Sulfate threshold target to control methylmercury levels in wetland ecosystems

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ARTICLE INFO

ABSTRACT

Sulfate contamination has a significant environmental implication through the stimulation of toxic hydrogen sulfide and methylmercury (MeHg) production. High levels of MeHg are a serious problem in many wetland ecosystems worldwide. In the Florida Everglades, it has been demonstrated that increasing MeHg occurrence is due to a sulfate contamination problem. A promising strategy of lowering the MeHg occurrence is to reduce the amount of sulfate entering the ecosystem. High surface water sulfate concentrations in the Everglades are mainly due to discharges from the Everglades Agricultural Area (EAA) canals. Water and total sulfur mass balances indicated that total sulfur released by soil oxidation, Lake Okeechobee and agricultural application were the major sources contributing 49,169, 35,217 and 11,775 mtons year^{-1}, respectively. Total sulfur loads from groundwater, levees, and atmospheric deposition contributed to a lesser extent: 4055; 5858 and 4229 mtons year^{-1}, respectively. Total sulfur leaving the EAA into Water Conservation Areas (WCAs) through canal discharge was estimated at 116,360 mtons year^{-1}, and total sulfur removed by sugarcane harvest accounted for 23,182 mtons year^{-1}. Furthermore, a rise in the mineral content and pH of the EAA soil over time, suggested that the current rates of sulfur application would increase as the buffer capacity of the soil increases. Therefore, a site specific numeric criterion for sulfate of 1 mg L^{-1} was recommended for the protection of the Everglades; above this level, mercury methylation is enhanced. In parallel, sulfide concentrations in the EAA exceeded the 2 μg L^{-1} criterion for surface water already established by the U.S. Environmental Protection Agency (EPA).

1. Introduction

Methylmercury (MeHg) is a neurotoxin that has the tendency to bioaccumulate in the muscle tissues of organisms, posing harm to the environment and to human health (Selin, 2009; Zhang and Hsu-Kim, 2010). Due to its ability to bioaccumulate, MeHg concentrations in organisms increase up the food chain, with very high concentrations in animals such as large fish and predatory birds. Effects of MeHg exposure are most severe in fetuses, causing damage to the developing brain and nervous system (Crump et al., 2000). Human exposure to toxic MeHg comes mainly from eating contaminated fish (Ni et al., 2010). MeHg can be formed naturally, but some environments, such as wetlands, seem to favor its development, posing a risk to the organisms in the ecosystem (Selin, 2009). Formation of MeHg has been observed worldwide, usually resulting from an increase in an identifiable source of elemental mercury into the environment. For example, in the Humboldt River Basin of Nevada (USA), the formation of MeHg has been linked to nearby mercury mines (Gray et al., 2002). In the Pantanal region of Brazil, the presence

of MeHg can be traced back to gold mining operations that increased mercury levels in local water and sediments (Yokoo et al., 2003). Also, in the Minamata Bay (Japan), MeHg poisoning was caused by polluted industrial effluents impacting a naturally sulfate rich environment (Kudo et al., 1998). One specific ecosystem that appears to be a hotspot for MeHg formation is the Florida Everglades, one of the largest wetlands in the world. Regularly, the Florida Department of Health (http://www.doh.state.fl.us/floridafishadvice/) publishes fish consumption recommendations based on mercury testing from specific water bodies. Currently (2011), there is a "no consumption" advisory for certain fish species from the Everglades.

High MeHg concentrations observed in Everglades flora and fauna have emphasized the need to reduce the amount of MeHg produced within the aquatic system. Controlling the amount of mercury that enters the environment has been the primary strategy of the Florida Department of Environmental Protection (FDEP) for dealing with this problem, since mercury is obviously necessary for the formation of MeHg (Axelrad et al., 2006). The FDEP is required to develop a Total Maximum Daily Load (TMDL) analysis for mercury in the Everglades because the water body does not meet the State's current standards for mercury (Atkeson et al., 2003). Unfortunately, controlling the amount of mercury entering the South Florida environment is not an easy task. Atmospheric deposition is usually the major pathway

through which mercury enters aquatic ecosystems (Caffrey et al., 2010). When mercury enters the environment through atmospheric deposition, the source of the mercury is not necessarily local and may originate from quite distant locations where local policy will not have much effect on the anthropogenic sources of mercury, such as coal combustion and waste incineration (Caffrey et al., 2010; Selin, 2009). Florida has reduced local mercury emissions, but the observed mercury levels have not decreased (Gabriel et al., 2010). Therefore, the source of the mercury is from a global source and cannot be locally controlled (Gabriel et al., 2010). Since nothing else can be done on a regional level to control the amount of mercury entering the environment, it is now necessary to develop new management strategies to decrease the MeHg levels in the Everglades (Orem, 2007).

