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Projecting Changes in Everglades Soil Biogeochemistry for Carbon and Other Key Elements, to Possible 2060 Climate and Hydrologic Scenarios

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Abstract Based on previously published studies of elemental cycling in Everglades soils, we projected how soil biogeochemistry, specifically carbon, nitrogen, phosphorus, sulfur, and mercury might respond to climate change scenarios projected for 2060 by the South Florida Water Management Model. Water budgets and stage hydrographs from this model with future scenarios of a 10 % increased or decreased rainfall, a 1.5 °C rise in temperature and associated increase in evapotranspiration (ET) and a 0.5 m rise in sea level were used to predict resulting effects on soil biogeochemistry. Precipitation is a much stronger driver of soil biogeochemical processes than temperature, because of links among water cover, redox conditions, and organic carbon accumulation in soils. Under the 10 % reduced rainfall scenario, large portions of the Everglades will experience dry down, organic soil oxidation, and shifts in soil redox that may dramatically alter biogeochemical processes. Lowering organic soil surface elevation may make portions of the Everglades more vulnerable to sea level rise. The 10 % increased rainfall scenario, while potentially increasing phosphorus, sulfur, and mercury loading to the ecosystem, would maintain organic soil integrity and redox conditions conducive to normal wetland biogeochemical element cycling. Effects of increased ET will be similar to those of decreased precipitation. Temperature increases would have the effect of increasing microbial processes driving biogeochemical element cycling, but the effect would be much less than that of precipitation. The combined effects of decreased rainfall and increased ET suggest catastrophic losses in carbon- and organic-associated elements throughout the peat-based Everglades.

Keywords Climate Change · Everglades · Biogeochemistry · Soil · Carbon · Nutrients

Introduction

Biogeochemical processes in soils play a key role in wetland ecosystems, including the Greater Everglades Ecosystem (GEE). These processes help regulate water quality, and provide conditions suitable for biological productivity. For example, important nutrient elements like nitrogen (N) and phosphorus (P) sequestered by wetland plants are released back for reuse through microbial biodegradation of senescent plant organic matter. Anaerobic microbial processes in wetland soils such as nitrate reduction, iron and manganese reduction, sulfate reduction, and methanogenesis can greatly alter the oxidation states and solubilities of metals and nonmetals (Reddy and Delaune 2008). Important metal pollutants like mercury (Hg) are transformed to more toxic and bioaccumulative forms by microbial processes (sulfate and iron reduction and methanogenesis) occurring in wetland soils.

In this paper, we examine the impacts that various climate scenarios to 2060 may have on the biogeochemical cycling of key elements in the GEE. A map of the GEE and

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Fig. 1 Map of the Greater Everglades Ecosystem (GEE) and its environs, showing major locations mentioned in the text

its subcompartments is presented in Fig. 1. The primary focus here is on the effects of the climate scenarios on carbon (C), because C accumulation and cycling drives much of the biogeochemical cycling of other key elements, such as N, P, sulfur (S), and Hg within the GEE. The paper is divided into sections discussing the general biogeochemistry of each of these elements. We also outline current conditions for each of these elements within the ecosystem in order to provide a baseline from which to compare the effects of various climate change factors. The effects of a 10 % increased rainfall scenario and a 10 % decreased rainfall scenario (both possible outcomes of climate change in south Florida) are discussed for each element. The effects of a 1.5 °C temperature increase and a 0.5 m rise in sea level were anticipated to be similar for all of the elements, and are discussed in separate sections rather than repetitive discussions for each element. While this paper discusses impacts of these climate changes on biogeochemical processes in soils in the GEE, results are applicable to many similar types of wetland ecosystems worldwide. This is part of a series of papers related to how the same climate scenarios will impact various aspects of the GEE (Havens and Steinman 2013), resulting from a workshop on climate change and the GEE held at Florida Atlantic University in February 2013 (www.ces.fau.edu/climate_change/ecology-february-2013/).

