Scheidt and Kalla, 2007). All labs used similar sample collection and processing methods, and ion chromatography for sulfate determinations (U.S. Environmental Protection Agency, 1993). In cases where samples overlapped in time and space, sulfate values from different labs were nearly identical.

Spatial Distribution of Sulfate

Average surface water sulfate concentrations for each site, based on data from 1993 through 2005 are plotted in Figure 2. Across the freshwater Everglades, the highest average surface water sulfate concentrations are found in canal water in (and just downstream of) the EAA. Average sulfate concentrations in Everglades marshes over the period of record ranged from <0.05 mg l^{-1} at sites distant or protected from canal discharge, to 100 mg l^{-1} at sites near canal discharge (Payne et al., 2009). At interior marshes within the WCAs, there is an overall gradient in sulfate concentration from north to south, with the exception of WCA-1 (the Arthur R. Marshall Loxahatchee National Wildlife Refuge), which is somewhat protected from canal inputs by a rim canal. Recent data show that during the wet season sulfate from canal water penetrates into WCA-1's interior marsh (Wang et al., 2009). Elevated sulfate concentrations occur near major canals throughout the ecosystem, even in areas to the south such as along the L-67 canal in southern WCA-3A and where the L-67 terminates in ENP.

A detailed analysis of the USEPA REMAP findings for sulfate is presented in Scheidt and Kalla (2007). Sulfate data at REMAP sites are in close agreement with the SFWMD and ACME findings for sulfate concentrations and distributions. Surface water sulfate concentrations across the Everglades tend to be highest during the wet season due to the pumping of stormwater from the EAA into the Everglades for flood control (Scheidt et al., 2000).

All datasets indicate that the most sulfate-enriched marshes are in WCA-2A, and northern WCA-3A. In WCA-2A average sulfate concentrations were >40 mg l^{-1} at all sampling sites. STA 2 discharges water with sulfate concentrations as high as 100 mg l^{-1} during the wet season into WCA-2A, the highest sulfate concentration of any of the STAs (Scheidt and Kalla, 2007). Compared to phosphorus, sulfate penetrates much farther into the marsh from STAs and canal discharge points. Sulfur is a plant nutrient required at roughly the same levels as phosphorus (Hawkesford and DeKok, 2007). However, sulfur is discharged into the northern Everglades at mg l^{-1} levels compared with μg l^{-1} levels for phosphate. MSR in soils also removes sulfate from surface water, sequestering sulfate as reduced sulfur in soils, but

this process is slow relative to sulfate loading rates to the northern marshes. Hence, as water flows across the marshes of WCA-2A and northern WCA-3A, phosphate is rapidly attenuated with distance from the canals by plant uptake, whereas sulfate is removed only slowly.

Over the last 15 years, surface water sulfate concentrations in WCA-3A have generally been highest in the north and east, and at sites near the Miami and L67 Canals (Figure 2). Sulfate concentrations up to 100 mg l^{-1} were observed in surface water at sites in WCA-3A near points of canal discharge, though average levels in most of northern WCA-3A range from 5–20 mg l^{-1}. Sulfate concentrations in WCA-3A decrease toward the south and west.

In the freshwater parts of ENP, sulfate concentrations in surface water were generally <1 mg l^{-1}, except for sites near canal discharge and a zone of relatively high sulfate (20–40 mg l^{-1}) in Taylor Slough east of an abandoned agricultural area (the Hole in the Donut). REMAP data from the 1995, 1996, 1999, and 2005 wet seasons indicate elevated sulfate levels (5–10 mg l^{-1}) well into the Shark Slough marsh near the L-67 canal terminus within ENP (Scheidt and Kalla, 2007; Stober et al., 2001). In BCNP sulfate concentrations were generally <1 mg l^{-1}, except for marshes just north of BCNP (2–3 mg l^{-1}) and canals such as the L28 (10 mg l^{-1} sulfate) that surround BCNP.

The STAs generally receive high sulfate loads from EAA canals, and have elevated surface water sulfate concentrations. For example, concentrations of sulfate in STA-1W generally range from 20 to 60 mg l^{-1}, while sulfate levels in STA-2 are reported as 70–100 mg l^{-1} (Garrett and Ivanoff, 2008; Scheidt and Kalla, 2007).

Temporal Changes in the Distribution of Sulfate

Sulfate concentrations in marsh surface waters exhibit substantial temporal variability due to changes in rainfall and canal discharge, seasonal drying and rewetting cycles, and perhaps the timing of additions of agricultural chemicals to soils in the EAA. For example, in any given year, sulfate concentrations at sites F1 in WCA-2A near the S-10C canal discharge structure, and U3 in the center of WCA-2A, have ranged from 5 to 100 mg l^{-1} (Figure 3).

Long-term temporal trends are superimposed on this shorter-term variability. For example, surface water sulfate concentrations at marsh sites in eastern WCA-2A have shown significant downward trends over time (Figure 3). This pattern reflects a decrease in water discharge volume through S-10 outflow structures on the Hillsborough Canal into northeastern WCA-2A, rather than a decline in sulfate concentration in canal water (Gilmour et al., 2007b).

Significant declines in surface water sulfate were also observed at site 3A 15 in central WCA-3A, more remote from the EAA. Sulfate concentrations here dropped from roughly 10 mg l^{-1} in the mid-1990s to <1 mg l^{-1} by
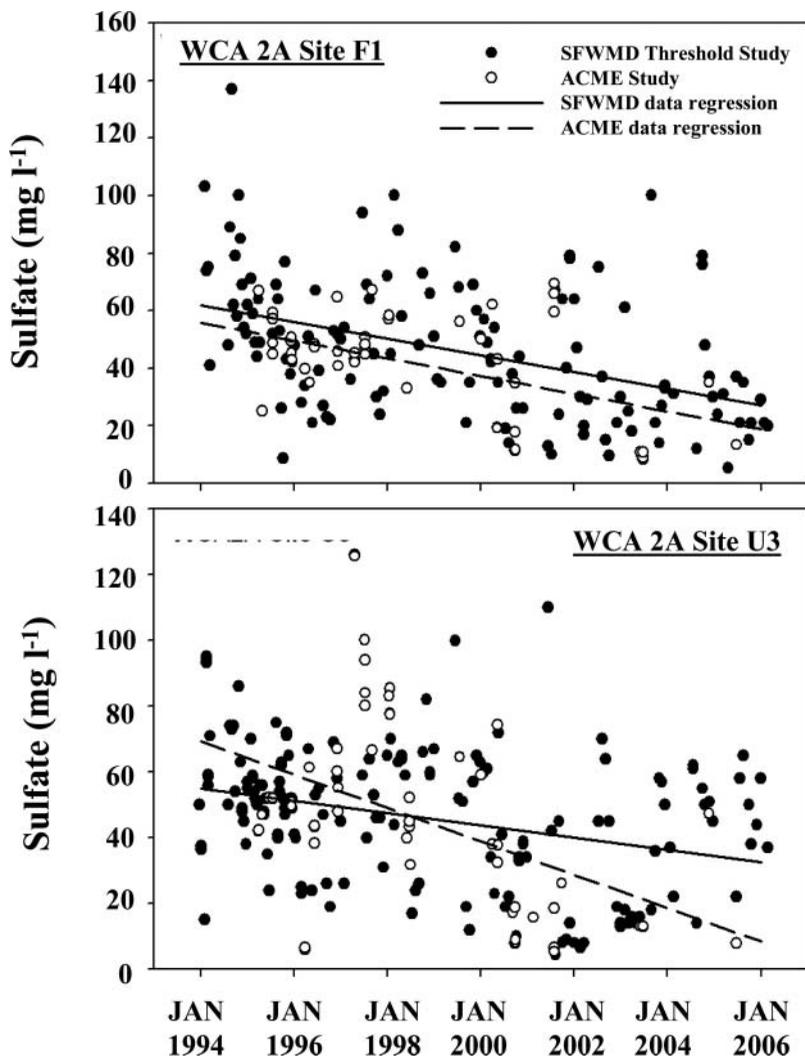
FIGURE 3. Surface water sulfate concentrations (mg l^{-1}) through time (1996–2007) at two sites in WCA-2A (blue dote = SFWMD data; pink dots = USGS ACME data). Lines represent linear regression fits for each data set, and indicate decreasing sulfate over time at these locations. Figure adapted from Gilmour et al. (2007b).

about 1999, and have remained low since then. The reason for this decline is more difficult to assess because canal loads to WCA-3A occur through levee breaks rather than control structures. However, sources of sulfate to this site probably include Miami and L-67 canal water, and the observed decline in sulfate here may reflect changes in water management accompanying the Everglades restoration effort.