One promising management strategy for the control of MeHg within the Everglades is to inhibit the process through which mercury is methylated into its more toxic form. Sulfur plays a substantial role in this process, as both sulfate and sulfide. The presence of high levels of sulfate stimulates the methylation process, while increased levels of sulfide inhibit it. The production of MeHg is aided by the presence of mercury (Hg (II)) and sulfate in the sediment porewater because the methylation process is carried out by sulfate-reducing bacteria (SRB) (Harmon et al., 2007; King et al., 2000). One mechanism that can be used to curtail the high levels of MeHg observed in the environment is to limit the amount of sulfate which enters the Everglades ecosystem. Since sulfate plays such a major role in the methylation process, the establishment of site-specific water quality criterion for sulfate may prove to be a promising management strategy for the control of MeHg within the Everglades. A decrease in sulfate levels will help to reduce the methylation process.

Currently, there is no specific water quality criterion for sulfate to help manage the MeHg problem. World-wide sulfate water quality guidelines have only been developed to regulate sulfate levels in drinking water and not in surface waters (BC Ministry of Water, Land and Air Protection, 2000). In Florida, under the Safe Drinking Water Act, the FDEP maintains a secondary water quality standard for sulfate of $250 \, mg \, L^{-1}$ in drinking water. Unlike primary water quality standards, secondary standards exist for esthetic reasons and are not enforceable (USEPA, 2001). The current sulfate secondary water quality standard of $250 \, mg \, L^{-1}$ was established because above this concentration, sulfate contributes a salty taste to drinking water (USEPA, 2001). Although, at present, there is no standard regulating levels of sulfate in surface waters, there is a numerical limit for sulfide established by the U.S. Environmental Protection Agency (EPA). The EPA classifies sulfide as a non priority pollutant and has established a $2 \, \mu g \, L^{-1}$ criterion for surface waters to protect aquatic life (USEPA, 2007). Nevertheless, since sulfate plays a key role in the production of sulfide and also of MeHg, it is important to establish a numerical criterion for sulfate, for the protection and restoration of the Everglades.

Background sulfate levels in the Everglades are estimated to be $\leq 1 \, mg \, L^{-1}$, but recent analyses have shown that about 60% of the ecosystem has sulfate concentrations in surface water above this level (Bates et al., 2002; Orem, 2004). Sulfate entering the ecosystem tends to show a north to south concentration gradient, with the highest levels observed in canal water crossing the Everglades Agricultural Area (EAA) (Bates et al., 2001). Numerous studies have identified sulfate (originating from the EAA) to be one of the key mechanisms to enhance MeHg production and the subsequent degradation of the Everglades (Bates et al., 2001, 2002; Orem, 2004). Many of these studies have focused on understanding the sulfur geochemistry, identifying and tracing sources of sulfate, and have also examined different strategies for mitigation of sulfate contamination (Bates et al., 2001, 2002; Gilmour et al., 2007; Orem, 2007; Ye et al., 2010). However, estimates and measurements of the major sulfate sources in the EAA are limited. A holistic quantification of the sources is critical

for predicting the impacts of future modifications in sulfate loading on the Everglades habitats. Furthermore, a specific sulfate limit for the Everglades Protection Area is needed in order to protect the fauna and flora in this ecosystem. Therefore, the goal of this study was to identify the major total sulfur (sulfate + sulfide) sources and estimate, through water and total sulfur mass balances, flowing in and out of the EAA. Although the methodology used in the present study was applied locally for the EAA, it could be adopted to other sites worldwide, where high MeHg concentrations are also observed. In addition, this information would support stakeholders in decision making about the necessity of setting limits for sulfate to control MeHg production.

2. Material and methods

2.1. Study area

The Everglades Agricultural Area (EAA), approximately 718,000 acres in size, is considered one of Florida's most important agricultural regions. Fig. 1 presents the study area map, located between Lake Okeechobee (LO) and the Water Conservation Areas (WCAs), contains about 500,000 acres of highly productive agricultural land mostly sugar cane and seasonal vegetable crops (Abtew et al., 2010). There are four major canals crossing north to south through the EAA: West Palm Beach Canal, Hillsboro Canal, North New River Canal, and Miami Canal; and three connecting canals: Bolles Canal, Cross Canal, and Ocean Canal. Water flowing from Lake Okeechobee and runoff from the EAA are discharged into Stormwater Treatment Areas (STAs) via these four canals to mitigate flooding from the local drainage area. The STAs are included as part of the EAA in the calculation of the water and sulfate mass balances.