Model Scenarios and Hydrologic Conditions

The model used in our analysis was developed by Obeysekera and others, and details on the model development, scope, and application can be found there (Obeysekera et al. 2011, 2014). The model incorporates simulations of many of the principal processes associated with the hydrologic cycle, such as rainfall (RF), evapotranspiration (ET), surface and ground water levels, and agricultural and urban water demand. Climate variables driving the model, such as RF and ET, are derived from data for the period 1965–2005, and for sea level along the coastal boundary of the model domain from daily tide gage data. The complexities of water management in south Florida with the many operational rules including water shortage policies are simulated in the model. The model is flexible enough so that current or future urban and agricultural demands and any future changes to the operating rules of the system can be implemented as components of planning alternatives. Modeling that assumes climate remains constant so that past conditions can be used to represent future scenarios (i.e., the "stationary approach") has been rejected in water resource planning (Milly et al. 2008). Therefore, to assess the effects of climate change on the GEE, several different scenarios using a "non-stationary" approach were evaluated (Obeysekera et al. 2014). Briefly, because no standard datasets for water resource planning were available, South Florida Water Management Model (SFWMM) modelling scenarios were developed from the projections of global circulation models (GCMs) and statistically downscaled data for the region. Both GCMs and downscaled data showed a positive change in temperature, with a median value of 1.5 °C. However, the precipitation responses were not consistent and could be either positive or negative dependent on the model used, so a ±10 % range was selected as representative and it was toward the middle of the range of values produced (Obeysekera et al. 2014). The sea level rise projection was the unified value from the Southeast Florida Regional Climate Change Compact (SFRCC 2011). The resultant SFWMM model runs subsequently incorporated these different climate scenarios; *a* ± 10 % −RF and +RF, a 10 % +ET, a 1.5 °C temperature increase, and a 0.5 m rise in sea level. In addition, Everglades restoration has a 50-year planning horizon; therefore, this timeframe was used to assess change.

The effect of the climate change scenarios on biogeochemical processes is closely tied to the resultant hydrologic conditions, particularly the spatial extent and duration of different hydroperiods. We examined the hydroperiods for current (base; water use demands and operations as of February 2012) and end-member conditions (−RF, +ET and +RF, +ET) for the 41 year average (1965–2005). Under base conditions annual hydroperiods throughout much of the Water Conservation Areas (WCAs) average 330–365 days, with a few zones in northern WCA1 and WCA3A and central WCA2A averaging 300–330 day hydroperiods, and WCA2B divided between equally divided into long and medium hydroperiods (Fig. 2a). Within Everglades National Park (ENP), Shark River Slough (SRS) generally has 300–330 days hydroperiods, while for the wet prairies to the northwest of SRS hydroperiods range from 180 to 300 days and the southern marl prairies/rocky glades have considerably shorter hydroperiods, ranging from <60 to 180 days. The increased RF scenario is very similar to the base, with the most notable response being increased groundwater levels near the coast due to increased sea level associated with elevated temperatures. More subtle, but distinct changes include increased hydroperiods in SRS and the wet prairies to its northwest (Fig. 2b). However, the scenario that has the greatest impact on hydroperiod is −RF, +ET (Fig. 2c). With reduced RF, the entire system experiences significantly shortened hydroperiods, SRS narrows, and sea level rise affects the coast. Given that climate patterns vary on any given year, reduced RF effects may be more extreme than those reflected under this average scenario, and in fact, in a dry year (e.g., 1989, a LaNina year), reduced RF will result in the majority of the GEE experiencing drastically shortened hydroperiods of 0–60 days (Fig. 2d).

Our approach in examining the impacts of climate change on biogeochemical processes in wetland soil was to employ (1) a big picture perspective, (2) identify regional impacts at areas of particular concern to the ecosystem (hot spots), and (3) examine trends at the ecosystem scale. To assess the impacts of climate change (increased temperature, increased/decreased RF, etc.) on biogeochemical processes in soils, we evaluated the GEE in context of their hydrologic units, but with a focus on key zones within each unit (overdrained, ponded, nutrient-enriched, etc.). The impacts of different climate change scenarios were evaluated qualitatively, with the evaluation presented (very negative, −; negative, −; neutral, 0; positive, +; very positive, ++) in terms of relative plus or minus impacts on the element in question (C, N, P, S, Hg). A change in hydroperiod of ±30 days was considered within the modelling error in terms of impact, while a ±60 day change was considered to have a significant effect on soil chemistry. We used habitat hydroperiods from McVoy et al. (2011) to guide decisions on accumulation versus loss of different soil types (peat, marl, etc.). We also wanted to assess gaps in the current understanding of the system that might be areas for future research related to biogeochemical processes in wetland soils and the impact of climate change on these processes.

