Appendix 3B-2: Sulfur as a Regional Water Quality Concern in South Florida

Mark Gabriel, Garth Redfield and Darren Rumbold[1]

Contributors: Pam Lehr, Ming Chen, Thomas Dreschel,
Nenad Iricanin, Binhe Gu, Don Axelrad[2], Susan Newman
and Dan Scheidt[3]

SUMMARY

Sulfur has become a focus of concern in the greater Everglades due to elevated concentrations in water and sediments of the northern Everglades[4], its impact on the cycling of geochemical surface water constituents, and its potential role in plant species distributions. Previous research, monitoring, and assessment together indicate a possibility that sulfur enrichment to the remnant Everglades originates through Everglades Agricultural Area (EAA) canals. There is also a likelihood that the main source for sulfur within these canals is from past and/or current agricultural sulfur application within the EAA. However, considering the high sulfate content of groundwater underlying many South Florida regions, the hypothesis that agricultural sulfur application is the primary source cannot be confirmed until additional source delineation investigations are performed. Information on potential agricultural, suburban, and urban sources of sulfur outside the EAA is also needed. At this stage, it would be beneficial to the South Florida Water Management District (SFWMD or District) and the Florida Department of Environmental Protection (FDEP) to focus efforts on addressing fundamental issues, such as developing a sulfur budget, identifying the most significant sulfur source(s) and, if applicable, collecting information on the history of each source causing sulfur enrichment. Information on sulfur loads from each source should be quantified over the typical climatic variation of South Florida in association with sulfur application practices in the EAA and other areas as each could be factors in the amount and timing in source release of sulfate. Additional investigations should also address organic sulfur fluxes in the Everglades, the potential for internal eutrophication, and Best Management Practices for agricultural and other sources of sulfur.

Increasing the quantity and quality of water to the Everglades, which is a major goal of the Comprehensive Everglades Restoration Program, has the potential to increase the amount of sulfate entering the Everglades. In turn, this water redistribution could exacerbate the methylmercury problem in some areas and pose other adverse effects on the ecosystem. In terms

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[1] Florida Gulf Coast University, Fort Myers, FL

[2] Florida Department of Environmental Protection, Division of Resource Assessment and Management, Mercury and Applied Science Program, Tallahassee, FL

[3] U.S. Environmental Protection Agency, Region 4

[4] In this appendix, northern Everglades refers to the northern Everglades Protection Area

of managing the Everglades mercury problem, a key evaluation at this stage is to determine what reduction in sulfate loading would result in declines in methylmercury reduction to a point where fish mercury levels drop below the Florida or U.S. Environmental Protection Agency fish criterion for human consumption. Since methods to decrease mercury loading to South Florida ecosystems can be far-reaching, particularly from an atmospheric deposition standpoint, an alternative option is to manage factors that stimulate methylmercury production.

INTRODUCTION AND BACKGROUND

The primary purpose of this document is to improve stakeholder understanding of sulfur as a water quality concern in South Florida. It is hoped that this information will aid concerned citizens and their decision makers in formulating sound and effective decisions on sulfur as we move toward a more sustainable South Florida ecosystem. This document is not intended to be a detailed technical reference, which is the function of Chapter 3B of this volume. Overall, this document begins with background information on sulfur as an important constituent in natural systems, provides an overview of sulfur's key interactions and effects, summarizes information on sulfur in South Florida, and concludes with recommendations on activities needed to fill information gaps for decision making.

Sulfur (S) is an essential element used by cells for protein synthesis. Several sulfur forms are found in nature. Some of the principal forms include elemental sulfur (S^0), sulfate (SO_4^{2-}), and hydrogen sulfide (H_2S). The form most essential for all plant life is the inorganic form, sulfate (SO_4^{-2}), which serves as a secondary, but important, nutrient. Primary sources for sulfur in surface water systems include mineral weathering, atmospheric loading (precipitation and dry deposition), runoff from agriculture and urban land uses, and groundwater interactions. In freshwater ecosystems, the background quantity of sulfur is generally sufficient to meet the demand of various organisms. Therefore, unlike phosphorus, sulfur is not limiting to growth or development of plants under most circumstances.

Sulfur holds a unique niche in nature, as it has a suite of direct and indirect effects on the cycling of other elements. Sulfur is actively involved in the cycling of micronutrients (i.e., iron, manganese) and macronutrients (i.e., phosphorus, nitrogen) that are important to system productivity and the overall health of plants and animals (Wetzel, 2001). Sulfur cycles through nature in a complex manner (**Figure 1**). Important processes include the formation and reduction of sulfur forms. The biochemical reduction of sulfate is done by bacteria and takes place primarily under oxygen-free conditions, typically occurring in sediments and soils. During sulfate reduction, sulfate-reducing bacteria (SRB) utilize sulfate instead of oxygen in metabolizing organic matter. During this process, SRB change (reduce) sulfate to another important form of sulfur: sulfide.

In general, sulfate is a highly reactive, water-soluble substance. Sulfide, however, displays different chemical properties, including reactions with metals to form highly stable substances such as pyrite (FeS_2) and cinnabar (HgS) and reactions with organic matter to form numerous organic-sulfur compounds. Under acidic conditions sulfide is transformed to hydrogen sulfide (H_2S) which can be released to the atmosphere. A visitor to a salt marsh or estuary may experience the "rotten egg" smell of hydrogen sulfide produced through sulfate reduction.