2.2. Water balance

The main water sources to the EAA considered in the present study include Lake Okeechobee, rainfall, discharges from levees, and groundwater. The major sources of water loss are evapotranspiration and water delivered to the WCAs. Flow, rainfall, potential evapotranspiration (crop coefficient estimated at 0.75), and stage data from 1995 to 2009 were downloaded from an online database (DBHYDRO) maintained by the South Florida Water Management District (http://www.sfwmd.gov/dbhydroplsql/show_dbkey_info.main_menu). The location of the water quality monitoring stations used in this study is shown in Fig. 1. A steady-state water balance is presented in Eq. (1). The left and right sides of the equation refer to the yearly inflows and outflows to and from the EAA, respectively. Eq. (1) follows the comprehensive approach proposed by Budyko (1958) and Milly (1994) assuming that the steady-state water balance is controlled by atmospheric conditions, water demand and availability. Groundwater recharge was estimated according to Eq. (2), using the annual average value of each one of the components of the water balance. Negative flow values from the data sets accounted for the back pumping from the EAA to the Lake and from the WCAs to the EAA, and were subtracted to obtain the net flow in and out of the EAA.

$$Q_{LO} + Q_L + Q_R + Q_{GW} = Q_{WCA} + Q_E \qquad (1)$$

$$Q_{GW} = (Q_{WCA} + Q_E) - (Q_{LO} + Q_L + Q_R) \qquad (2)$$

where Q_{LO} is the Lake Okeechobee inflows to the EAA, Q_L is the levee inflows, Q_R is the rainfall, Q_{GW} is the groundwater recharge, Q_{WCA} is the EAA outflows to the WCAs, and Q_E is the evapotranspiration. All parameters are in million $m^3 \, year^{-1}$.
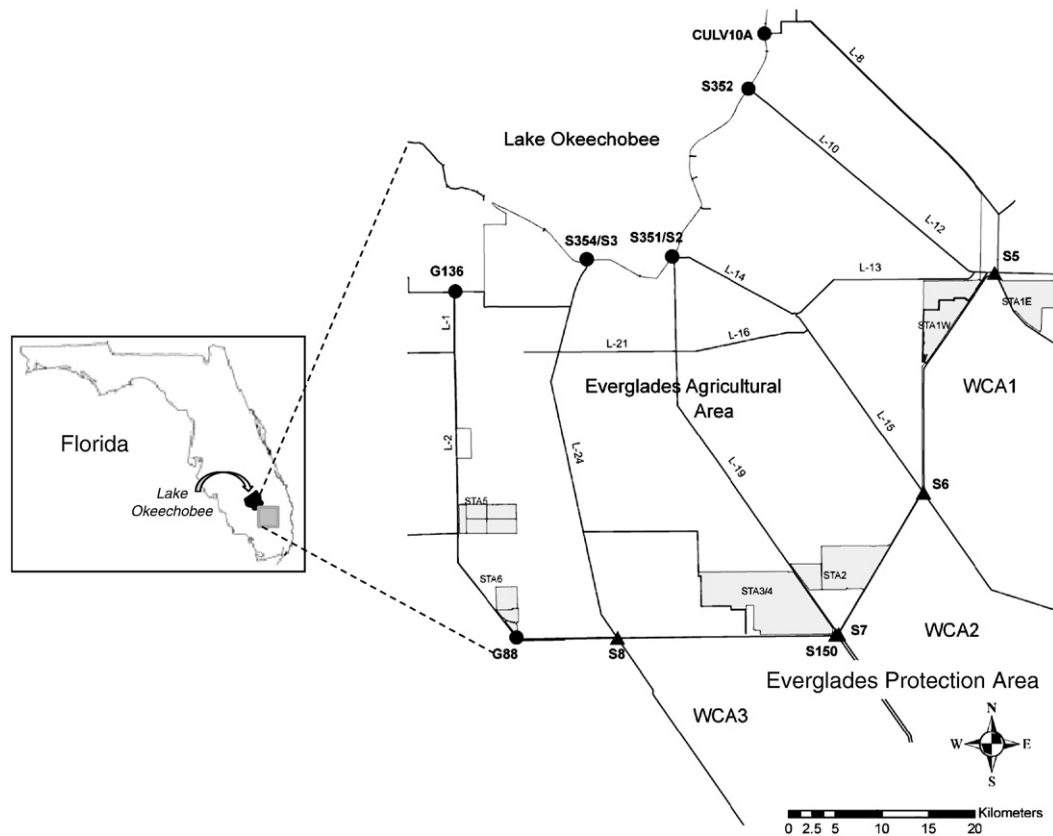
Fig. 1. Location of Florida, South Florida and the study area (EAA: Everglades Agricultural Area). WCA are the water conservation areas 1, 2 and 3. STAs are the stormwater treatment areas (constructed wetlands). The inflow (●) and outflow (▲) stations used in the water and total sulfur (TS) mass balance calculations in the EAA are represented in the map.