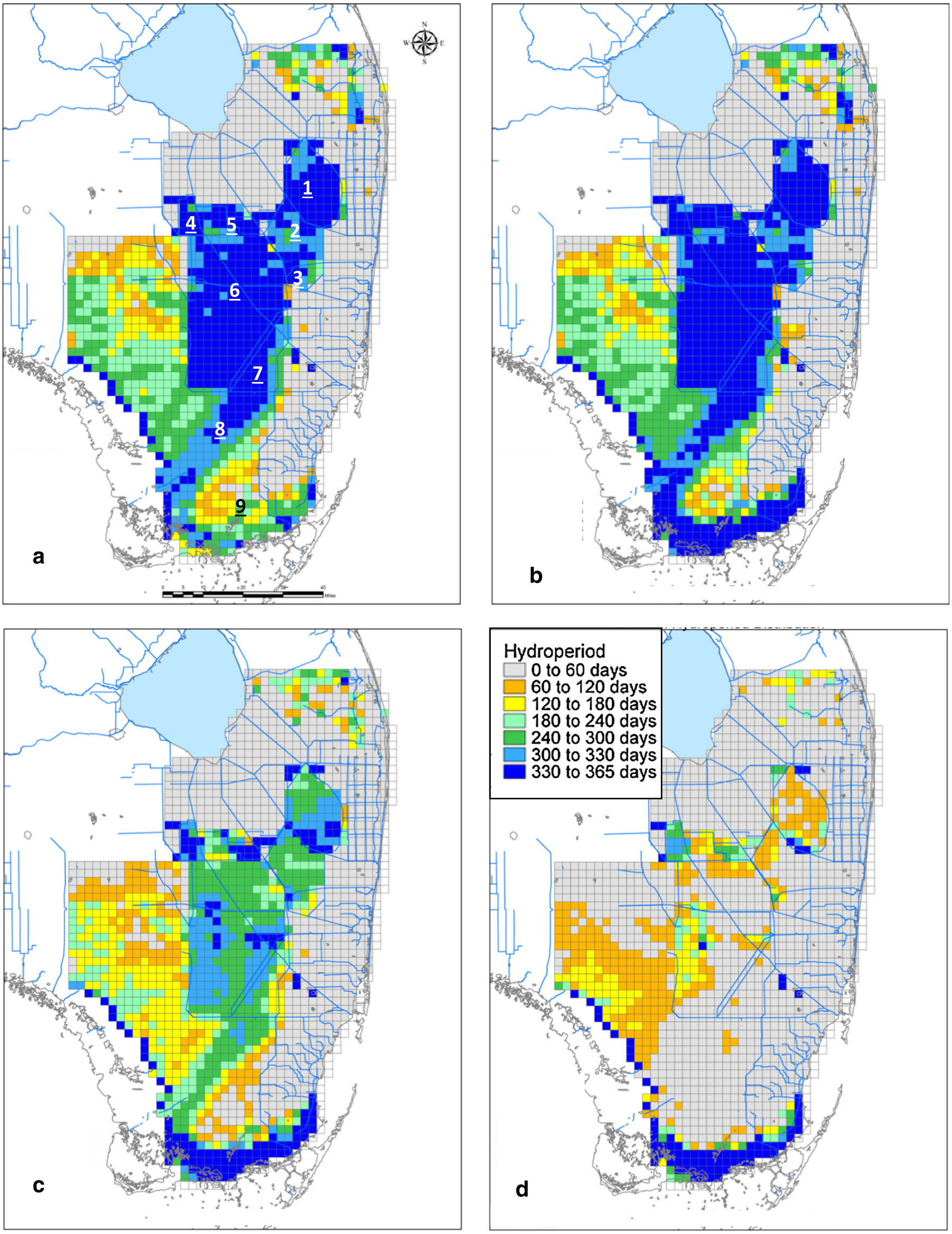

Fig. 2 Average systemwide hydroperiods produced by the SFWMM throughout different Greater Everglades Ecosystem hydrologic areas; 1-WCA1, 2-WCA2A, 3-WCA2B, 4-Rotenberger, 5-Holey Land, 6-WCA3A, 7-WCA3B, 8-Shark River Slough, 9-Taylor Slough. *Blue lines* on map are canals. Maps represent **a** base average of the 41-year simulation period (1965–2005), **b** increased RF, increased ET 41 years average, **c** decreased RF, increased ET 41 years average, **d** annual average decreased RF and increased ET hydroperiods for a dry year, 1989. Modeling scenarios and assumptions described in the text (Color figure online)