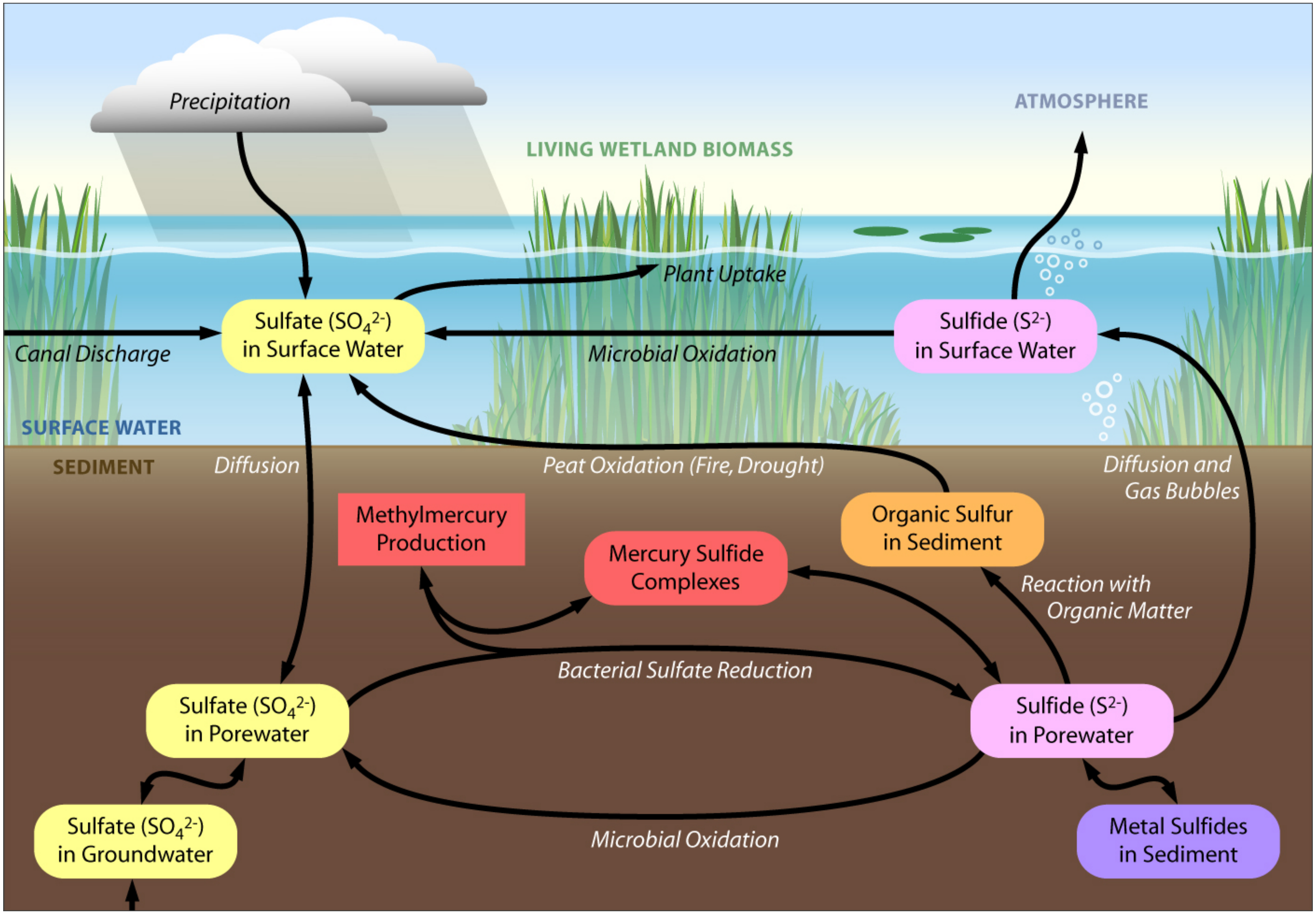

Figure 1. The Everglades sulfur cycle (adapted from Orem, 2004; illustration by C. King, SFWMD).

SULFUR INTERACTIONS IN AQUATIC ENVIRONMENTS

The cycling of sulfur (**Figure 1**) viewed in the context of living ecosystems provides a framework for understanding the far-reaching and complex interactions between sulfur and the aquatic food web. Sulfate, the oxidized form, and sulfide, the reduced form, are the cornerstones of natural interactions involving sulfur. There are many gaps in knowledge regarding sulfur dynamics, particularly in the South Florida environment. As noted by the Peer Review Panel for the 2007 South Florida Environmental Report – Volume I (Jordan et al., 2007), more information is needed on the environmental role of sulfur, especially its sources and effects. However, there is a large body of scientific documentation on key interactions and impacts that can occur in the aquatic ecosystems of South Florida. Many of these studies are highlighted in the 2007 South Florida Environmental Report – Volume I, Chapter 3B (Axelrad et al., 2007) and associated appendices (Gilmour et al., 2007a, 2007b). Sulfur interactions in marshes can be summarized as a triad: sulfate-induced nutrient mobilization, toxic influences on plants, and exacerbation of mercury bioaccumulation. In the following section, the roles of sulfur in agriculture, marsh nutrient cycling, marsh vegetation dynamics, and in the mercury cycle are briefly summarized.

SULFUR IS HISTORICALLY AN IMPORTANT NUTRIENT FOR CROP PRODUCTION AND SOIL AMENDMENT

Sulfur (S) is a secondary nutrient for plant growth and is the fourth primary nutrient in crop production following nitrogen, phosphorous, and potassium. Since the 1920s sulfate has been applied to the Everglades Agricultural Area (EAA) to enhance crop productivity (Allison et al., 1927). It has long been recognized that application of copper sulfate is absolutely necessary to bring new areas of Everglades peat into production (Allison et al., 1927; Jones, 1948). During the early years, sugarcane ordinarily received 200 pounds (lbs) of muriate or potash per acre during planting, plus copper, zinc, and manganese sulfate to improve plant growth regardless of condition (Jones, 1948). Traditional practice also included applying 20 to 40 lbs of copper sulfate to Class II and III muck lands (Jones, 1948). In later years, the University of Florida Institute of Food and Agricultural Sciences (IFAS) recommended using elemental sulfur to lower soil pH when the pH exceeded 6.6 for the purpose of improving the availability of macronutrients needed for sugarcane growth. Currently, the IFAS maximum recommended rate is 500-S/ha. Such a load may actually result in 70 lb–S/ha-yr (78 kg-S/ha-yr) if application only occurs over vegetables that contain soils with a pH above 6.6 (Schueneman, 2001).