In contrast, sulfate has increased in the northwest corner of WCA-2A. Prior to 2000, rainfall was the primary source of water to this area and

sulfate concentrations ranged from 5–17 mg l^{-1} (Garrett and Ivanoff, 2008). Since the opening of STA-2 in 2000, which releases treated effluent into northwest WCA-2A, the average sulfate concentration has risen to 60–70 mg l^{-1}, consistent with sulfate levels found in STA-2 discharge water (Garrett and Ivanoff, 2008). Surface water ammonium and dissolved organic carbon, and pore water total dissolved phosphorus, ammonium, and total dissolved Kjeldahl nitrogen concentrations also increased significantly in this area after 2000.

The temporal variability of sulfate concentrations in different parts of the ecosystem highlights the many factors that influence sulfate levels, most importantly the discharge of sulfate-enriched canal water. Some temporal trends can be linked to changes in water management operations (e.g., initiation of new inflow points from STAs), while the causes of others is less clear. Unfortunately, canal water and STA discharge water is highly enriched in sulfate (>60 mg l^{-1} on average for canal water). The use of this sulfate-enriched canal water to increase hydroperiod in some areas to the south (e.g., ENP) as part of the restoration plan will increase sulfate loading to these areas. This has significant consequences for the ecosystem, as discussed later.

3   SOURCES OF SULFATE TO SURFACE WATER

Canals within the EAA have the highest surface water sulfate concentrations in the greater Everglades region (Bates et al., 2001, 2002; Chen et al., 2006; Gilmour et al., 2007b; Scheidt et al., 2000). Everglades marshes with the highest sulfate levels are located near points of canal discharge. In general, sulfate concentrations decrease with distance from the EAA, both to the north and south (Figure 2). Thus, surface water sulfate distributions suggest that a major source of sulfate exists within the EAA, and that canal water is the principal conduit-delivering sulfate to the Everglades. But what is the source of the sulfate within the EAA?

Wet and Dry Deposition of Sulfate

Rainfall has sulfate concentrations that are too low to account for the high levels of sulfate in EAA canals. Rainwater from the northern Everglades has sulfate concentrations ranging from <1 to 2.5 mg l^{-1} (Bates et al., 2002; McCormick and Harvey, 2011), and rainwater from ENP has an annual volume-weighted mean of 0.5–0.7 mg l^{-1} sulfate (National Atmospheric Deposition Program, 2008). Also, sulfate in rainfall has sulfur isotopic (δ^{34}S) compositions of +2 to +6‰ compared to +15 to +23‰ for sulfate in canal water (Bates et al., 2002; Katz et al., 1995). Rainwater may be an important
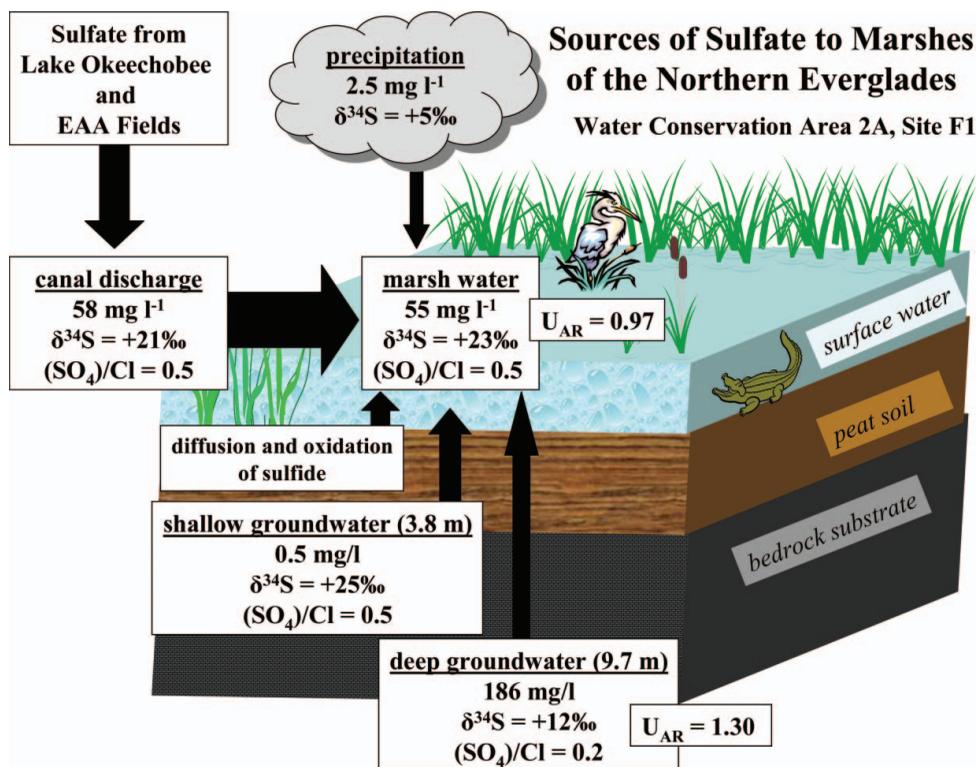
FIGURE 4. Sources of sulfate to a marsh site in the northern Everglades, WCA-2A. Sulfate concentration and geochemical data indicate that canal water is the principal source of sulfate to surface water at marsh sites. Figure based on ACME data from WCA-2A and nearby canals. (This figure is available in color online).

source of sulfate to unenriched areas, but cannot account for the high sulfate levels in canals or sulfate-enriched marshes (Figure 4).

Data on dry deposition of sulfate and total sulfur in south Florida are not readily available. Data from other areas of North America show that dry deposition of sulfate and total sulfur is always less than or equal to wet deposition (USEPA, 2006). Thus, dry deposition is unlikely to be a major contributor to the total sulfate flux to the Everglades.

Groundwater as a Source of Sulfate

Shallow groundwater (<9 m) under WCA-2A and the southern EAA has sulfate concentrations of <2 mg l^{-1} (Bates et al., 2002; Figure 4). The Biscayne Aquifer, a shallow aquifer under the southeastern portion of WCA-3 and ENP (J. A. Miller, 1990), has median sulfate levels of 17 mg l^{-1} (Radell and Katz, 1991). Overall, sulfate levels in shallow groundwater are low compared to those in EAA canals and sulfate-enriched marsh sites. Shallow groundwater is easily impacted by infiltration of contaminated surface water (Klein and

Hull, 1978), and more likely to be enriched with sulfate from surface sources than to be a source of sulfate.

Groundwater >9 m below the surface may have high sulfate concentrations (Bates et al., 2002; Figure 4). Miller (1988) found sulfate concentrations of 25–580 mg l^{-1} in EAA groundwater at 20 locations at a depth of 15 m, with the highest concentrations in the eastern EAA. A 1976–77 study of groundwater in the EAA reported sulfate concentrations of 20–490 mg l^{-1} (CH2MHILL, 1978). Thus, deep groundwater (>9 m) underlying the EAA has sulfate levels exceeding those found in surface water, and could be a source of sulfate to canals and marshes in the Everglades.

Several lines of geochemical evidence (Figure 4), however, indicate that deep groundwater is not a major source of sulfate to surface water in canals or marsh areas: (a) Marshes with high surface water sulfate concentrations have pore water sulfate profiles that exponentially decrease with depth, indicating no advective flux of sulfate-rich groundwater (Orem et al., 1997); (b) Deep groundwater has a sulfur isotopic composition (δ^{34}S) of about +12‰, distinct from values (+18 to +25‰) typical of sulfate in canals and enriched marsh sites (Bates et al., 2002); (c) Sulfate/chloride values are 0.2 in deep groundwater, compared to 0.5 in canal water and high-sulfate marsh sites (Bates et al., 2002; Chen et al., 2006); (d) The uranium concentration and ^{234}U/^{238}U activity ratio (AR) of groundwater (AR = 1.30) is distinct from that of canal water (AR = 0.98) and surface water of Everglades marshes (AR = 0.97), indicating that groundwater is not a major water source to canals or marshes in the northern Everglades (Zielinski et al., 2000). These geochemical results are evidence that the high sulfate levels in canal and marsh water in the northern Everglades are not derived primarily from shallow or deep groundwater.

Sulfate Contributions From the Kissimmee-Okeechobee Watershed

No sulfur budgets presently exist for portions of the Kissimmee-Okeechobee watershed, and sulfate data are limited. The soils that predominate in upland areas of the watershed are typically poor in sulfate, although not in all locations. The most significant anthropogenic source of sulfate in the watershed likely comes from fertilizer applications to improved pastures and other agricultural lands, which collectively account for 52% of the land-use in the watershed (Zielinski et al., 2006). However, quantitative information on fertilizer application rates is lacking for most land-use types. Sulfate concentrations have remained stable from 1974–2006 at both the upstream end of the Kissimmee River (mean of 9 mg l^{-1}), and at the downstream end as it enters Lake Okeechobee (mean of 12 mg l^{-1}). Concentrations measured near the mouth of the Kissimmee River during 1940–41 (Parker et al., 1955) averaged 6 mg l^{-1}. Thus, there is some indication that development in the watershed after 1945 increased sulfate loads to the lake.