Carbon

Carbon Cycle and Biogeochemistry

A characteristic common to many wetlands is the accumulation of organic matter (OM) derived from internal or external primary productivity. The presence of saturated or inundated conditions for significant time periods promotes anaerobic conditions that reduce the rate of OM oxidation with respect to the rate of production. The majority of the GEE, in its natural state, accumulates OM derived from primary productivity (vascular plants and periphyton) as organic soil. Under historic hydrologic conditions, this accretion process resulted in vast peat deposits (0.5− 3+ m in depth) representing >5,000 years of soil genesis. In shorter hydroperiod areas (low organic soil accumulation), dominated by calcareous periphyton, large amounts of inorganic C in the form of calcite (marl) are deposited in soils (Gleason and Spackman 1974).

The ability of the GEE, and wetlands in general, to serve as OM, and thus C, sinks is greatly influenced by several factors. General biotic factors include OM production and quality (DeBusk and Reddy 2005; Cadisch and Giller 1997) and rate of microbial decomposition (DeBusk and Reddy 1998; Wright and Reddy 2001a); however, abiotic factors such as hydrology (Corstanje and Reddy 2004), temperature (Inglett et al. 2012; Fierer et al. 2005), nutrient availability (Wright and Reddy 2001b; Amador and Jones 1995), and presence of alternative electron acceptors (McLatchey and Reddy 1998; Reddy and DeLaune 2008) may have equal or greater influence on C accretion rates.

Organic soil accumulation in the GEE is a slow process, with only 1–2 mm accreting at the soil surface annually (Craft and Richardson 1993; Reddy et al. 1993). The predominance of long hydroperiods (8–12 months a year) maintains anaerobic conditions and allows for the continued accretion of organic soils. In the event of drawdown or prolonged dry periods, aerobic conditions facilitate microbial oxidation of soil organic matter at a rate ~20× faster than accretion. Portions of the historic GEE south of Lake Okeechobee and north of WCA1 have been drained for agricultural development resulting in subsidence in excess of several meters in the last 75 years (Snyder 2005; Stephens 1956). This massive loss of organic soil serves as a potent example of how tenuous organic soil resources can be in the GEE region.

Similarly, anthropogenic alteration of hydrology and nutrient conditions (eutrophication) have had significant detrimental effects on soils within the remnant ecosystem (Reddy et al. 2011; Scheidt and Kalla 2007; Davis and Ogden 1994). Soil oxidation resulting in subsidence is of considerable concern due to subsequent loss of ecosystem services (C storage) and environmental integrity. On average, C represents 47 % of OM by mass in modern day GEE soils (Reddy et al. 2005). The remaining mass includes plant essential elements such as N, P, S, and contaminants such as Hg as well as others, that are bound in the OM matrix (Osborne et al. 2011a). Therefore, processes governing the cycling of C in the GEE are of important not only for their effect on C, but also because they exert control over cycles of nutrients and contaminants bound in the soil matrix (Osborne et al. 2011a). Mineralization of organic C is a microbially mediated process in which macrophyte litter, periphyton biomass, and soil are decomposed to smaller, more readily available organic compounds. These compounds move through the dissolved organic C (DOC) pool ultimately being assimilated into microbial biomass or reduced to CO_2 or CH_4 via respiration or methanogenesis, respectively (Fig. 3) (Qualls and Richardson 2003; Bridgham and Richardson 1992; Wetzel 1992). Abitoic leaching of DOC from detritus or soil also contributes to the DOC pool in the soil interstitial waters or overlying water column (Osborne et al. 2007).