Sugarcane is a crop that requires relatively high annual sulfur supply (94 kg/ha) compared to other field crops (corn: 47 kg/ha, rice: 20 kg/ha). However, research studies conducted by the IFAS extension indicate that actual sulfur application rates are lower than the IFAS recommendation. EAA growers typically only apply sulfur as needed because it is more economical to correct pH-related micronutrient deficiencies with either foliar sprays or band placement instead of broadcasting large amounts of sulfur (Schueneman, 2000).

SULFUR LOADING CAN CAUSE NUTRIENT MOBILIZATION

There are several processes within the sulfur cycle that can lead to deleterious impacts to aquatic plants and animals. As previously discussed, bacteria reduce sulfate to sulfide as they decompose organic matter. In the process, phosphorus originally bound within the sediment organic pool can be released and become available for plant uptake. The presence of excess sulfate could lead to internal nutrient eutrophication, a process well documented by Dutch scientists in the shallow lakes and mineral-rich fens of the Netherlands (Lamers et al., 1998; Smolders et al., 2006). Two primary mechanisms are involved in internal eutrophication: (1) production of sulfide resulting in the release of nutrient species, particularly ammonium (nitrogen) and phosphate and (2) enhanced phosphate and ammonium remobilization through alkalinity generation (Smolders et al., 2006; Gilmour et al., 2007a). The following items provide details on how sulfate loading can lead to increased nutrient mobilization:

1. In anaerobic sediments and soils, sulfate-reducing bacteria may utilize sulfate to metabolize organic matter, thereby releasing phosphate and ammonium from organic material; this is termed “internal eutrophication or “sulfate-mediated eutrophication.”
2. Sulfate may directly outcompete phosphate for adsorption onto sediments, thereby releasing phosphate.
3. Sulfate reduction results in alkalinization (increased pH; decreased acidity) of sediment porewater, in that way providing more suitable conditions for microorganisms to consume organic matter. This consumption of organic matter may release phosphorus and nitrogen. It has been widely demonstrated that acidic conditions favor accumulation of peat (organic matter).
4. Sulfate reduction, and the concomitant reduction of Fe, leads to the formation of ferric sulfide species (FeS_x), which may result in a strong decrease in the phosphate-binding capacity of sediments as FeS_x has low phosphate-binding potential (Lamers et al., 1998; Smolders et al., 2006).
5. The acidity produced from sulfate-surface water mixing can remove phosphate bound to organic material.

Due to the potential for phosphate release, enrichment spurred by sulfur addition can therefore jeopardize the performance of Stormwater Treatment Areas and could impair efforts to reduce phosphate loading to the Everglades. Along with phosphate release from sulfate additions, when sulfide is produced during sulfate reduction, sulfide may bind with iron to produce ferrous sulfide (FeS) (Axelrad et al., 2007). Production of ferrous sulfide creates immobilization of iron, which is a plant micronutrient. For South Florida, an area for investigation is the balance between these processes and the net effect on our environments, particularly those recovering from nutrient enrichment. To date, it is unclear what balance in sulfate and phosphorus concentrations are needed to create internal eutrophic conditions and sulfide immobilization of iron for the greater Everglades.

SULFUR CAN HAVE INHIBITORY EFFECTS ON MARSH VEGETATION

A number of studies have demonstrated the inhibitory effects of sulfide to wetland plant growth and species distribution (McKee et al., 1988; McKee and Mendelssohn, 1989; McKee et al., 1990; Mendelssohn and Morris, 2000; Li and Mendelssohn, 2007). Sulfide has the ability to bind iron thus making this essential micronutrient unavailable for plant uptake (Koch et al., 1990). In addition, sulfide can also increase oxygen-deficiency stress by increasing biochemical reduction intensity in sediments. It has been shown that cattail (*Typha domingensis*) has a greater ability to transport oxygen to its roots than sawgrass *(Cladium jamaicense*) (Gilmour et al., 2007a), thereby allowing it to produce a more extensive oxygenated root rhizoshpere. In the rhizosphere, oxygen reacts with sulfide to produce sulfate. The resultant sulfate can then be utilized by plants (Pezeshki et al., 1996). Therefore, the dominance of cattail may be maintained or enhanced when sulfur is present in significant amounts in nutrient-enriched marshes. However, further research is needed on this process and its consequences on the competition between sawgrass and cattail in South Florida, as most evidence has been drawn from laboratory investigation.

SULFUR IS LINKED TO MERCURY METHYLATION

It is widely accepted that sulfate may promote the production of toxic methylmercury (MeHg) by a process known as methylation under conditions when sulfate-reducing bacteria are thriving (Compeau and Bartha, 1985; Gilmour et al., 1992; Slowey et al., 2007). There is also increasing evidence that other types of bacteria can methylate mercury, namely iron-reducing and methanogenic bacteria (Fleming et al., 2006; Warner et al., 2003), though it is believed that SRB are the dominant mercury methylaters in natural systems.

Methylmercury is a potent neurotoxin which bioaccumulates as it moves through the food web. MeHg can bioaccumulate in top-predator fish to much as ten-million times the concentration in surface water. In fish, greater than 95 percent of total mercury is in the MeHg form (Grieb et al., 1990). The current U.S. Environmental Protection Agency (USEPA) human health mercury criterion for fish consumption is 0.3 milligrams per kilogram (mg/kg) and this level is often widely exceeded throughout the Everglades Protection Area (Rumbold et al., 2007; Axelrad et al., 2005, 2006, 2007).

Several factors, other than the concentration and availability of sulfate, influence mercury methylation (Choi and Bartha, 1994; Barkay et al., 1997; Gilmour et al., 2007b). The concentration and distribution of various organic and inorganic carbon compounds, sulfur and chloride species, pH, and metals (particularly iron and manganese) can impact mercury bioavailability and affect MeHg production rates. These factors are important to recognize because a decrease in sulfur concentration or load may or may not lead to a proportional reduction in methylmercury.