Concentrations of sulfate in Lake Okeechobee are lower than sulfate concentrations in EAA canals. Lake sulfate concentrations were about 25 mg l^{-1} during 1940–41 (Love, 1955), 28 mg l^{-1} from 1950–1952 (Brown and Crooks, 1955), and 22 mg l^{-1} in 2005 (Scheidt and Kalla, 2007). Lake Okeechobee receives most of its sulfate input (98%) from surface inflows (McCormick and James, 2008). Drainages flowing into the lake from the north account for 64% of annual average sulfur loads: 28% from the Indian Prairie/Lake Istokpoga basin, 18% from the Kissimmee River, and 18% from other basins. Runoff (including backpumping) from the EAA accounts for 36% of the annual average sulfur load to the lake. Groundwater appears to contribute little or no sulfate to the lake, and rainfall contributes only a small percentage (about 2–3%) of the lake's sulfate (McCormick, 2009). The concentration of sulfate (and other ions) in the lake is significantly in excess of what would be expected based on inputs from surface flow alone due to significant evapoconcentration in this large shallow lake (James et al., 1995). The lake also lacks the ability to effectively sequester sulfur in its sediments. The rocky and sandy bottom of much of the lake and the resuspension of sediments from the relatively shallow lake bottom during even modest wind events prevents sequestration of reduced sulfur species in the lake sediments. Indeed, the residence time of sulfate in Lake Okeechobee is similar to that of unreactive chloride, about 2–3 years on average, showing that sulfate passes through the lake quickly (McCormick, 2009).

The highest recorded sulfate concentrations in Lake Okeechobee occurred during the 1970s, with average sulfate levels during this period in excess of 60 mg l^{-1}. During this period, large volumes of EAA runoff were routinely backpumped northward to the lake, accounting for roughly 50% of the lake's sulfate load. Changes during the 1980s reduced this backpumping in an effort to reduce nutrient loading that was contributing to lake eutrophication. These changes simultaneously resulted in greater discharges of EAA water southward to the WCAs and in a substantial decline in lake sulfate loads that led to a rapid decline in in-lake sulfate concentrations consistent with the short residence time for this ion in the lake. Since 1985, annual net exports of sulfate from the lake have exceeded imports from the EAA in most years. As a result, during the period of record for water-quality data collection (1974–2006), Lake Okeechobee represents a modest net input of sulfate (approximately 4500 mt yr^{-1} in surface flows) to the EAA canals and the Everglades, driven by surface runoff to the lake and evapoconcentration.

Evidence From Sulfur Isotopes

Stable isotopes (δ^{34}S) of sulfate in surface water of marshes and canals were used to examine sources of sulfate to the Everglades (Bates et al., 2001, 2002). Although complicated by fractionation during MSR, sulfur isotopes may still provide useful insights when used for source discrimination (Thode

et al., 1961). Surface waters from upstream portions of canals in the EAA had the highest sulfate concentrations and the lowest $\delta^{34}S$ values. Sulfate concentration decreased and $\delta^{34}S$ values increased moving downstream along the canals and out into the Everglades due to (a) progressive microbial sulfate reduction in canals and marsh soils, and (b) dilution by rainwater (Bates et al., 2002). Plots of sulfate concentration versus sulfur isotopic composition ($\delta^{34}S$) showed a wide range of $\delta^{34}S$ values (+15 to +35‰) at low sulfate concentration, reflecting the different sources and redox changes that contribute to the sulfate pool at unenriched sites. At higher sulfate concentrations the spread of $\delta^{34}S$ values decreased (+17 to +24‰) and a distinct trend emerged, suggesting a single dominant source of sulfate at elevated sulfate concentrations. The highest sulfate concentrations in EAA canal water had $\delta^{34}S$ values approaching +16‰, suggesting this is close to the $\delta^{34}S$ value of the principal sulfate source (Bates et al., 2002).

Extensive use of sulfur in agriculture in the EAA (Bottcher and Izuno, 1994) suggests that much of the sulfate in EAA canals may originate from agricultural application. (Bates et al., 2002). Elemental sulfur (S^0) is used as a soil amendment and fungicide in the EAA (Bottcher and Izuno, 1994). Sulfur isotopic analyses ($\delta^{34}S$) of S^0 used in the EAA (Bates et al., 2001, 2002) had a range of values (15–20‰) consistent with the isotopic composition ($\delta^{34}S$) of sulfate in EAA canals. Sulfate extracted from the upper 10 cm of soil in an active sugarcane field in the EAA had a $\delta^{34}S$ value of 15.6 ‰ (Bates et al., 2002), consistent with that of agricultural S^0. From these data, it is hypothesized that sulfur applications in the EAA are (a) oxidized to sulfate in the largely aerobic soils, (b) remobilized from the soils by rainfall and/or irrigation, (c) transported as sulfate in runoff to the canals in the EAA, and (d) discharged to the Everglades in canal water. Note that the isotopic data ($\delta^{34}S$) do not indicate whether the sulfate entering the canals in the EAA is derived from recently applied sulfur, sulfur released during soil oxidation (including historical agricultural applications of sulfur and natural sulfur), or both.

Sulfur in the EAA

Sulfur has three principal roles in agriculture: (a) as a plant nutrient, required in about the same amounts as phosphorus (Tabatabai, 1984), (b) as a soil amendment as S^0 to lower soil pH and increase the bioavailability of phosphorus and micronutrients (Boswell and Friesen, 1993; Ye et al., 2009), and (c) as a fungicide (Meyer, 1977). Sulfur is also present in some fertilizers as a counter ion to the principal nutrient (e.g., ammonium sulfate). Gypsum ($CaSO_4$) may also be added to soil to increase the sulfur content and for erosion control. Sulfate from oxidized S^0 and gypsum dissolution is highly mobile in organic-matter-rich soils (Rhue and Kamprath, 1973), and may be readily leached into drainage canals as sulfate. Elemental sulfur and sulfur-containing compounds (e.g., copper sulfate) are used as broad-spectrum

fungicides at 91 metric tons yr^{-1} for vegetables and 529 metric tons yr^{-1} for citrus within the management area of the SFWMD (McCoy et al., 2003).

The amount of total sulfur used in various soil amendments, fertilizers, and fungicides in the EAA is unknown. Also unknown is the total sulfate entering canals as runoff from EAA fields. Schueneman and Sanchez (1994) suggest that 500–1,700 kg ha^{-1} yr^{-1} of S^0 may be needed to reduce soil pH by 0.2–0.7 units for vegetables and 560 kg ha^{-1} yr^{-1} for multiyear sugarcane production in the EAA. A 1976–77 study of water quality in the EAA reported elemental sulfur applications (exclusive of fungicides) of 11 and 88 kg ha^{-1} yr^{-1} to sugarcane and vegetables, respectively (CH2MHILL, 1978). In a more recent publication, Schueneman (2000) estimated that about 37 kg ha^{-1} yr^{-1} of S^0 (about 111 kg ha^{-1} yr^{-1} converted from S^0 to sulfate) are presently added to EAA soil as an amendment. This estimate includes S^0 and sulfur in phosphorus fertilizer added to EAA soil, but not additions of sulfur in other fertilizers or in fungicides.

EAA Sulfur Mass Balance

Gabriel et al. (2010) completed a preliminary sulfur mass balance for EAA canals. Total sulfur fluxes into and out of EAA canals were estimated for a dry year (2007), a wet year (2004), and a year of intermediate rainfall (2003). Results show that wet and dry deposition are minor contributors during all years. In the dry year, sulfate levels in canals were somewhat lower and fluxes to canals were dominated by Lake Okeechobee water, as also shown by Bates et al. (2002). In dry years sulfate from soil oxidation and agricultural applications in the EAA remain on the land (e.g., not washed into canals by rainfall). For wet and intermediate rainfall years, sulfur fluxes to canals from EAA lands dominated (2–3 times higher than fluxes from Lake Okeechobee). Of the EAA land sources, sulfate from soil oxidation (legacy agricultural applications and natural soil sulfur) was about 5 times higher than new additions of agricultural sulfur. There are still significant uncertainties in the amounts of sulfur in all forms (soil amendments, fertilizers, fungicides, gypsum) added each year in the EAA.

Overall, it appears that much or most of the sulfate present in canals originates from the EAA lands. The broad use of sulfur in agriculture (present and legacy in soil), and the elimination of other sulfur sources (groundwater, wet/dry deposition) to canals suggests that soil oxidation and present sulfur use in the EAA accounts for the major proportion of the sulfate load to the Everglades.