Baseline Conditions

Recent system wide soil surveys (Reddy et al. 2005; Scheidt and Kalla 2007) provide a detailed view of soil OM and C content (Fig. 4) from which to make baseline evaluations. There is generally a north–south gradient in peat depths, with deepest peats measured in WCA 1 (Corstanje et al. 2005) followed closely by WCA2A (Rivero et al. 2007, 2009). WCA3A contains the largest contiguous peatlands (Bruland et al. 2006, 2007); however, WCA3B, Holey Land and Rotenberger Wildlife Management Areas (HLRB), and northern WCA3A have all experienced significant soil losses in the last 50 years (Osborne et al. 2011a; Scheidt and Kalla 2007). Everglades National Park is unique in the GEE system as it is bounded by marl prairies where limestone is often exposed at the surface on both east and west sides of the main natural water conveyance feature, SRS, where organic soils persist (Osborne et al. 2011b). To a lesser extent, Taylor Slough, a much smaller drainage feature to the east of SRS, also contains limited organic soils (Osborne et al. 2013).

Currently, northern WCA1 and a majority of WCA2A are experiencing some level of peat oxidation during dry years, and accretion of peat during wet years. Soil P enrichment in these areas not only accelerates OM production but also accelerates OM processing. The northernmost portion of WCA1 is dry long enough to be accretion neutral or even somewhat negative with respect to net soil accretion annually (Fig. 4a). Northern WCA3A, WCA3B, and HLRB are accretion neutral under normal conditions and negative in dry years. Central/south WCA3A is chronically flooded (Watts et al. 2012), and thus positive

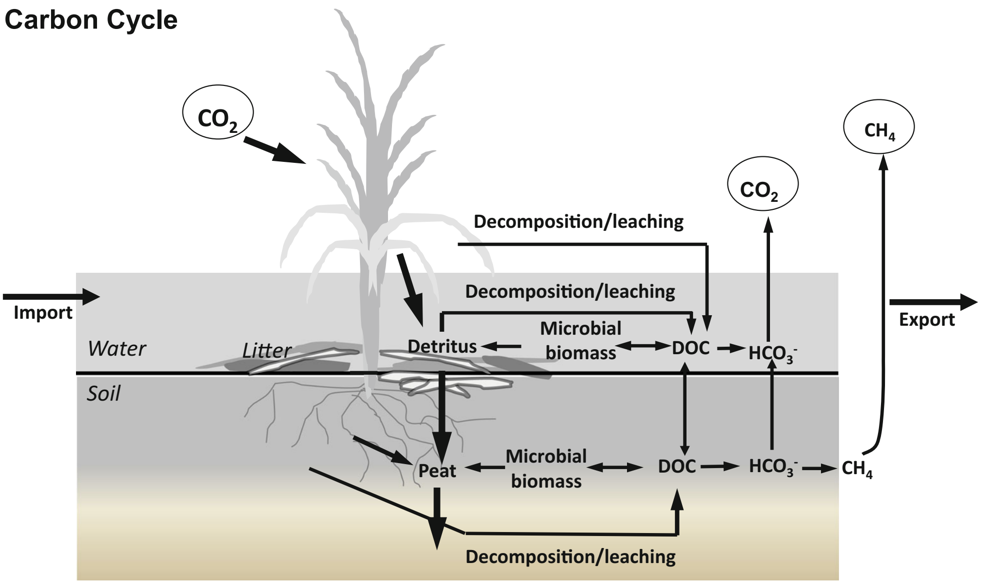

Fig. 3 The carbon cycle for a freshwater wetland like the Everglades (adapted from Reddy and Delaune 2008)