Fish consumption advisories have been posted throughout the Everglades by the Florida Department of Health due to the danger mercury-laden fish pose to human health, especially to pregnant women and children. Mercury enters the Everglades almost entirely through wet and dry deposition (rainfall and dust) following atmospheric transport from human and natural sources such as the burning of fossil fuel, incineration of medical waste, outgassing from geologic formations, cement kiln operation and volcanic activity. Mercury delivered to ecosystems through atmospheric deposition is in a highly reactive form and thus can undergo several biogeochemical transformations including methylation.

Sulfate loading is an important factor in causing increased mercury methylation in the Everglades (Benoit et al., 1999, 2001, 2003; Bates et al., 2002; Gilmour et al., 2007a). The effect of sulfur on mercury methylation in the Everglades appears to be determined by the balance between sulfate and sulfide. Previous studies suggest mercury methylation in Everglades surface waters is generally highest between 2-20 milligrams per liter (mg/L) of sulfate and where porewater sulfide concentrations are moderate (5-150 micrograms per liter, or µg/L) (Gilmour et al., 1998; Benoit et al., 2003; Gilmour et al., 2007b). Currently, the lower parts of WCA-2A and WCA-3A have average surface water sulfate concentrations within this optimal range (2-20 mg/L) (Gilmour et al., 2007b). In areas that contain sulfate levels higher than the optimal range, sulfide levels are typically high enough where they begin to inhibit methylation. This point is commonly dubbed the sulfur "break point." At this point, excess sulfide reduces MeHg production by complexing with available mercury. In pristine areas (relative to sulfate), the sulfide break point is typically not reached because there is no initial pool of sulfide to provide a base for the break point. As a result, in pristine areas MeHg can be exacerbated by lack of available sulfide for inhibition of methylation. Based on previous findings it suggested that any decrease in sulfate load should result in less MeHg production across the Everglades Protection Area (EPA), except in a few highly impacted areas of WCA-2A and far northern WCA-3A. This is supported by strong declines in fish THg in WCA-2A and at site WCA-3A15 over the last decade (C. Gilmour, Smithsonian Environmental Research Center, personal communication).

SULFUR DISTRIBUTION IN THE SOUTH FLORIDA REGIONAL ECOSYSTEM

Water quality monitoring and assessment in the Florida Everglades ecosystem from the 1980s to present has largely focused on phosphorus, which is regarded as the primary pollutant leading to changes in plant communities: replacement of sawgrass by cattail and reductions of other sensitive plants such as bladderwort and spike rush. However, recently, information on sulfur has suggested that it, too, plays an important role in plant species distribution (Axelrad et al., 2005, 2006, 2007). Compared to phosphorus, relatively little is known about the biogeochemistry and impacts of sulfur on Everglades water quality (Axelrad et al., 2005; Weaver and Payne, 2005). The freshwater Everglades in its undisturbed state is naturally low in sulfate (less than 1 mg/L) (Orem et al., 1997). Inputs from stormwater runoff have increased sulfate concentrations in surface waters above background levels in nearly fifty percent of the freshwater Everglades, and sulfate concentrations are up to two orders of magnitude above historical levels in heavily effected areas (Orem, 2004). The observed sulfate contamination is believed to be contributing to declines in native plants by altering chemical conditions in sediments (Gilmour et al., 2007a).

Florida water quality standards suggest that “Substances in concentrations which injure, are chronically toxic to, or produce adverse physiological or behavioral response in humans, plants or animals — none shall be present” (Subsection 62-302.530(62), Florida Administrative Code). Until now, Florida has not adopted water quality criteria for sulfur. For sulfide, USEPA recommends a surface water criterion of 0.002 mg/L for protection of aquatic life, yet there are no water quality criteria recommended for sulfide in pore water (USEPA, 2004).

Pristine areas of the Everglades have virtually undetectable levels of sulfide in sediment porewater. Recent work by Gilmour et al. (2007a) reported an assessment of sources, trends, and effects of sulfur for the Everglades using historic data for sulfate and sulfide. They found varying sulfate concentrations throughout the Everglades but with consistently high sulfate concentrations in the northern Everglades. Despite some variation in the distribution of sulfate in surface water, overall, the data presents a clear north-to-south concentration gradient (see **Figure 2**). For example, they observed mean sulfate concentrations of 44 mg/L in WCA-2, which receives water from EAA discharge, to low concentrations (2.3 mg/L) in more southern parts of WCA-3. Sulfide showed a similar north-to-south gradient with extremely high porewater concentrations (up to 12,000 μg/L) in the north to low concentrations (0.1 μg/L) in more pristine southern areas.