4   BIOGEOCHEMISTRY OF SULFUR

Biogeochemical processes play an important role in the cycling of sulfur in Everglades wetlands, with the principal drivers being MSR, sulfur reoxidation

by chemical, photochemical and microbial processes, precipitation of metal sulfides, and the reaction of sulfide with organic matter to produce organic sulfur species. Sulfate-reducing activity in soils across the Everglades follows the distribution of sulfate in surface waters (Benoit et al., 2003), suggesting that MSR is sulfate-limited rather than substrate-limited in most Everglades soils. Sulfate-reducing bacteria can compete for substrate when electron acceptors that yield more energy than sulfate (oxygen, nitrate, and ferrous iron) are unavailable. Everglades soils exhibit rapid loss of oxygen with depth due to high rates of organic carbon production and soil oxygen demand. Nitrate and ferrous iron concentrations are too low in Everglades soils to support denitrification and iron reduction (Orem et al., 1997). Assays for microbial iron reduction in Everglades soils have yielded low or undetectable rates (Gilmour and Roden, 2009).

Microbial Sulfate Reduction

Figure 5 shows average depth profiles of sulfate, sulfate reduction rate, and some products of MSR across the ecosystem for the years 1995–1998. Net MSR is indicated by the declining concentration of sulfate with depth, and by the direct measurement of $^{35}SO_4^{2-}$ reduction to $^{35}S^{2-}$ in intact soil cores (Gilmour et al., 1998). MSR rates are usually maximal in the top few cm of sediments. At oligotrophic sites (e.g. TS-7 and TS-9 in ENP) sediment oxygen demand may be low enough that the sulfate reduction maximum is a few cm below the soil surface. Across the full sulfate gradient of the Everglades, average MSR rates ranged over two orders of magnitude. In the sulfate-enriched marshes in WCA-2A (F1 and U3 in Figure 5), MSR rates were exceptionally high, similar to rates in temperate tidal marshes (Mitchell and Gilmour, 2008).

Sulfide concentrations in Everglades soil pore water generally parallel surface water sulfate concentrations, and range from 13,000 to <0.1 μg l^{-1} at sulfate-enriched and unenriched sites, respectively. Sulfide concentrations in soil pore water often increase with depth to a maximum within the upper 20 cm (Figure 5). Dissolved sulfide is absent from surface water in the Everglades, except at heavily sulfate-enriched sites where 100's μg l^{-1} have been observed (Orem et al., 1997). Sulfide levels at these sites exceed EPA recommendations of 2 μg l^{-1} for sulfide in surface water (USEPA, 2006).

Only a portion of the sulfide produced in Everglades soils is permanently stored. Dissolved sulfide that accumulates in soil pore water may advect or diffuse back to surface water, where oxidation of organic and inorganic sulfides back to sulfate may occur, primarily through the activity of various sulfur oxidizing bacteria near the soil/surface water interface. Oxidation of sulfide remobilized from soils can influence both the concentration and $\delta^{34}S$ value of sulfate in surface water (Bates et al., 2001, 2002).
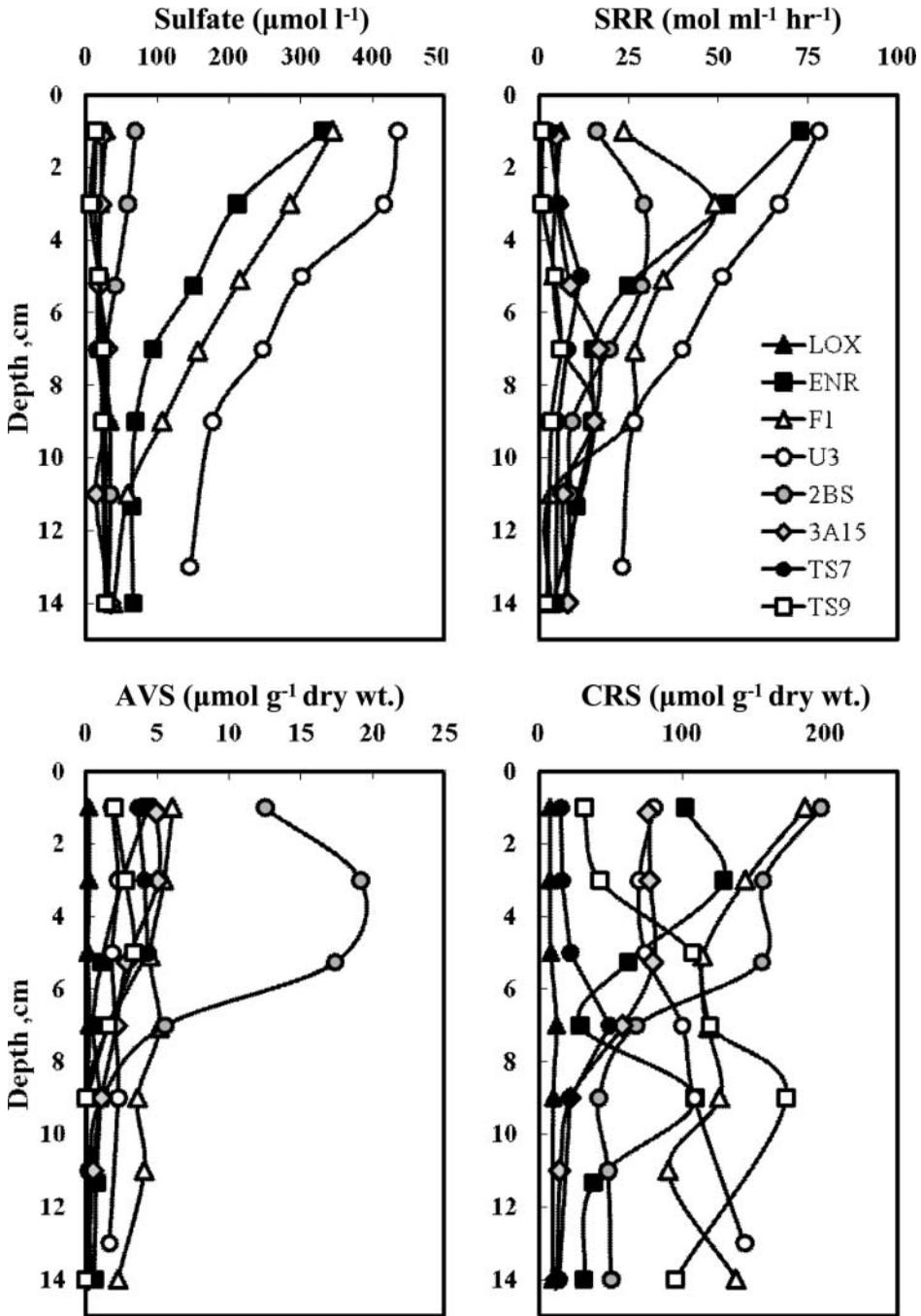
FIGURE 5. Indicators of sulfur cycling across a sulfate gradient in Everglades' marshes from ACME datasets (1995–1998): pore water sulfate concentrations (A), microbial sulfate-reduction rate (SRR) measured by the reduction of $^{35}SO_4^{2-}$ injected into intact cores (B), after Mitchell and Gilmour (2008), concentrations of acid volatile sulfides or monosulfides AVS (C), and chromium-reducible sulfur or disulfides like pyrite CRS (D), accumulated in soils.

Sulfur in Everglades Soil

The principal sink for sulfur within the ecosystem is reduced sulfur species in organic soils. Sulfur in Everglades soil originates from sulfur in the plant material forming the peat, and through reaction of sulfide with soil organic matter to form organic sulfur, and with metals (primarily iron) to form insoluble metal sulfides (Altschuler et al., 1983; Casagrande et al., 1979). Sulfur sequestration in soil requires reducing conditions, because reduced sulfur forms are those retained.

In the Everglades, the total sulfur (TS) content of soils ranges from 0.1 to 2.5% (dry wt. basis; Table 2). The highest TS contents in the freshwater Everglades are in WCA-2A and the periphery of WCA-1. Soil TS contents <0.5% are generally associated with soils containing >25% mineral matter (carbonates and quartz sand). Organic-rich soils (peats) from the brackish mangrove forests fringing Florida Bay have TS contents ranging from 2 to

TABLE 2. Accumulation rates of sulfur in the upper 10 cm of sediment from ACME sampling sites throughout the Everglades (1995–2000)

Site[1]	Status	Total Sulfur (mg g^{-1})	DBD[2] (g cm^{-3})	Sedimentation Rate[3] (cm yr^{-1})	Sulfur Accumulation Rate (g S m^{-2} day^{-1})
WCA 1-Center	Freshwater Marsh Unimpacted	10.2	0.074	0.01	0.21×10^{-3}
WCA 1-West	Freshwater Marsh P and S Impacted	12.4	0.096	0.13	4.2×10^{-3}
WCA 2A-F1	Freshwater Marsh P and S Impacted	8.9	0.057	0.36	5.0×10^{-3}
WCA 2A-F4	Freshwater Marsh P and S Impacted	10.2	0.094	0.27	7.1×10^{-3}
WCA 2A-U3	Freshwater Marsh S Impacted	10.4	0.097	0.12	3.3×10^{-3}
WCA 3A-15	Freshwater Marsh Slight S Impacted	3.00	0.083	0.38	2.6×10^{-3}
ENP TS7	Freshwater Marsh Unimpacted	7.1	0.170	0.048	1.6×10^{-3}
ENP TS9	Freshwater Marl Prairie Unimpacted	0.8	0.343	0.051	0.38×10^{-3}
ENP TS16	Brackish Water Mangrove/Sawgrass	18.8	0.125	0.14	9.0×10^{-3}
ENP TC2	Brackish to Marine Dwarf Mangrove Forest	46.5	0.116	0.020	3.0×10^{-3}

[1]WCA = Water Conservation Area.
[1]ENP = Everglades National Park.
[1]TS = Taylor Slough.
[2]DBD = sediment dry bulk density.
[3]Sedimentation rate from ^{210}Pb analysis.