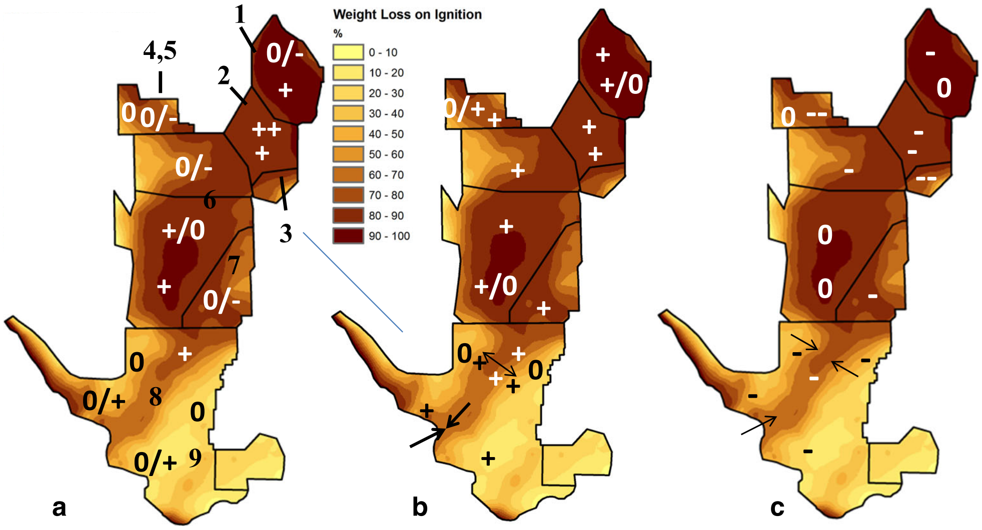

Fig. 4 Map of loss on ignition (LOI) for the Greater Everglades Ecosystem, a proxy for organic carbon in the ecosystem. Conditions for carbon accumulation/no change/loss in wetland soil is indicated for various areas of the ecosystem using the terminology (++, +, 0, −, −−) described in the text. **a** Baseline, **b** 10 % increased RF, **c** 10 % decreased RF. *Arrows* indicate flow directions or narrowing of channels. Modified from Osborne et al. (2013). Greater Everglades Ecosystem hydrologic areas; 1-WCA1, 2-WCA2A, 3-WCA2B, 4-Rotenberger, 5-Holey Land, 6-WCA3A, 7-WCA3B, 8-Shark River Slough, 9-Taylor Slough

net accretion is occurring there in both wet and most dry years. Shark River and Taylor Slough both are net positive (+) in wet years and net negative (−) in dry years giving an average net change of 0 (Fig. 4a). Similarly, the marl prairies, which do not accrete organic matter (except in solution holes, where some organic-rich soil is accreted), rather inorganic calcite is not generally affected by wet or dry years. The northern-most portion of SRS, due to nutrient enrichment (Osborne et al. 2013) and baseline flow, maintains a net positive accretion for wet and most dry years under current conditions. Coastal interfaces in the mangrove fringe of southern ENP are not greatly affected by wet or dry years. Most accretion in these areas is due to mangroves and thus is net neutral to positive.

Climate Scenario Increased Rainfall

Under the climate change scenario of a 10 % increase in annual RF, it is predicted that overdrained areas of WCA1, WCA2A, WCA2B, HLRB, northern WCA3A, and 3B will receive more water promoting peat accretion (Fig. 4b). Areas of net peat accretion in the baseline condition

(Fig. 4b) will continue to do so under similar hydroperiods. Uncertainty exists with respect to some areas such as southern WCA3A where ponding depths are already known to be inhibitory to vegetation (Watts et al. 2012), hence the assignment of a neutral/positive (+/0) accretion score. These areas, under increased RF, may be susceptible to becoming open water habitats. Dry years are anticipated to cause persistent soil oxidation in areas currently experiencing subsidence under baseline conditions, such as northern WCA1, 2A, 3A, and HLRB. Increased freshwater flow down SRS and Taylor Slough expand the inundation and hydroperiod of adjacent areas (east and west) of the sloughs and under wet years will promote peat accretion in these areas, but likely no change under average years (0). Further, increased flow is anticipated to reduce saltwater intrusion and subsequent peat erosion.

Climate Scenario Decreased Rainfall/Increased Evapotranspiration

For soil oxidation and resulting C mineralization, this scenario of decreased RF and increased ET is the most concerning (Fig. 4c). Under this scenario, what is considered a dry year under baseline condition may become the normal condition. Additionally, increased ET will accelerate drying and in effect shorten the hydroperiod even further. This will result in HLRB, WCA1, 2A, 2B, 3A, and 3B being significantly drier under dry year conditions; leading to significant peat oxidation. Hence, areas already known to be experiencing oxidation were substantially negative with respect to accretion of organic matter and received two negative (−) scores (Fig. 4c). ENP, at end of the water flow pipeline, will experience significant drying. This will result in narrowing of Shark River and Taylor Sloughs and increased oxidation of peat (−). Decreased hydroperiod will also reduce marl deposition in marl prairies to the east and west of SRS, especially in the northern extent of ENP (−). Decreased flow in Shark River and Taylor Sloughs will result in increased salt water intrusions that will exacerbate peat erosion.