2.3. Sulfate mass balance

Different sources of sulfate and sulfide were identified in order to develop a total sulfur (TS) mass balance in the EAA. It is worth noticing that in aerobic water the TS is mainly constituted of sulfate. These sources include Lake Okeechobee, atmospheric deposition, agricultural sulfur applications, and soil oxidation (Bates et al., 2002; Gabriel et al., 2010; Gilmour et al., 2007; Orem, 2007; Ye et al., 2010). This study considered groundwater and discharges/recharges from levees as additional sources of TS. The present study assumed that the TS load could leave the EAA through surface water flowing to the WCAs and through sugar cane harvesting. Total sulfur (TS) contained in the soil (legacy) and TS in the canals were also estimated for the EAA. Daily TS concentrations in surface water were retrieved from DBHYDRO (http://www.sfwmd.gov/dbhydroplsql/show_dbkey_info.main_menu) for stations located at Lake Okeechobee outflows, at levees discharging to the EAA, and at the WCAs inflows. The same database was also used to collect data of TS concentration in groundwater, and to estimate, by extrapolation, shallow groundwater TS concentrations. Fig. 1 shows the location of the stations from

DBHYDRO that were used to establish the mass balance. The TS (dry + wet) atmospheric deposition data was determined from the U.S. EPA Clean Air Status and Trends Network (CASNET) and the averaged annual values were determined from two monitoring sites located in South Florida (FL11 and FL99) and used in the mass balance determination. The values considered in the present study for estimating the amount of agricultural TS applied to soil, TS removed from the EAA by sugar cane harvest, TS content in soil and the rate of oxidation were obtained from literature (Bates et al., 2002; Gabriel, 2009; Schueneman, 2001; Wright et al., 2008). Table 1 summarizes the values and the references used to establish the mass balance. The TS mass balance equation considered in this study was developed following the principle of mass conservation, which for steady-state flow processes can be expressed using Eq. (3) (Chapra, 1997). The left hand side reflects all sources of TS feeding into the EAA.

$$TS_{LO} + TS_L + TS_{AD} + TS_A + TS_{SO} + TS_{GW} = TS_{WCA} + TS_H \qquad (3)$$

where TS_{LO}, TS_L and TS_{AD} represent the total sulfur load from Lake Okeechobee, from levees and from atmospheric deposition,

Table 1
Data used for the total sulfur (TS) mass balance.

	Units	Value	Source
Total area of the EAA	ha	290,600	SFWMD
TS from agricultural applications	kg ha^{-1} year^{-1}	37.0	Wright et al. (2008)
TS from soil oxidation	kg ha^{-1} year^{-1}	243	Schueneman (2001)
Soil oxidation rate	cm year^{-1}	1.4	Wright and Snyder (2009)
TS concentration in the EAA soils	%	0.35	Bates et al. (2002)
TS removed by harvest	mton year^{-1}	25,500	Gabriel (2009)
Density of soil	g cm^{-3}	0.356	Izuno (1994)

respectively. TS_A, TS_{SO} and TS_{GW} characterize the total sulfur load from agricultural applications, soil oxidation and from groundwater, respectively. TS_{WCA} is the total sulfur load to WCAs, and TS_H stands for total sulfur load out from the EAA by sugarcane harvest. All equation terms are in mtons year^{-1}.

Although the values presented in Table 1 have been derived from peer-reviewed published papers or from studies conducted by recognized agencies or universities, these numbers are averaged across the EAA. The spatial variability is to be investigated with further monitored data at different locations within the EAA in order to increase the accuracy of the numbers presented in Table 1.

2.4. Determination of the sulfate target

Data for the monitored sulfate and methylmercury levels (from 1992 to 2005) were obtained from the mercury Everglades National Park database (http://www.evergladesfoundation.org/pages/current-research-news/) in order to establish the relationship between these two parameters and to suggest a sulfate target for the Everglades Protection Area. The target was then compared to the Comprehensive Everglades Restoration Plan (CERP) adopted performance measure of <1 mg L^{-1} for sulfate in surface water to minimize the methylation of mercury.

3. Results and discussion

3.1. Water balance in the EAA

Annual average rainfall was 1174 mm, serving as the major source of water to the EAA corresponding to 47% of the total inflows (Fig. 2). The average flow from groundwater, Lake Okeechobee and levees were estimated to supply 811, 1565 and 366 million m^3 year^{-1} (13, 22, and 5%), respectively. Average annual potential evapotranspiration was 1508 mm, representing 53% of the water loss in the EAA. Water discharged from the EAA to WCAs through major canals was estimated to be 2867 million m^3 year^{-1}, contributing 47% of the total water outflow. These results suggest that hydrology in the EAA is driven by meteorological factors rather than by groundwater recharge or water delivered through canals. Inflow and outflow estimates were comparable with values reported by the SFWMD. Historical average outflows from Lake Okeechobee and WCAs inflows are 1815 and 2873 million m^3 year^{-1} (1,470,820 and 2,328,080 acre-feet per year), respectively. Rainfall and evapotranspiration annual averages are approximately 1118 and 1448 mm, respectively (Abtew et al., 2010).

Approximately 45,423 m^3 of storage capacity was calculated using primary and secondary canals averaging a water level of 3.47 m (11.37 ft).