9% (Table 2) due to high-sulfate seawater, organic-rich soils, and reducing conditions. In Lake Okeechobee, TS contents range from 0.6 to 1.1% in peaty sediments from South Bay, and from 0.1 to 0.4% in sand/silt sediments from the center of the lake.

Soils from across the EAA have TS contents ranging from 0.1–5% (Gabriel, 2009). Bates et al. (2001) reported TS concentrations of 0.1 to 0.6% in the upper 20 cm and up to 2.3% below 100 cm in limited EAA soil sampling. The relatively low TS contents in the upper 20 cm may reflect oxic conditions and high mineral matter content in the surface soils that inhibit sulfur retention. Under oxic conditions, organic sulfur, metal sulfides, and sulfur added in fertilizers and soil amendments are oxidized to sulfate, and leached from the soil during rain events. However, water saturated soils below 100 cm in the EAA may have anoxic conditions and higher organic matter contents that favor greater retention of sulfur in reduced form (organic sulfur and metal sulfides).

Vertical profiles of TS in Everglades marsh soils show various patterns, but in many cores TS concentrations decrease with depth (Bates et al., 1998). This may reflect both the diagenetic recycling of sulfur as well as increased sulfur loads to the ecosystem during the past 50 years. However, in southern ENP, TS often increases with soil depth. Pore water analyses indicate that this vertical pattern results from high sulfate and sulfide levels at depth from tidally driven movement of marine water along the base of the peat column in southern ENP approaching Florida Bay (Orem, 2009). Irregular vertical profiles of TS often reflect changing soil mineral matter content.

Accumulation rates for TS in surface soils range from 0.38×10^{-3} to 9.0×10^{-3} g m^{-2} day^{-1} across the ecosystem (Table 2). Sedimentation rates were determined at these sites using ^{210}Pb profiles and the CRS model of Binford (1990). The highest accumulation rates for TS occur in brackish water mangrove swamps and sulfur-enriched freshwater marshes. Average TS accumulation rates for unenriched freshwater marsh sites, sulfur-enriched sites, and mangrove sites (brackish water) were 1.6×10^{-3}, 4.5×10^{-3}, and 6.0×10^{-3} g m^{-2} day^{-1}, respectively. Enriched sites in the Everglades accumulate on average nearly 3 times as much TS in the soil as unenriched sites, and approach values found in brackish water areas.

Sulfur Species in Soils

Organic sulfur is the major sink for sulfur in Everglades peat, accounting for 50–85% of the TS (Altschuler et al., 1983; Bates et al., 1998; Casagrande et al., 1977). Disulfides (e.g., pyrite, chromium-reducible sulfide) and sulfates are the next most important sulfur species, accounting for 10–30% and 5–30% of the TS, respectively (Bates et al., 1998). Acid-volatile sulfides (monosulfides) are only a small fraction of the TS in Everglades soils, ranging from 0–2%

and generally <1% (Bates et al., 1998), possibly due to iron limitation of monosulfide fixation.

Remobilization of Sulfur From Soil by Drought and Fire

Drought and fire are natural processes that have historically shaped the Everglades (Gunderson and Snyder, 1994). Changes to the ecosystem (construction of canals, levees, and pumping stations) and water management practices, however, have altered the natural hydrology and increased the frequency and severity of drought and fire (Lockwood et al., 2003; Wu et al., 1996).

Sequestered forms of reduced sulfur in wetland soils (metal sulfides and organic sulfur) may be oxidized to sulfate by drought or fire. Fire may also volatilize sulfur to the atmosphere. Rewetting following drought/fire mobilizes the sulfate formed by the oxidation process and reestablishes anoxic conditions in the soil, stimulating MSR.

In May and June 1999 drought and fire affected most of northern WCA-3A. Prior to the burn, surface water sulfate concentrations in this area averaged about 7 mg l^{-1} (Orem, 2000). One month after the burn (June 1999), surface water sulfate levels at 14 sites in the burned area averaged 58 mg l^{-1}, and some sites had sulfate concentrations in the 100's of mg l^{-1} in surface water and pore water (Gilmour et al., 2004). The large increase in sulfate concentration following burn and rewet stimulated MSR and MeHg production for several months after the rewet (Gilmour et al., 2004, 2007a, 2007b). A year later (September 2000), sulfate levels at these 14 sites averaged 5 mg l^{-1}, similar to preburn levels.

Controlled laboratory experiments using soil core microcosms were conducted to further evaluate sulfur release from Everglades soils following dry down and rewet (Gilmour et al., 2004, 2007b). Soil cores from central WCA-3 and STA-2 were dried for 40 days under simulated natural lighting conditions, and then rewet with site water. Several types of controls were also run. Rewet soils from WCA-3 showed sulfate concentrations in overlying water of >200 mg l^{-1} immediately after rewetting, compared to <1 mg l^{-1} in control and ambient site overlying water concentrations (Gilmour et al., 2004, 2007b). STA-2 soils also showed sulfate concentrations of >200 mg l^{-1} in overlying water upon rewetting, but the high-sulfate canal water used to refill these cores contributed about 50 mg l^{-1} of the sulfate in this experiment (Gilmour et al., 2004). The presence of sulfide in the rewet cores from both sites indicated active MSR. MeHg production was also stimulated in the soils from both locations in these dry/rewet experiments (Gilmour et al., 2007b). Results confirm that dry down of Everglades organic soil oxidizes reduced sulfur species to sulfate, which is mobilized following rewet, and stimulates MSR and mercury methylation as soon as anoxic conditions are reestablished in the soil.

5 IMPACTS OF SULFUR ON THE ECOSYSTEM

The excess sulfate entering the Everglades has fundamentally changed its biogeochemistry through stimulation of MSR. The microbial community structure in soils over wide areas has been altered from one dominated by methanogenesis to one dominated by MSR. Impacts of increased sulfate loads may include (a) stimulation of MeHg production, (b) buildup of sulfide to levels that may be toxic to flora and fauna, (c) enhanced release of nutrients from organic soils, (d) changes in soil redox conditions, and (e) changes in metal speciation through formation of insoluble metal sulfides.

Impacts on MeHg Production and Bioaccumulation

Elevated levels of MeHg in gamefish caused Florida to issue fish consumption advisories for all of the Everglades (Florida Department of Health, 2003). Ecological risk assessments have indicated that populations of top predators such as wading birds could be adversely affected by MeHg contamination (Duvall and Barron, 2000). MeHg levels in top predator fish in ENP are among the highest levels in the nation for freshwater fish (Axelrad et al., 2009), and represent a threat to fish-eating avian and mammalian wildlife (Rumbold et al., 2008). Total mercury concentrations and spatial patterns in soil and water in the Everglades do not explain the bioaccumulation and distribution of mercury in prey fish; therefore other biogeochemical factors must be at play (Scheidt and Kalla, 2007; Stober et al., 2001).

Sulfate is known to be an important control on the production of MeHg in aquatic ecosystems (Benoit et al., 2003; Gilmour et al., 1992), including the Everglades (Gilmour et al., 1998). MeHg production in most ecosystems reflects a balance between microbial sulfate reduction, and sulfide accumulation in soil or soil pore waters (Benoit et al., 2003). Field observations, laboratory experiments, and mesocosm studies have shown positive correlations between net MeHg production and surface water sulfate concentrations across the Everglades over the range of 0.5–20 mg l^{-1} sulfate (Gilmour et al., 2007a). REMAP data for 2005 indicate that sulfate was correlated with MeHg in Everglades surface water and benthic periphyton (Scheidt and Kalla, 2007). However, at pore water sulfide concentrations >1 mg l^{-1} the buildup of sulfide becomes inhibitory to MeHg production, and the positive correlation between sulfate and MeHg breaks down. In both the ACME and REMAP data sets, pore water sulfide is negatively correlated with MeHg concentration and bioaccumulation (Scheidt and Kalla, 2007). Sulfide may inhibit MeHg production through the formation of sulfide-Hg or sulfur-containing DOC-Hg complexes that restrict the bioavailability of Hg to methylating bacteria (Benoit et al., 2001).