Under dry year scenarios, fire, a natural disturbance in the GEE (Watts et al. 2012; Wade et al. 1980), has the potential to be devastating. Excessively dry conditions can foster extensive peat fires that are likely to burn unhindered due to logistical difficulty in suppressing peat fires in back country locales. Under dry conditions, fire frequency will also likely increase, further exacerbating loss of organic soils to fire. Finally, saltwater intrusion may also be extensive resulting in dramatic mortality of salinity sensitive vegetation. Loss of vegetation results in loss of soil cohesion and subsequently will accelerate soil losses from peat erosion.

Nitrogen

Nitrogen Cycle and Biogeochemistry

Both N and C are major constituents of organic matter and as such, are tightly coupled. Greater than 95 % of the total N in wetland soils is present in the organic N pool, while the remaining inorganic N is primarily ammonium N. Major sources of N to wetland ecosystems include atmospheric deposition, sediment and nutrient loading, and biological N_2 fixation (Fig. 5). The amount of N accumulated in wetland soils depends on the balance between plant production and decomposition and the balance between allochthonous import and particulate export. Because C and N are tightly coupled, N accumulation is highly correlated to C accumulation, with 0.064 g N m^{-2} $year^{-1}$ per g C m^{-2} $year^{-1}$ as observed in the GEE WCA2A (Reddy et al. 1993). Nitrogen fixation is the process whereby atmospheric N_2 is converted to ammonia by certain types of bacteria and algae, where N is generally incorporated into cell structures. Most N fixation occurs in the aerobic water column by algae and N-fixing bacteria, although some bacteria can fix N in anaerobic soil. Biological N_2 fixation contributes approximately an equivalent amount of N to wetlands as atmospheric deposition (0.5–1.0 g m^{-2} $year^{-1}$). In eutrophic areas of the GEE (e.g., areas receiving discharges of agricultural drainage), P inputs have led to increasing N limitation of the system as evidenced by a lowered water column N:P (TN:TP <30) and algal nutrient limitation assays (McCormick et al. 1996; Inglett et al. 2004). Nitrogen transformations in the GEE are controlled by the same interdependent variables that regulate wetland formation and development; climate, hydrology, soils, and vegetation. Nitrogen is unique as it is governed by a range of oxidation–reduction reactions and array of biotic and abiotic transformations in which it participates, and the diversity of states (soluble, gaseous) in which it exists. Several N transformations are influenced by changing climatic conditions (see reviews by Hefting et al. 2004; Buresh et al. 2008; Reddy and Delaune 2008; White and Reddy 2009). Soil organic N is the single largest pool of N in the GEE followed by live plant biomass and available inorganic N (White and Reddy 2000).

Changes in organic N mineralization rates by external drivers alter both the biological components of wetlands (D'Angelo and Reddy 1994; Wright et al. 2008) as well as the organic matter composition (Chen and Xu 2008). Mineralization, second to primary productivity, is an important ecosystem process that regulates recycling of nutrients stored in organic matter to bioavailable nutrients. Accretion and mineralization of organic N is governed by the turnover of OM which is influenced by oxygen status and availability of P (White and Reddy 2000). Both