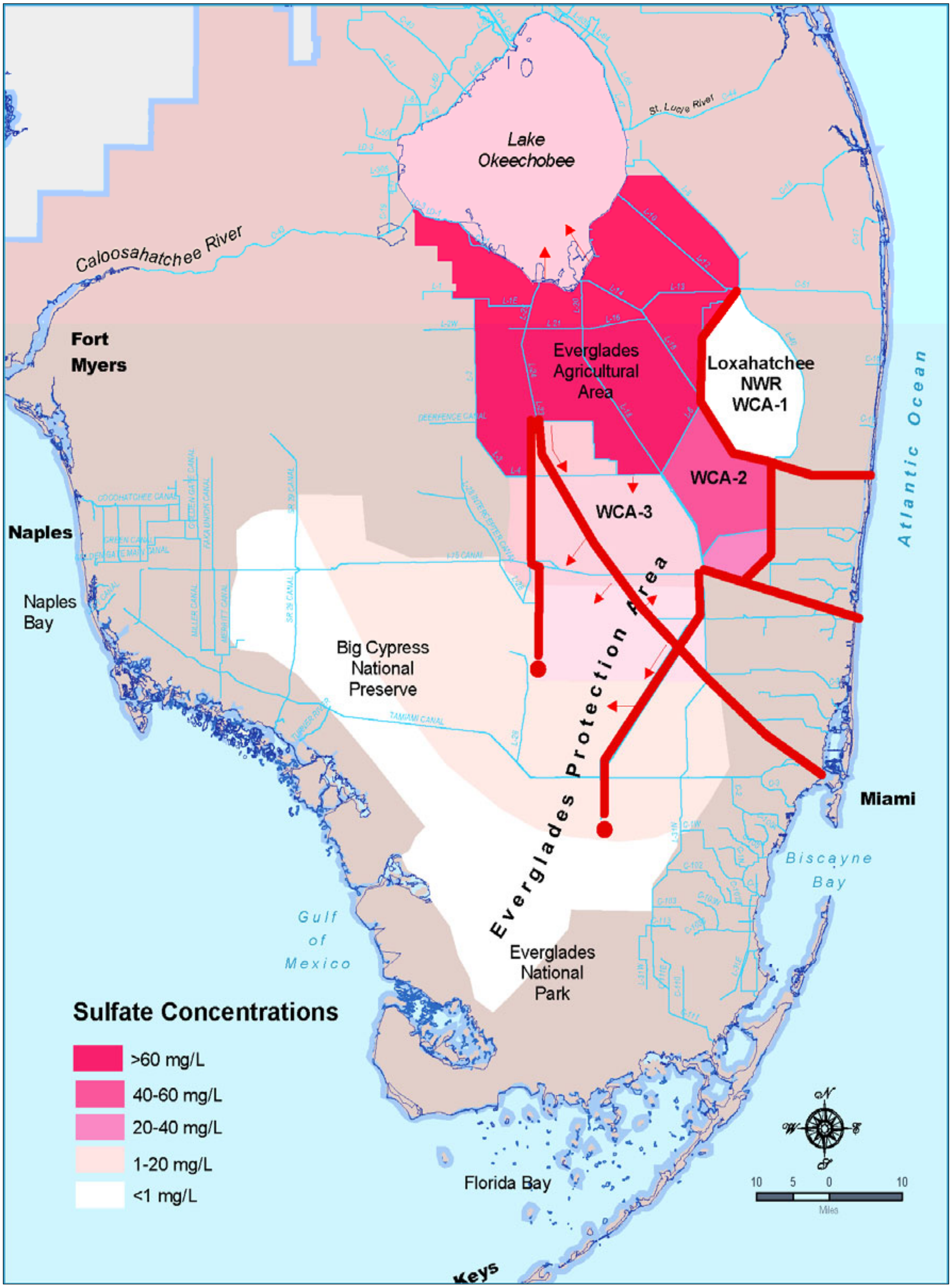

Figure 2. The distribution of sulfate concentrations (mg/L) in surface waters across the Greater Everglades (adapted from Axelrad et al., 2007). Large dots indicate terminal discharge areas; arrows indicate discharge points and leakage areas.

SULFATE CONCENTRATIONS WITHIN WATER CONSERVATION AREA MARSHES

Sulfate concentrations across the Water Conservation Areas (WCAs) exhibit a wide range. Concentrations in WCA-2, for example, vary from 5 to 50 mg/L. Sulfate, which is not rapidly removed in large amounts from surface waters by aquatic plants, penetrates much further into the marsh from its point of origin when compared to phosphorus. Likewise, in the largely pristine WCA-1 (the Arthur R. Marshall Loxahatchee National Wildlife Refuge), sulfate concentrations rapidly decrease from about 15 mg/L to less than 0.2 mg/L along a transect from the Hillsboro Canal to the center of WCA-1 (Gilmour et al., 2007a). The low level of sulfate in the interior of WCA-1 is associated with the hydrology of the system, since canal water does not migrate to the interior marsh, which instead receives most of its water from rainfall. Average sulfate concentrations in areas of WCA-2A and 2B are often high, with most sites exhibiting sulfate levels greater than 40 mg/L. In contrast to WCA-1, the canal discharges flow throughout WCA-2 in a general north to south pattern, allowing sulfur to penetrate the system. In WCA-3, sulfate concentrations are found to be generally highest in the north and east, although average concentrations in northern WCA-3A are more generally in the range of 10 to 20 mg/L. Sulfate concentrations in WCA-3 decrease toward the south and west, dropping to less than 1 mg/L.

SULFATE CONCENTRATIONS WITHIN CANALS, RIVERS, AND LAKE OKEECHOBEE

The highest surface water sulfate concentrations (excluding estuarine and marine sites) are observed in canals in the EAA. Average sulfate concentrations from U.S. Geological Survey (USGS) sampling in EAA canals from 1995–2000 ranged from about 55 to over 70 mg/L (Gilmour et al., 2007a). Some studies have observed sulfate concentrations in canal water approaching 200 mg/L (Bates et al., 2002; Orem, 2004). Sulfate concentrations in Lake Okeechobee range between 20 and 50 mg/L. No significant vertical trends in sulfate concentrations are observed in the water column of the lake. The Kissimmee River, Taylor Creek, and Fisheating Creek are the three principal drainages entering Lake Okeechobee, and average sulfate concentrations in these drainages are 16, 30, and 11 mg/L, respectively, based on the USGS data set (Gilmour et al., 2007a). Some of the sulfate in northern canals may also reflect contributions from agriculture (cattle ranching and citrus), where some agricultural chemicals containing sulfur are used. The high concentrations of sulfate in Lake Okeechobee (compared to most freshwater lakes) likely represent contributions from both the rivers feeding into the lake from the north and backpumping of water from the EAA. Backpumping inputs, however, have been reduced by changes in regional water management and will be reduced to a minor fraction of total inputs by the projects being constructed to improve conveyance and storage under the Long-Term Plan for Achieving Water Quality Goals in the Everglades Protection Area.