Net MeHg production is the balance between total MeHg production and MeHg degradation. There are multiple pathways of MeHg degradation,

with microbial and photochemical processes probably dominating in Everglades soils and waters, respectively. Marvin-DiPasquale et al. (2000) showed that net methylation in the Everglades reflects MeHg production rather than degradation patterns, the latter being less variable across the Everglades. Indeed, mercury methylation rates in the Everglades are strongly correlated with MeHg concentrations (Benoit et al., 2003). Strong correlations between methylation rates and MeHg, but weak correlations between demethylation rates and MeHg have been observed elsewhere (Drott et al., 2008). This suggests that net MeHg levels in most ecosystems, including the Everglades, are driven by controls on production rather than degradation.

The opposing effects of sulfate stimulation and sulfide inhibition on MeHg production, and the north to south gradient in sulfate concentrations in the Everglades provides geographic context to MeHg distributions and methylation rates (Figure 6). Unenriched areas of the ecosystem with sulfate <1 mg l^{-1} exhibit low levels of MeHg due to sulfate limitation of MSR. In sulfate-enriched areas (>20 mg l^{-1} sulfate) buildup of sulfide inhibits MeHg production. Areas with intermediate concentrations of sulfate ($1–20$ mg l^{-1}) have sulfate and sulfide levels that promote maximum MeHg production. During the mid to late 1990s, the highest MeHg levels in soil (Gilmour et al., 1998), fish (Stober et al., 1996, 2001), and wading birds (Frederick et al., 1997) in the Everglades were observed near the center of WCA-3A. At that time, sulfate concentrations in surface water in central WCA-3A ranged from 2 to 10 mg l^{-1}, and pore water sulfide concentrations were low enough ($5–150$ μg l^{-1}) to prevent sulfide inhibition of mercury methylation (Orem et al., 1997; Stober et al., 1996, 2001).
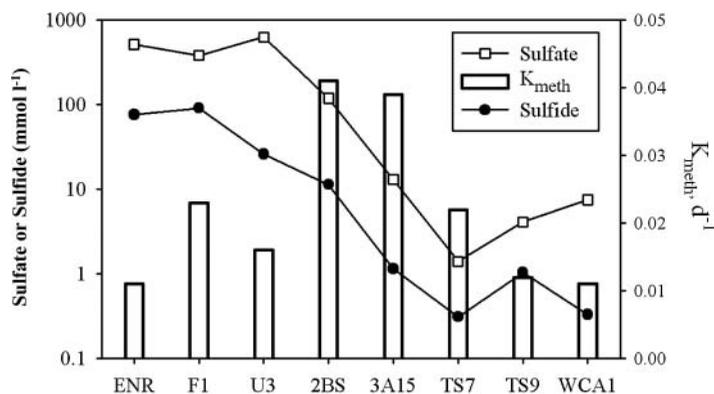
**FIGURE 6.** Plots of sulfate (mmol l^{-1}) and sulfide (mmol l^{-1}) concentration and the mercury methylation rate constant (K_{meth} d^{-1}) across the Everglades at ACME intensive sites (1995–1998). Mercury methylation rates were highest in the central portion of the curve (sites WCA-2BS and WCA-3A15) due to the combined influences of sulfate stimulation and sulfide inhibition of mercury methylation.

Since the late 1990s levels of MeHg in biota (fish, and wading birds) have declined in central WCA-3A, and this decline has been attributed to a decrease in local Hg emissions in south Florida (Atkeson et al., 2005). However, deposition of total Hg on the central Everglades has stayed relatively constant over the past 15 years (Axelrad et al., 2008), suggesting that local emissions are not the major control on Hg deposition on the Everglades. Sulfate (and sulfide) levels in central WCA-3A also dropped from the late 1990s to present, as discussed previously. Thus, a decline in sulfate loading appears to be the biggest control on declines in MeHg production and bioaccumulation in central WCA-3A over the past decade (Axelrad et al., 2008; Gilmour et al., 2007a). More heavily sulfur-enriched areas may have a longer recovery period, however.

Other factors, besides sulfate levels, impact MeHg production and distributions within an ecosystem. These may include inorganic mercury inputs and bioavailability, redox conditions, pH, and dissolved organic carbon (Aiken et al., 2011; Miskimmin et al., 1992). All of these factors, especially the high rate of mercury deposition in south Florida, are factors in the high levels of MeHg production and bioaccumulation in the Everglades (Gilmour et al., 1998, 2007a). In many respects, the south Florida ecosystem represents an ideal environment for mercury methylation: (a) it is a shallow wetland area with anoxic conditions in organic-rich soils, (b) there is high deposition of inorganic mercury in abundant rainfall, (c) it has high dissolved organic carbon concentrations that hold mercury in solution and can enhance methylation, (d) pH is circumneutral, (e) water temperature is high, and (f) it receives high sulfate loads to drive MSR. Conditions (d) and (f) are lacking within the interior of WCA-1, which may explain why this area tends to have low mercury in mosquitofish and low bioaccumulation factors (Scheidt and Kalla, 2007).

Sulfide Toxicity

Sulfide is toxic to plants (Armstrong et al., 1996; Koch and Mendelssohn, 1989; Koch et al., 1990; Mendelssohn and McKee, 1988) and animals (National Research Council, 1979). Rooted plants in saturated soil develop an oxidized rhizosphere around their roots that can detoxify sulfide, and the extent of the rhizosphere can determine the ability of plants to tolerate various levels of sulfide (Chabbi et al., 2000).

Aquatic macrophytes show varying degrees of sensitivity to sulfide toxicity. Rice is impacted at pore water sulfide levels >70 μg l^{-1} (Allam and Hollis, 1972). The freshwater macrophyte *Nitella flexilis* shows toxic effects at sulfide levels as low as 1700 μg l^{-1} (Van der Welle et al., 2006), while *Phragmites australis* shows sulfide toxicity at levels of 6,800–10,200 μg l^{-1} (Hotes et al., 2005). In a greenhouse experiment, Li et al. (2009) demonstrated that *Cladium jamaicense* is more sensitive to sulfide toxicity

than *Typha domingensis*. *Cladium* was impacted at sulfide levels of about 7480 μg l^{-1}, but *Typha* was unaffected by sulfide toxicity up to 23460 μg l^{-1}. At locations in the Everglades where *Typha* has displaced *Cladium*, pore water levels of sulfide approach 13000 μg l^{-1} (Gilmour et al., 2007b). These locations are also heavily enriched with phosphorus from agricultural runoff, and eutrophication has been suggested as the principal cause of this change in macrophyte dominance (Childers et al., 2003; Miao et al., 2000). Sulfide toxicity may also play a role, however, because the observed sulfide levels can exceed those toxic to *Cladium* (Li et al., 2009). The effects of sulfide on other Everglades flora are not known.

Sulfide is also toxic to aquatic fauna (Wang and Chapman, 1999). Sulfide toxicity for fish ranges from 47–1000 μg l^{-1} in water (Adelman and Smith 1970; Thurston et al., 1979; USEPA 1976). A shrimp (*Crangon crangon*) showed 50% mortality at sulfide concentrations of 680 μg l^{-1} (Vismann, 1996). The freshwater oligochaete *Ophidonais serpentina* showed toxic effects from sulfide at 1,700 μg l^{-1} (Van der Welle et al., 2006). Some aquatic animals are able to avoid the toxic effects of sulfide by oxidizing it to thiosulfate, if sufficient oxygen is present (Grieshaber and Völkel, 1998). Sulfide levels in surface water in Everglades marshes are generally <0.1 μg l^{-1}, but reach 100s of μg l^{-1} in heavily sulfate-enriched areas. Aquatic fauna in Everglades surface water are unlikely to routinely experience acute toxic effects from sulfide, though impacts of chronic low level sulfide exposure are unknown. Much higher levels of sulfide (up to 13,000 μg l^{-1}) are found in soil pore water from heavily sulfate-enriched areas of the Everglades. Organisms that spend part or all of their life cycles in soils could experience acute sulfide toxicity, but studies of this have not been conducted.

Nutrient Remobilization Via Internal Eutrophication

Sulfate loading to wetland soils can lead to enhanced mobilization of N and P via several redox-related mechanisms, collectively called internal eutrophication (Lamers et al., 1998; Smolders et al., 2006). Mesocosm studies conducted in central WCA-3A of the Everglades examined the impacts of sulfate on nutrient release via internal eutrophication (Gilmour et al., 2007b). Results showed that sulfate loading released ammonium and phosphate from Everglades soils at dosing levels >20 mg l^{-1}. Phosphate and ammonium were enhanced in both surface water and pore water in the dosed mesocosms by up to 50 and 20 times, respectively, relative to controls. Both phosphate and ammonium release increased with increased sulfate loading, though the relationship was not linear. Additional studies of internal eutrophication in sulfate-enriched parts of the Everglades are needed.