3.2. Total sulfur mass balance in the EAA

Results of the TS mass balance suggest that soil oxidation is the largest source with about 45% of the TS loaded into the EAA (Fig. 3), in agreement with previous studies (Schueneman, 2001). Lake Okeechobee outflows transport 32% (35,217 mtons year^{-1}) of TS, representing an important pathway of sulfate input to canal waters. This value is also consistent with earlier studies, which have reported annual average inputs from Lake Okeechobee to the EAA of approximately 32,000 mtons year^{-1} (Gabriel et al., 2010; McCormick and James, 2008; Schueneman, 2001). Agricultural applications, levees, atmospheric deposition and groundwater loads were found to contribute 11,775, 5858, 4229 and 4055 mtons year^{-1} (11, 5, 4 and 4%), respectively. TS flowing out from canal waters to WCAs represents the main mechanism of sulfate loss with about 116,360 mtons year^{-1}; an estimate relatively similar to the one calculated by Gabriel (2009) for a high precipitation year (Gabriel et al., 2010). Furthermore, this result corroborates several studies that have suggested that, although Lake Okeechobee sulfate concentrations are elevated, average loadings are significantly lower than those in the canals discharging to WCAs (Bates et al., 2002; Gilmour et al., 2007; Orem, 2004). TS removed by crop harvest accounts with 23,182 mton year^{-1}, 17% of the TS loss from the EAA. The total average load from all TS sources to the EAA was 110,303 mtons year^{-1}, whereas the TS leaving the EAA was 139,542 mtons year^{-1}, indicating that there is 29,239 mtons year^{-1} (21%) of TS loads from different sources not accounted for in the present study.

TS accumulated in the EAA soil was estimated to 831,994 mtons, representing the legacy of sulfur applications to the EAA soil. This was calculated using an average value adopted from Bates et al. (2002) of 0.35% dry weight of TS in the first 30 cm of the EAA soil. Concentration of TS in the EAA soil is a very important aspect to evaluate since it could be a potential source to canal waters through the release of TS by soil oxidation and subsequent runoff from the agricultural fields. Bates et al. (2001) found that TS content near the soil surface (first 30 cm) was between 0.10 and 0.60% (dry weight) and greater than 2% at depths below 122 cm, suggesting that reduced sulfur, which has accumulated for many years in the top soil, has been oxidized and washed out to EAA canals or filtered into the soil during rainfall events (Bates et al., 2002).
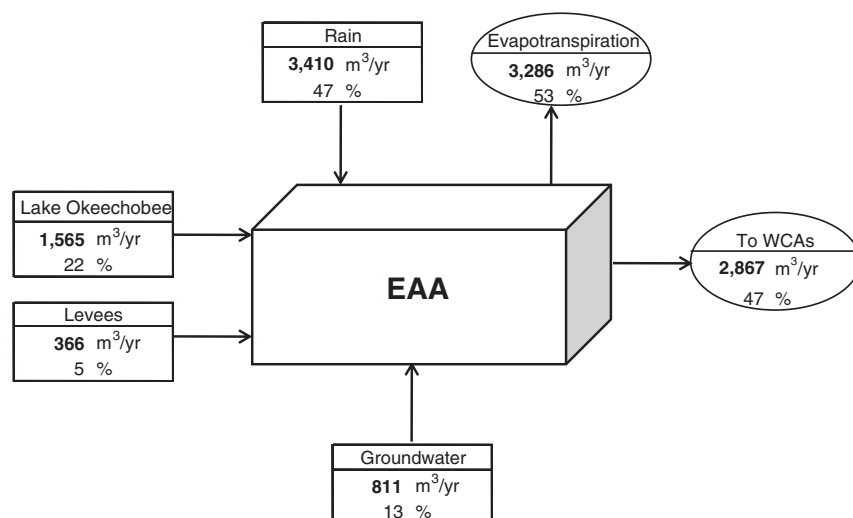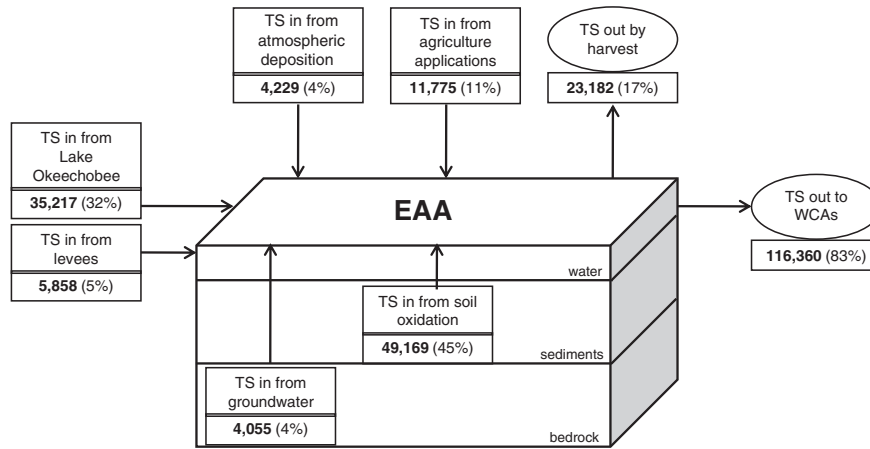

Fig. 2. Water balance results in the Everglades Agricultural Area (EAA) (average values from 1995 to 2009). Flow (in bold, million m^3/year) and percentage (%) of contribution to the total inflow and outflow are indicated. Rectangles and circles represent inflows and outflows, respectively.