SULFUR REMOVAL BY STORMWATER TREATMENT AREAS

The Stormwater Treatment Areas (STAs) are designed to reduce phosphorous inputs to the Water Conservation Areas through plant uptake and subsequent storage in sediments (Orem, 2004; Chimney and Goforth, 2006). Sulfate removal in the STAs is primarily through microbial sulfate reduction in soils and the storage of reduced sulfur as organic sulfur compounds and iron sulfides in sediments. Because sulfur is a secondary plant micronutrient, plants may also remove some sulfate from inflow waters.

A comparison of inflow and outflow sulfate loads through time in the STAs suggests that these wetlands can remove some incoming sulfate, but typically much less compared to phosphate. For example, the total sulfate load from 2001 to 2005 for STA-5 outflow (structures G-344A, B, C, D) was 47 percent lower than the incoming sulfate load (inflow structures G-342A, B, C, D). During the same period of record STA-6 showed a 42 percent reduction in sulfate loading (inflow structure G-600 and outflow structures G-354 and G-393) and STA-2 showed a 10 percent reduction (inflow structures S-6 and G-328 and outflow structure G-335).

POTENTIAL SULFUR SOURCES

Defining sources and sinks of sulfur in South Florida is critical to developing a better understanding of the sulfur cycle and determining controls. Recognized potential sources of sulfur include dry and wet atmospheric deposition, shallow and deep ground water (connate water or relict seawater), Lake Okeechobee, and surface flow (including canals). An assessment of each potential source is presented below.

Atmospheric Deposition

A significant source of sulfur for many ecosystems is atmospheric deposition. In South Florida, sulfate deposition is at the medium to low end of deposition rates seen nationwide (**Figure 3**). A few potential factors contributing to South Florida's sulfur deposition signature are the type and amount of regional industry, climate, and agricultural practices. Across the Everglades Protection Area (EPA), rainwater sulfate concentrations at almost all of the 15 collection sites in the Water Conservation Areas, Everglades National Park, and around Lake Okeechobee average between 1 and 5 mg/L (Gilmour et al., 2007a). These rainwater sulfate concentrations are considerably lower than sulfate concentrations found in surface water from Lake Okeechobee, EAA canals, and sulfur-enriched marshes of the Everglades. Rainwater sulfate concentrations, however, are often higher than values observed in pristine areas of the Everglades (the interior marshes of WCA-1, Everglades National Park, and Big Cypress National Park) and, therefore, rainwater may be the principal source of sulfate in these areas of the ecosystem. In some instances, rainwater is as low as 0.5 to 0.7 mg/L in parts of Everglades National Park (D. Scheidt, USEPA Region 4, personal communication). On the other hand, the sulfate concentration of rainwater is far too low to be the principal source of sulfate in the canals. Furthermore, sulfate from rainwater in Central and South Florida has a stable isotope profile different than that in surface water from EAA canals or the northern Everglades (Katz et al., 1995; Bates et al., 2001 and 2002). Dry atmospheric deposition of sulfur within the Everglades Protection Area has been difficult to quantify to date due to problems with sample contamination. Although this source requires further investigation, the U.S. Environmental Protection Agency's Clean Air Status and Trends Network Program estimated that dry sulfur deposition contributed less than half of total atmospheric deposition in 2005 (USEPA, 2005). With respect to marine influences, dry and wet deposition of sulfate-laden sea aerosol undoubtedly impacts the Everglades Protection Area and deposition is likely uniform along a north-to-south gradient. It is unlikely that sea aerosol has a major impact on the sulfate composition of highly enriched areas in the EPA; however, it may be a major component to the sulfate content in pristine areas (Bates et al., 2002). Therefore, based on current sulfate concentration and loading data, it is clear that atmospheric deposition cannot account for most of the sulfate content observed in sulfur-enriched areas of the EPA.