Suppression of Redox Conditions

The redox state of aquatic soils is usually established by microbially mediated reactions accompanying the degradation of organic matter (Berner, 1980).

Systems that are highly reducing typically have large amounts of bioavailable organic matter and terminal electron acceptors for driving microbial redox reactions. Excess sulfate entering the Everglades has greatly enhanced the electron acceptor capacity of the ecosystem, driving down redox conditions in soils over large areas. Areas of the ecosystem in close proximity to canal discharge have lower redox potential compared to sites remote from canals (Drake et al., 1996). A close correspondence exists between redox potential and sulfide concentration for Everglades soils (Gilmour et al., 2007b). The nutrient uptake and growth of aquatic macrophytes may be impacted by lower soil redox conditions (Lissner et al., 2003).

Effects of Sulfide on Metal Speciation

Sulfide is reactive with many transition metals, forming highly insoluble metal sulfide species. Thus, buildup of sulfide in soil pore water from stimulation of MSR may alter the concentrations and bioavailability of metals. The formation of insoluble iron mono- and disulfides has been shown to cause iron deficiency in some species of rooted macrophytes in other wetlands (Smolders et al., 1995; Van der Welle et al., 2006). The combined impacts of iron deficiency from the precipitation of iron sulfides, sulfide toxicity, and ammonium toxicity (ammonium released by internal eutrophication) has been shown to be the cause of the decline of *Stratiotes aloides* L., a formerly abundant and keystone freshwater macrophyte in the Netherlands (Smolders et al., 2003). Little is known about how sulfur loading affects metal speciation in the Everglades.

6 CONCLUSIONS AND MANAGEMENT OF SULFUR FOR RESTORATION

Sulfur is a major concern for Everglades restoration due to the high loading to the ecosystem, the large area of the ecosystem enriched with sulfate, and the myriad impacts of sulfur. Most of the sulfur loading originates within the EAA and is evident as sulfate in EAA canal water. Various lines of geochemical evidence are consistent with EAA soil oxidation (the EAA is pumped dry to allow crop production; Institute of Food and Agriculture Services, 2007), and agricultural use of sulfur in the EAA as the principal sources of the sulfate in EAA canal water. Additional work is needed to better quantify the different sources of sulfate to the canals and the discharge of high sulfate canal water to the Everglades. Sulfate loading to the Everglades increases MSR in soils, leading to depressed redox conditions, enhanced cycling of nutrients in soils, production of toxic sulfide, and high MeHg production and bioaccumulation that may threaten wildlife.

Need for Sulfur Management

There are no USEPA or Florida numeric water quality criteria for sulfate concentration in the context of ecosystem protection. CERP adopted a performance measure for surface water sulfate of <1 mg l^{-1} throughout the Everglades (Comprehensive Everglades Restoration Plan, 2007). Surface water sulfate concentrations <1 mg l^{-1} reflect maximum concentrations found in the unenriched areas of the Everglades. Presently, about 60% of the Everglades have levels of sulfate exceeding the 1 mg l^{-1} performance measure (Scheidt and Kalla, 2007).

Among the risks arising from sulfate enrichment, sulfide toxicity in surface waters probably affects the smallest area. The USEPA (2006) has a recommended level of 2 μg l^{-1} for sulfide (as H_2S) in surface water in order to protect aquatic life (primarily aquatic fauna). Surface water H_2S levels at heavily sulfate-enriched sites in the northern Everglades may exceed 100 μg l^{-1} and USEPA guidelines (Orem et al., 1997). However, the area affected probably represents $<5\%$ of the Everglades (Scheidt and Kalla, 2007), is concentrated in areas near canal or STA discharge (surface water sulfate >40 mg l^{-1}), and may be seasonal in nature (e.g., exceeding EPA standards only during the warmer/wetter time of the year). Also, some aquatic fauna may escape the high sulfide waters by swimming to less sulfidic areas.

Sulfide toxicity to plants and infauna, arising from sulfide buildup in marsh soils, may have a somewhat greater impact. Li et al. (2009) demonstrated that sulfide impacts *Cladium* at 7,480 μg l^{-1} in soil pore water. This level of sulfide occurs in areas where surface water sulfate concentrations routinely exceed 40 mg l^{-1} ($<5\%$ of the Everglades; Scheidt and Kalla, 2007). The levels of sulfide in soil toxic to other Everglades plants and to infauna are unknown.

Release of nutrients from aquatic soils due to sulfate loading (internal eutrophication) appears to occur from consistent sulfate loading of >20 mg l^{-1} (Gilmour et al., 2007b). This level of sulfate loading impacts up to 10% of the Everglades (Scheidt and Kalla, 2007), primarily marsh areas where canal or STA water is discharged.

Control of Everglades MeHg production and bioaccumulation would necessitate the largest reduction in sulfate loading compared to that needed to control other sulfate-induced detrimental effects. MeHg production increases with sulfate loading between 1 and 20 mg l^{-1} at most locations. The 1 mg l^{-1} performance measure would minimize MeHg risk to wildlife and human consumers throughout the Everglades. It is important to point out, however, that any reductions in sulfate loading would lead to decreased risk from production and bioaccumulation of MeHg on an ecosystem-wide scale.

Agricultural Best Management Practices for Sulfur

Research findings suggest that past and present EAA agricultural practices introduce much of the sulfate entering EAA canals, and that a reduction in

sulfate loading would yield significant environmental benefits to the Everglades. Reductions in the amount of sulfur presently used in EAA agriculture could be achieved via implementation of BMPs, which may be defined as agricultural practices that allow sustainable and economic use of agricultural land with minimal environmental consequences.

Potential BMPs for EAA sulfur soil amendments and fertilizers overlap, as sulfur soil amendments lower soil pH to make phosphorus and plant micronutrients more bioavailable. Sulfur as a plant nutrient is unlikely to be deficient relative to crop needs in organic EAA soils (Rice et al., 2006). Development of BMPs for reduction of sulfur use may require (a) sulfur data from soil and plant tissue for minimization of sulfur use while maintaining crop yield, (b) examining means of lowering soil pH without use of sulfur, (c) investigating aerial application of micronutrients (e.g., Mn, Zn, Cu, Mg, Si, Fe) to crops, (d) replacing fertilizers using sulfate as a counter-ion (e.g., $MgSO_4$, K_2SO_4) with sulfate-free versions (e.g., $MgCl_2$, KCl), and (e) examining alternatives for sulfur-containing fungicides. Also, research on crop yield as affected by varying regimes of increased phosphorus applications and decreased sulfur applications with measurements of resultant phosphorus and sulfur runoff from EAA fields may yield useful insights. While this approach may seem counterintuitive given that phosphorus is a known pollutant in the Everglades, several factors argue for consideration of this option: (a) Sulfur is also a known pollutant; (b) Sulfur is applied to EAA soils in order to release phosphorus, some of which may run off into EAA canals, and so reduction or elimination of EAA sulfur application may mitigate the effect of additional phosphorus fertilizer application; (c) Present elevated sulfate levels in the Everglades may cause release of soil phosphorus and so contribute to imbalance of the ecosystem; and (d) The present STAs are designed to remove phosphorus but remove much less sulfate. Thus, the net effect of reducing EAA sulfur application and increasing application of phosphorus could be positive.

The importance of the EAA as a source of phosphorus to the Everglades was recognized in the State of Florida's 1988 Surface Water Improvement and Management Plan (SWIM) for the Everglades. The Federal District Court, however, viewed the 1988 SWIM Plan as inadequate in regard to protection of Everglades water quality, especially concerning its effectiveness in minimizing EAA phosphorus inputs to the Everglades. Ultimately, the State passed the Florida Everglades Forever Act in 1994, which mandated both STAs and BMPs for management of EAA phosphorus (Bottcher and Izuno, 1994). A BMP approach for sulfur has not been implemented, but could represent a tool to reduce sulfur loads to the ecosystem.