Fig. 3. Total sulfur mass balance results in the Everglades Agricultural Area (EAA) (average values from 1995 to 2009). Load (in bold, mtons year^{-1}) and fraction (%) of total sulfur (TS) in and out of the EAA are indicated. Rectangles and circles represent the total sulfur load in and out of the EAA, respectively.

Due to soil subsidence and oxic conditions in the EAA, the rate of sulfate released from oxidation is accelerated. Different rates of soil subsidence have been reported in the literature and have been used for TS mass balance estimates (Gabriel et al., 2010; Wright and Snyder, 2009). Gabriel (2009) reported a range from 0.5 to 1.5 inch year^{-1} (1.27 to 3.81 cm year^{-1}) and Wright et al. (2008) a rate of 0.55 inch year^{-1} (1.4 cm year^{-1}). A value of 243 kg ha^{-1} year^{-1} (adopted from Schueneman, 2001) was used in this study for mass balance calculations to represent the TS released by soil oxidation. The TS inputs from this source could originate from the natural or background sulfur present in soil and from the legacy sulfur agricultural applications considered as anthropogenic contributions (Orem, 2007).

Isotopic analysis has accredited agricultural fertilizers as a major contributor to sulfate content in the agricultural soil and in the adjacent canals (Bates et al., 2002; Orem, 2004). Average mass balance estimations of TS loadings from farmers' applications accounted for 10% of the total TS input to the EAA. However, the usage of sulfur as a soil amendment for pH adjustment is likely to increase in the long term. Comparison of two studies conducted at the EAA soil (Porter and Sanchez, 1992; Janardhanan and Daroub, 2010) reveals that pH and mineral content in the soil had increased over time (Fig. 4). Currently, agricultural applications are estimated at 37 kg ha^{-1} year^{-1} (33 lb ac^{-1} year^{-1}) based on surveys (Schueneman, 2001). Nevertheless, as the soil subsidence continues, the mineral matter contained in the organic soil becomes a major component of the soil matrix (Wright

and Snyder, 2009). The proportion of minerals, such as clay, sand, or calcium carbonate, would augment in the soil profile, making the soil continuously more alkaline and increasing its buffering capacity. In addition, investigations at the Everglades Research and Education Center (EREC) in the EAA, showed that up to 4483 kg ha^{-1} (4000 lb ac^{-1}) of sulfur was needed to diminish the pH by one unit, demonstrating the high buffering capacity of soils in the EAA (Beverly and Anderson, 1987). Therefore, farmers will be required to apply larger quantities of sulfur-based fertilizer each year in order to achieve neutralization of the soil.

Research on groundwater discharge as a source of sulfate has been limited. Bates et al. (2002) analyzed groundwater samples collected at different depths in the Everglades Nutrient Removal Area (ENR) in 1998, area currently known as STA1W, and found that sulfate concentrations tend to be more elevated at greater depths (Bates et al., 2002). Sulfate concentrations in groundwater present a high spatial variability throughout the Everglades (Orem, 2007). For the purpose of mass balance calculation, an average TS concentration of 5 mg L^{-1} was used. This concentration is considered to be representative of shallow groundwater for all the EAA based on data extrapolation from Bates et al. (2002) (Fig. 5). It is also based on studies that evidence the dominant contribution of groundwater in the ENR is from shallow sources with relatively low sulfate concentrations (approximately less than 10 mg L^{-1}), rather than
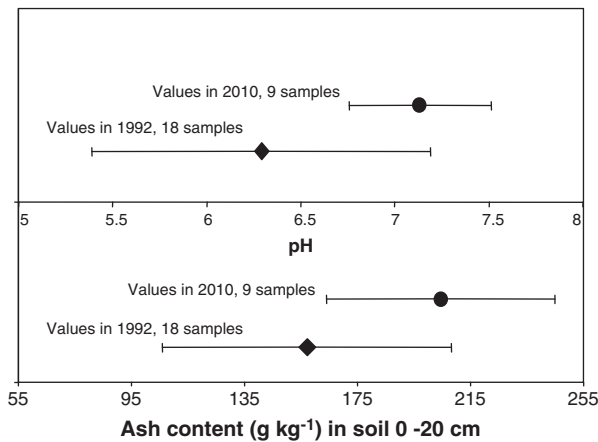
Fig. 4. Comparison of the Everglades Agricultural Area (EAA) soil pH and mineral content in 1992 and 2010. The values were taken from Porter and Sanchez (1992) and Janardhanan and Daroub (2010).
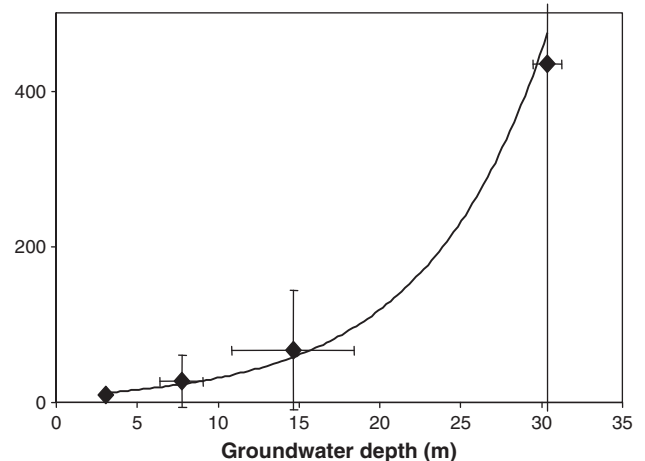
Fig. 5. Groundwater sulfate concentration extrapolation analysis at different depths. The values were taken from Naja et al. (in press).