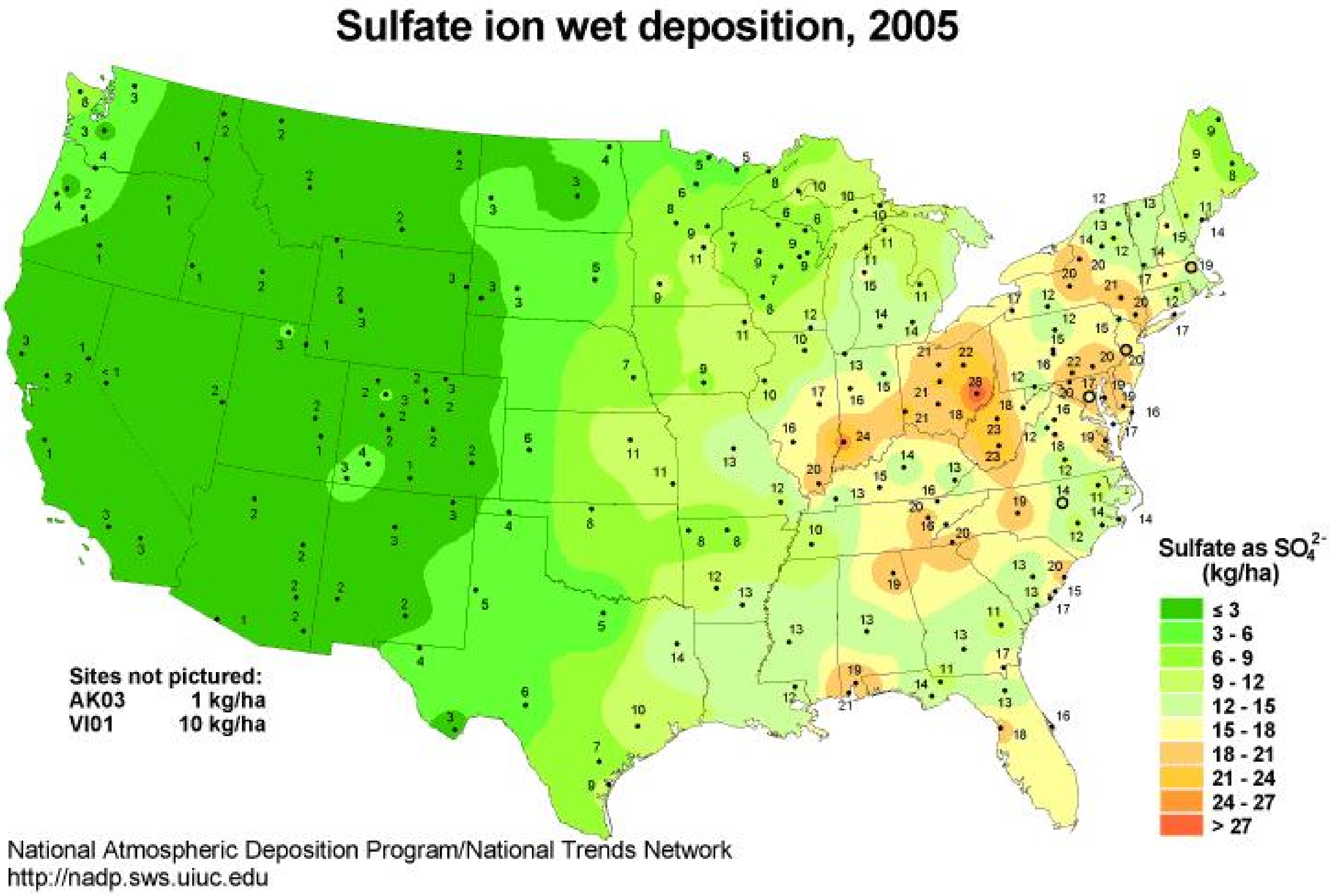

Figure 3. Wet deposition of sulfate as SO_4^{2-} (kg/ha) in 2005. Data from National Atmospheric Deposition Program website at http://nadp.sws.uiuc.edu/isopleths/maps2005/so4dep.gif, July 2007.

Surface Water

To date, the highest sulfate concentrations (excluding estuarine and marine sites) within the EPA are observed in canal water in the EAA. Average sulfate concentrations from USGS sampling in EAA canals from 1995–2000 averaged 72.8 mg/L in the Hillsborough Canal; 55.8 mg/L in the North New River Canal; and 65.6 mg/L in the Miami Canal (Gilmour et al., 2007a; Axelrad et al., 2007). Studies conducted by Chen et al. (2006) also found consistently high sulfate values (45 to 119 mg/L) in EAA farm canals. A big question at this stage is what the dominant source of sulfur is to canals. As previously discussed, sulfur has been, and in some cases continues to be, used in agricultural and urban grounds-keeping through practices involving fertilizers, fungicides, pesticides, and herbicides. With respect to fertilizing, agricultural sulfur (comprising 98 percent elemental sulfur) is used as a soil amendment in the EAA to solubilize micronutrients (Schueneman, 2000) and enhance uptake of phosphorus by crop plants (Bottcher and Izuno, 1994; Rice et al., 2006). Oxidation of elemental sulfur to sulfate in soils produces acidity in the soil which helps in mobilizing applied phosphorus fertilizer for more effective uptake by crops, especially sugarcane. Knowing that sulfur has been used in EAA farming activities, one must consider the possibility that applied sulfur is a source to EAA canals through surface runoff. Using stable isotope signatures, Bates et al. (2002) summarize evidence on the importance of agricultural-use sulfur as a sulfur source. In this study, sulfur isotope signatures were generated for several agricultural sulfur samples sold by farm stores and agricultural chemical distributors within the EAA. These values were very similar to isotope signatures from the upper 10 cm of soil in an active sugarcane field in the EAA (Bates et al., 2001 and 2002), as well as to isotope signatures in EAA canal water (Bates et al., 2002). Thus, until otherwise demonstrated, these findings are consistent with agricultural sulfur applications being a dominant contributor to the sulfate content of EAA agricultural soils and canal water; however, more definitive investigations on possible sulfur sources are needed. Bates et al. (2002) findings and current isotope results also do not indicate whether the sulfate entering the canals in the EAA is derived from recently applied agricultural sulfur, or whether historical applications are slowly released during soil oxidation.

Groundwater

Groundwater is another potential source for sulfate in surface water, both in the EAA and generally in South Florida, however data is somewhat limited and results are mixed. Data collected by USGS researchers show that shallow groundwater [less than 9 meters (m)] in WCA-2A has consistently shown lower (tenfold or more) sulfate concentrations compared to surface water (Bates et al., 2001). Deep groundwater (greater than 9 m) underlying WCA-2A has also shown levels too low to account for the high sulfate concentrations in the surface water (Gilmour et al., 2007a). However, deep groundwater from a depth of 30.5 m at the S-10C structure (located along the Hillsboro Canal that discharges into WCA-2A) has displayed sulfate concentrations as high as or higher than surface water (concentrations up to 186 mg/L). Concentrations of sulfate from deep groundwater (greater than 9 m) beneath STA-1W are also as high as sulfate in the canals in the EAA. Research conducted by CH2M Hill (1978) for the Florida Sugar Cane League indicated that shallow groundwater (12 wells, 8-10 feet in depth) had high concentrations, ranging from 20 to 490 mg/L. Therefore, based on available data, it is clear that more work is needed to better define groundwater as a potential source for sulfur since groundwater can contain sulfate concentrations similar to those of surface water (canal water). To adequately define groundwater as a sulfur source, more robust spatial and temporal sampling studies are needed in addition to evaluating the possibility of groundwater-canal flow interactions and upwelling in downstream areas.