Sulfur Mitigation Using STAs

Contamination of the Everglades by phosphorus use in the EAA (Craft and Richardson, 1993; Koch and Reddy, 1992) led to the development of the
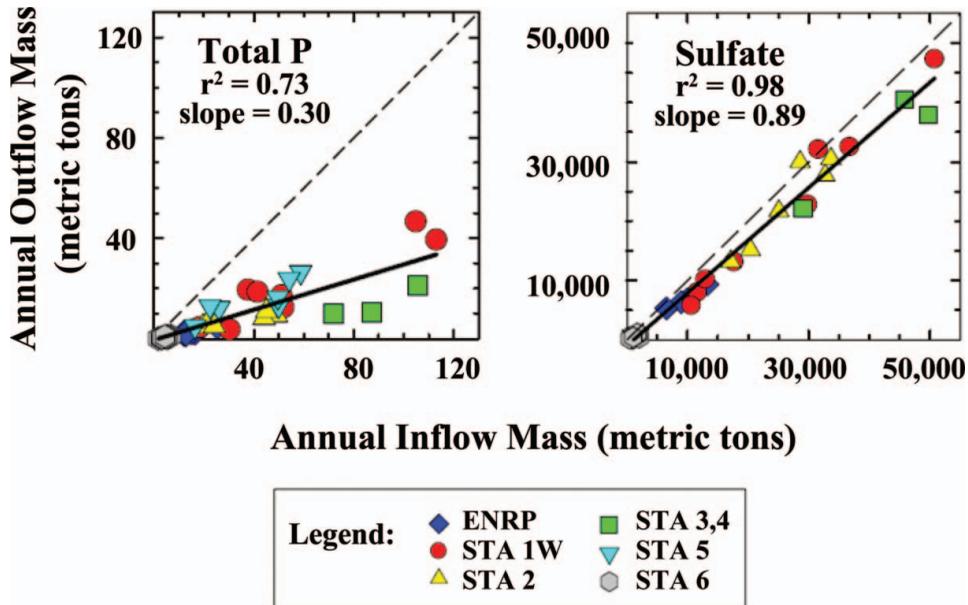
FIGURE 7. Annual inflow and outflow mass (metric tons) for total phosphorus and sulfate in six STAs for the period 1994–2007. Data points that fall below the diagonal dashed line indicate net mass removal by STAs. Figure adapted from: Pietro et al. (2009). Results show that STAs are effective at removing total phosphorus, but not sulfate. Note differences in scale between total phosphorus and sulfate loading to the STAs. (This figure is available in color online).

STAs, constructed wetlands designed for phosphorus removal and sited between the EAA and the Everglades. The STAs remove phosphorus through uptake by emergent, submerged, and floating aquatic vegetation, and total phosphorus (TP) loads have been reduced by 70% over the past 15 years (Pietro et al., 2009).

While reduction of TP loads to the Everglades using BMPs and STAs have achieved success, approaches for removing other contaminants such as sulfate have not been developed. STAs designed to remove TP from EAA canal water remove only about 11% of the sulfate (Figure 7). One factor in the poor removal of sulfate compared to TP by STAs is that the mass inflow of sulfate to STAs exceeds that of TP by a factor of over 1,000, while plant requirements for sulfur and phosphorus are roughly equivalent (Tabatabai, 1984).

Sequestration of sulfur in STA anoxic soils primarily involves MSR-producing sulfides and the subsequent formation of solid phase organic sulfur and metal sulfides. Substantial amounts of sulfur may be sequestered in aquatic soils in this manner (Morgan, 1990; Morgan and Good, 1988). A major factor limiting this process is the slow diffusion of sulfate into aquatic soils where MSR occurs (Krom and Berner, 1980). Reducing STA flow-through rate (increasing residence time) and possibly adding an iron

source could be ways of improving the capacity of STAs for retention of inflowing sulfate (Orem, 2007).

Other Sulfur Mitigation Strategies

In addition to the use of BMPs on sulfur use in the EAA, and sulfate removal using existing STAs, other approaches for removing sulfate from surface water flow have been reviewed by Orem (2007). The relative effectiveness and cost of these various approaches for sulfate removal are summarized in Table 3.

Permeable reactive barriers (PRBs) represent a relatively new approach for in situ passive treatment of contaminated water (Scherer et al., 2000). The reactive barrier is made of materials for the chemical sequestration, chemical breakdown, or microbial breakdown of the contaminant (Scherer et al., 2000). Some minerals such as feldspar (Priyantha and Perera, 2000), and modified synthetic zeolites have been shown to be effective in removing sulfate from water (Haggerty and Bowman, 1994). The creation of zones in the STAs that resemble PRBs designed for sulfate sequestration might be effective in increasing sulfate removal, but need to be tested in pilot studies.

Maree (U.S. Patent No. 5,035,807, 1991) used a chemical approach to remove sulfate from water that relies on the insolubility of barium sulfate. The process doses the sulfate-enriched water with barium sulfide, using CO_2 to keep the pH acidic. Barium sulfate is precipitated and may be collected and disposed of, or may be regenerated to barium sulfide by heating in a kiln to 1200°C. The sulfide from the barium sulfide is converted to H_2S under the acidic conditions, and is bubbled from the water to the atmosphere. Treated water is neutralized with limestone to adjust pH to near neutral and released to the system. The process was shown to reduce sulfate in treatment water to about 5 mg l^{-1}.

Nanofiltration and reverse osmosis are effective approaches for sulfate removal from water, and can reduce sulfate levels in drainage water by 95–99% (Bakke et al., 1992; Visser et al., 2001). However, nanofiltration suffers from a number of problems for cleaning natural waters, including expensive operating costs and membranes; clogging of the membrane pores by particulate, colloidal, and dissolved organic substances; and biofouling (Nyström et al., 1995). Ion exchange is also an effective method for removing ionic contaminants such as sulfate from water (Darbi et al., 2003), but high levels of dissolved organic carbon or particulate load can coat resins and decrease the efficiency of ion exchange. Darbi et al. (2003) suggested that ion exchange may be preferred over nanofiltration for removing ionic substances from natural waters. To date, nanofiltration and ion exchange approaches have only been used at the individual farm scale for removing dissolved ions such as sulfate from discharge water. These approaches may be impractical

TABLE 3. Relative effectiveness and costs among different active and passive sulfate mitigation strategies for the Everglades (L = Low, M = Moderate, H = High). Table adapted from Orem (2007)

Sulfur Mitigation Method	Effectiveness of Sulfate Removal	Initial Costs	Maintenance Costs	Notes
Biological Removal (STAs, PASTAs)	L-H[a]	L-M[b]	L[c]	(a) effectiveness depends on type of STA used, residence time of water, etc. (b) STAs already exist, may require some modification (c) little maintenance cost once operating
Permeable Reactive Barriers (PRBs)	M-H	M[d]	L[e]	(d) construction of barriers from bio-waste, zero-valent iron, and crushed limestone (e) essentially none until replacement is needed
Mineral Removal (limestone, feldspar zeolites)	L-M	M[f]	L[g]	(f) construction of trenches for mineral emplacement (g) essentially none until replacement is needed
Chemical Treatment (Barium Sulfide)	M-H	M-H[h]	M-H[i]	(h) construction of reaction ponds or chambers (i) collection and disposal of precipitated $Ba\,SO_4$
Membrane Filtration (nanofiltration)	H[j]	M-H[k]	H[l]	(j) also removes other ions of concern, e.g. PO_4^{3-} (k) costs include pre-filters, nanofiltration filter setup, pumps, and operator training (l) frequent replacement of nanofilters may be necessary due to biofouling
Ion Exchange	M-H	M-H[m]	M-H[n]	(m) costs include pre-filters, ion exchange cartridges and setups, operator training (n) frequent replacement of pre-filters and ion exchange resins may be needed due to high particulated and dissolved load

for handling the volumes of water with a large particulate and dissolved organic load on the scale of the Everglades.

Management of Sulfur for Restoration

Restoration of the Everglades to a condition approximating its predevelopment state by reestablishing natural sheet flow of water, and moving more water to areas (mostly in the south) that presently lack sufficient water will

require using water originating in Lake Okeechobee and passing through the EAA. This water is contaminated with a number of chemicals harmful to the ecosystem, including sulfate. Sulfate is a particular concern because of its high concentration and many adverse impacts. Resource managers should recognize that there may be unintended adverse ecological impacts as a result of actions taken to improve water distribution without addressing all of the important water quality issues.

Reduction of sulfate loading to the Everglades might begin with BMPs for sulfur use in agriculture, balancing agricultural needs with minimizing sulfate runoff. However, even if BMPs on sulfur use in the EAA are successful, significant sulfate loading will likely continue from EAA soil oxidation and sulfate inputs from Lake Okeechobee. Mitigation strategies will be needed to further reduce sulfate loading to the ecosystem. Various mitigation approaches were summarized earlier (Table 3), and discussed by Orem (2007). Modification of existing STAs for more effective sulfate removal is especially appealing.

Although reduction of sulfate runoff to the CERP performance measure of 1 mg l^{-1} is desirable, it should be noted that any reduction in overall sulfate loads will benefit the Everglades. The variety and magnitude of sulfur sources will make attaining the CERP goal for sulfate a challenge. Nevertheless, studies have demonstrated that any significant reduction in present sulfate loads to the Everglades will have beneficial results in the near term, especially with regard to levels of MeHg. Considering that most of the mercury deposited on the Everglades appears to originate from distant sources (outside the reach of state and federal regulators), reductions in sulfate loading to the Everglades may represent the most viable approach for reducing MeHg production and bioaccumulation within an ecosystem that has some of the highest levels of MeHg in biota of any wetland in the United States. The success of BMPs and mitigation strategies using STAs for reducing phosphate loads to the Everglades suggests that similar approaches for sulfate reduction may be effective.

ACKNOWLEDGMENTS

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