from deeper groundwater where high sulfate concentrations were found (Bates et al., 2002; Choi and Harvey, 2000; Orem, 2007). Comparing the sources of TS evaluated in this study, groundwater did not demonstrate a significant contribution to the total load to the EAA. This finding supports results from earlier studies suggesting that shallow groundwater had TS concentrations too low to account for the sulfate concentration observed in the EAA canal waters (Bates et al., 2002; Gilmour et al., 2007).

Data from atmospheric deposition in South Florida from USEPA's CASTNET were used to estimate an annual average TS load to the EAA of 4229 mtons year^{-1}, which is very close to the estimate of approximately 4000 mtons year^{-1} by Gabriel (2009) for average and dry years. As concluded in the previous studies, dry and wet TS atmospheric deposition showed to represent a minor input to the EAA.

Point sources of TS contamination such as direct discharges from levees, mainly from the C-139 basin, where included for the first time in a TS mass balance for the Everglades. In comparison with other surface water inputs, annual average TS load from levees (5858 mtons year^{-1}) was 6 times less than Lake Okeechobee loads, suggesting that levee inputs are not a considerable source of TS to the EAA.

Sulfate entering the EAA from different sources stimulates SRB and sulfide production. The EPA's National Recommended Water Quality Criteria establishes a numerical limit for sulfide of 2 µg L^{-1} in surface waters. The EPA Gold Book indicates that sulfide concentrations in excess this level would "constitute a long-term hazard" to aquatic wildlife (USEPA, 1986). This criterion for sulfide is currently being exceeded in the Florida Everglades (Fig. 6). Studies have detected sulfide concentrations in areas of the Northern Everglades to be as high as 300 µg L^{-1} in porewater and peat (Gilmour et al., 1998). In addition, as shown in Fig. 6, available data of sulfide concentration in surface water from DBHYDRO at the STA1W, showed that levels of sulfide are well over the EPA National Recommended Water Quality Criteria of 2 µg L^{-1} (0.002 mg L^{-1}), and tend to increase over time, posing a risk to fish and other aquatic life in the ecosystem.

3.3. Sulfate target

There is no EPA recommended water quality criterion for sulfate like there is for sulfide. However, the Comprehensive Everglades Restoration Plan (CERP) has already adopted a performance measure of <1 mg L^{-1} for sulfate in surface water. It is important to suggest a site specific sulfate criterion so that the FDEP has sound scientific rational for establishing a water quality standard for sulfate in the Everglades. A sulfate threshold of 1 mg L^{-1} (background sulfate concentration) is recommended to control the formation of MeHg. Above this level, particularly above 2 mg L^{-1} (Fig. 7), the ecological risk to the ecosystem increases because at intermediate levels of sulfate the methylation of mercury is optimized. Consequently, a site specific numeric criterion for sulfate of 1 mg L^{-1} should be established in the Florida Everglades for the protection of aquatic and human life. Sulfate concentrations within the Everglades should not reach levels that optimize the methylation process and contribute to higher levels of MeHg in the aquatic environment. In order to establish the sulfate criterion, best management practices (BMP) dealing with sulfate amendments should be enforced in the EAA and the STAs are to be re-engineered to enhance the sulfate removal processes (Orem et al., 2010).