Lake Okeechobee

Lake Okeechobee has elevated sulfate concentrations from rivers entering the lake from the north draining both urban and agricultural lands, and also from EAA sources via backpumping. Although the lake has annual average sulfate concentrations less than half of those in EAA canals (Bates et al., 2002), it does contribute sulfate to the EAA canals (Zielinski et al., 2006; Axelrad et al., 2007). It is probable that during prolonged dry periods, most water and sulfate in the EAA canals comes from Lake Okeechobee (Bottcher and Izuno, 1994); however, during times of normal rainfall, EAA canal sulfate concentrations increase beyond Lake Okeechobee sulfate levels, plausibly as a result of runoff from the EAA.

ACTION PLAN TO SUPPORT DECISION MAKING ON SULFUR AS A WATER QUALITY CONCERN IN SOUTH FLORIDA

Considering the importance of sulfur to phosphorus cycling, methylation of mercury and sulfide toxicity, it is important that resource agencies collaborate to generate more information that addresses critical questions regarding the sulfur issue in South Florida. Existing information from monitoring and research must continue to be synthesized, analyzed and made available. Additional priority research and analysis activities need to be undertaken to identify potential management options. To address the current needs, several high-priority projects are recommended. The projects outlined below are fully consistent with the findings and recommendations of the 2007 Peer Review Panel (Jordan et al., 2007, pages 23–24).

1. **Sulfur budget.** The South Florida Water Management District and the Florida Department of Environmental Protection must continue to gather information on sulfur contributions from all known primary sulfur sources within South Florida (surface water, (canals and rivers), atmospheric deposition, groundwater, and Lake Okeechobee) to establish a more refined/up-to-date sulfur budget for the greater Everglades ecosystem. Loading estimates should be obtained using high resolution spatial sampling frameworks and over various time periods to capture particular hydrometeorological conditions (i.e., dry and wet seasons). In addition, investigation is needed on all potential sources, for example, cattle grazing areas, suburban and urban areas that practice fertilizer application, and areas with intense animal operations. Despite the low sulfur levels in dry deposition, further work is still needed as this delivery mechanism may be important during dry periods (particularly for pristine areas). Current sulfur application and IFAS fertilizer recommendations need to be fully considered and investigated for mass balances since both could potentially be large factors. Factors such as soil subsidence (mineralization of soil organic matter), crop rotation, farm operation, water management, irrigation, and groundwater intrusions also need to be considered.

2. **Content and decomposition of organic sulfur in the surface water and sediment associated flux.** Because plants require sulfur for growth, organic matter in surface water and sediment may have significant sulfur concentrations. To date, the extent of organic sulfur has not been investigated in South Florida ecosystems. Considering the large amount of organic sulfur cycling throughout the greater Everglades ecosystem a stand-alone research effort concentrating on organic sulfur fluxes is needed. Measurements of organic sulfur in the inflow, water column, sediment, and porewater will help provide a more complete sulfur budget and assist in developing an understanding of the sources and fates of sulfur.

3. **Sulfur cycle dynamics and relationships with internal eutrophication.** Sulfate reduction leads to the release of phosphorus originally bound to iron and organic matter. To develop a better understanding of the Everglades sulfur cycle and to determine the potential for or extent of internal eutrophication, the relationships between sulfate concentration, rate of sulfate reduction, abundance of sulfate-reducing bacteria, rate of organic decomposition and changes in iron and phosphate concentrations in sediment need to be defined. The dynamics of acid-volatile sulfide in pore water will also be evaluated. The same set of analyses should be performed for Stormwater Treatment Areas (STAs), specifically, to determine if the presence of excess sulfur in the STAs limits phosphorous removal efficiency. Currently there is much speculation about the role of sulfur in STA performance. Some Everglades scientists argue that the role of sulfur within STAs is very important — while others argue that it is trivial. Given the large investment in construction and maintenance of the STAs, it is important that a conclusive determination be made regarding sulfur impacts on phosphorous mobilization.

4. **Sulfur Best Management Practices.** Water quality treatment in the Everglades has traditionally focused on reducing phosphorus inputs to the ecosystem through (1) Best Management Practices (BMPs) and (2) the construction of Stormwater Treatment Areas (STAs), which are constructed wetlands designed to remove phosphorus from stormwater runoff before it is discharged to the Everglades. Through bacterial sulfate reduction and plant uptake a relatively small percentage of sulfur entering STAs is retained. However, the retention of sulfur is not nearly comparable to that observed for phosphorus (about 70 percent). Considering the presence of sulfur application in the EAA and other neighboring areas and the known deleterious impacts of sulfur to natural systems in excess amounts, a proactive step is to initiate investigation of sulfur BMPs. Potential directions for sulfur BMPs may include (1) reducing the amounts of agricultural sulfur used, (2) replacing agricultural sulfur with another soil amendment that would enhance phosphorus uptake by plants, and (3) using a different counter-ion in fertilizers and other agricultural products. Implementation of BMPs for sulfur use throughout the region, in concert with biochemical reduction, plant uptake, and sedimentation processes in aquatic environments, may reduce the amount of sulfate entering the Everglades.

CURRENT INTERAGENCY AND UNIVERSITY RESEARCH

1. Researchers at the Louisiana State University are conducting investigations on sulfur toxicity to emergent plants and the competitive advantage of cattails over sawgrass under different sulfate/sulfide porewater and surface water conditions. Further information on this research is available at www.research.lsu.edu/newsletter/environment.htm.

2. The U.S. Geological Survey and Smithsonian Environmental Research Center researchers, in cooperation with FDEP, have conducted extensive analysis of sulfate-related mercury methylation using mesocosm studies within WCA-2, WCA-3, and STA-2 (Gilmour et al., 1998; Gilmour et al., 2007b). From this work they have suggested optimal sulfate and sulfide levels for mercury methylation. Considering that wetland biogeochemistry can vary widely throughout the EPA, and, therefore, factors impacting methylation vary geographically, extended effort is proposed by FDEP to further explore methylmercury potential throughout the EPA. Additional information on past mercury research within the Everglades is available at www.serc.si.edu/labs/microbial/index.jsp.

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