In order for the FDEP to implement the suggested sulfate criterion as a site specific water quality standard, the following steps should be taken: 1) adopt 1 mg L^{-1} threshold for sulfate as the dimension of magnitude for this standard, as suggested in this paper. Above this threshold, a risk to aquatic life is expected; 2) establish a dimension of frequency of allowable excursions. This will determine how often the standard may be exceeded due to variations within the ecosystem while still maintaining a level that will protect aquatic life (Novotny, 2003); and 3) establish a dimension of duration for the length of time the 1 mg L^{-1} standard can be exceeded (Novotny, 2003). Should the FDEP decide to accept the suggested sulfate criterion as a water quality standard, it would also need to recognize that areas of the Everglades are well exceeding this threshold and would need to be classified as impaired. Once a water body is designated as impaired, a Total Maximum Daily Load (TMDL) process must be conducted. A TMDL assessment will help to ensure that established "water quality standards will be attained and maintained in a water body" (Novotny, 2003). Mandatory TMDL elements include the following: water body identification, loading capacity of the water body, present status in how much the water body deviates from the standard, source identification of the pollutant, waste load allocation, load allocation, a margin of safety, seasonal variations, future growth, and an implementation plan (Novotny, 2003). Establishment of a site specific sulfate standard of 1 mg L^{-1} for the Florida Everglades is the first step that needs to be taken to reduce the levels of sulfate in this ecosystem. Concentrations of sulfate below 1 mg L^{-1} will inhibit the methylation process, ultimately helping to decrease the levels of MeHg within the ecosystem as well (Jeremiason et al., 2006).

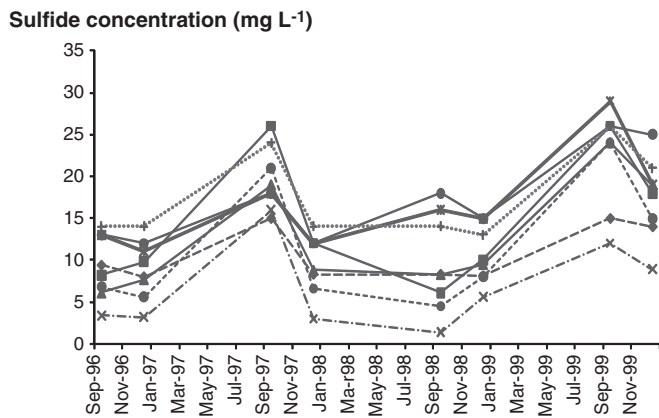**Sulfide concentration (mg L⁻¹)**

Fig. 6. Surface water sulfide concentration in the Everglades Nutrient Removal Area (ENR), currently known as STA1W, from 1995 to 1999. Data were downloaded from DBHYDRO database. The figure symbols correspond to sulfide concentration values at different locations within the ENR.
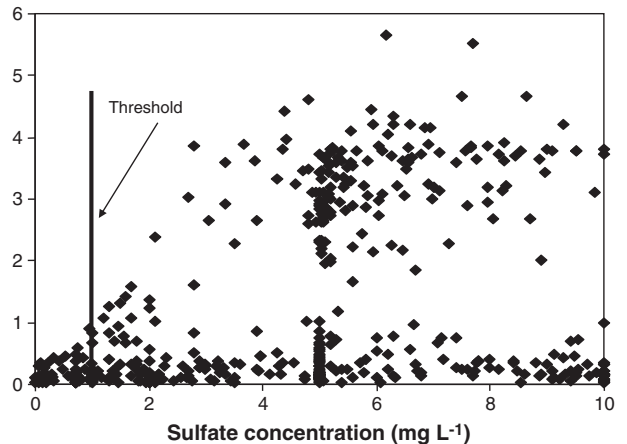
Methylmercury concentration (ng L⁻¹)

Fig. 7. Relationship between sulfate concentration and MeHg production. Data were obtained from the mercury Everglades National Park database (http://www.ever-gladesfoundation.org/pages/current-research-news/).

4. Conclusion

Total sulfur mass balance determination pointed to agricultural applications, soil oxidation and Lake Okeechobee as the primary sources to the EAA. Total sulfur sources, such as discharge/recharge of groundwater and levees, and atmospheric deposition were found to contribute to a lesser extent. The average mass balance estimations of TS loadings from farmers' applications and from soil oxidation accounted for 56% of the TS input to the EAA. This number will tend to increase because of the increase in the soil buffering capacity. It is worth noticing that there are still 21% of TS loads coming to the EAA from sources not accounted for in the present study. As overload sulfate enters the EAA, it stimulates production of toxic hydrogen sulfide, which is currently exceeding the criterion of $2\,\mu g\,L^{-1}$ established by the EPA for freshwater, and it also contributes to the production of MeHg within the Everglades. Controlling sulfate entering into the EAA is crucial to reduce MeHg concentration and bioaccumulation. One management mechanism to reduce sulfate loads, particularly from the main sources, is the establishment of a site specific sulfate criterion of $1\,mg\,L^{-1}$ for the Everglades, which is also the CERP's restoration goal. This criterion will be crucial for the restoration and protection of the greater Everglades wildlife.

Acknowledgments

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