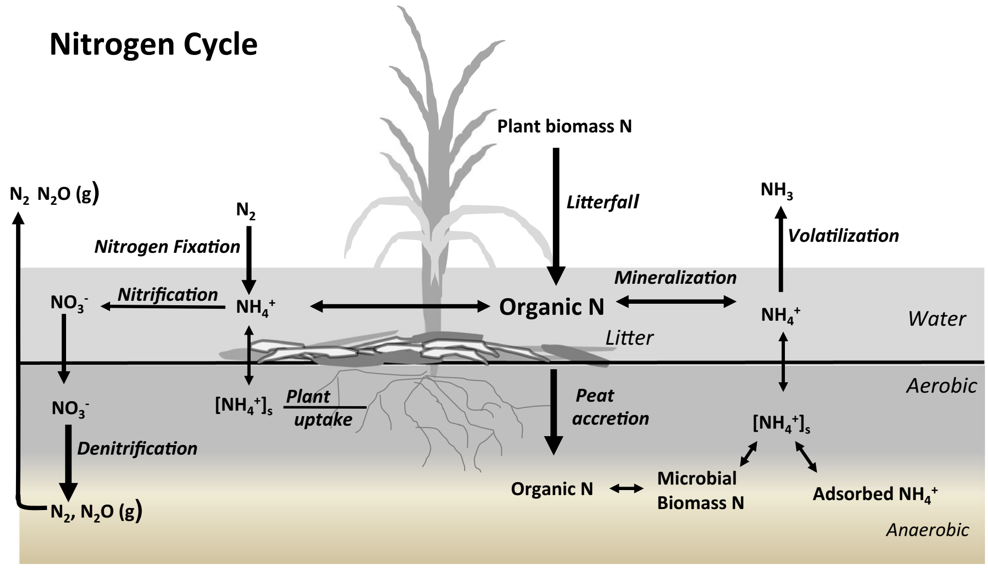

Fig. 5 The nitrogen cycle for a freshwater wetland like the Everglades (adapted from Reddy and Delaune 2008)

potentially mineralizable N (PMN) and substrate-induced N mineralization (SINM) in floc and soil layers were higher at the enriched sites of WCA2A than the unenriched sites (White and Reddy 2000). Potentially mineralizable N is significantly correlated with the microbial biomass N and soil total P. Ammonium N released during organic N mineralization is rapidly assimilated by microbes and plants. During the internal cycle between available NH_4, microbes, and vegetation, some N may be nitrified to NO_3 in aerobic portions of the soil. The NO_3 formed has several fates which may tend to either conserve N (uptake and dissimilatory reduction to NH_4) or lead to its loss (denitrification). Both nitrification and denitrification operate at rates far below their potential and under proper conditions (e.g., draining or fluctuating water levels) may accelerate and increase overall N loss from the system (White and Reddy 2003).

Baseline Conditions

Due to close coupling of N and C in OM, total N patterns in soils follow very closely the patterns described previously for LOI and C (Fig. 4). Average C/N molar ratios are 16–20, with the greatest range observed in WCA3A (range 10–59) and the smallest range in WCA2B (15–22). N/P molar ratios are wider ranging, averaging 129–207. Specifically, 207 (range 44–490, WCA1); 150 (range 25–513, WCA2A); 145 (range 127–385, WCA2B); 129 (range 22–304, WCA3AN); 183 (range 59–362, WCA3AS) 191 (range 83–337, WCA3B); 129 (range 14–371, HLRB); and 139 (range 40–345, ENP). The lowest N/P ratios are observed in areas adjacent to inflows that are enriched by P, suggesting that some of these areas may have switched from P limitation to N limitation.

The southern marshes of the GEE are located between the WCAs and the mangrove ecotone. This area of marshes is dominated by the ridge and slough ecosystem found in the longer hydroperiod areas of SRS and the marl and wet prairies to the east and west that make up the bulk of ENP landscape. This ecosystem is the transition from primarily P-limited to N-limited as the Gulf of Mexico becomes a source of P (Childers et al. 2006). Periphyton plays a dominate role in N cycling within the southern marshes (Inglett et al. 2011). Although N cycling is clearly important in various ecosystem components, many transformations and fluxes in the N cycle remain unquantified in the southern marshes. A recent study by Wozniak et al. (2012) showed that N cycling in southern marshes is actively occurring, particularly at the marsh-canal interface. This finding has implications for downstream coastal ecosystems and for the Everglades restoration. Hydrologic conductivity is important in the southern marshes for nutrient sequestration, litter decomposition, and cyanobacterial mats. The role of water depth on organic N and subsequent environmental variables, in the southern marshes, has yet to be determined.

Climate Scenario Increased Rainfall

Increased RF will increase the hydroperiod, which can potentially increase the rate of organic N accretion and slow the rate of organic N mineralization (Fig. 6a). Longer anaerobic periods resulting from increased RF can result in accumulation of ammonium in soils. Under these conditions, distinct aerobic zones at the soil–floodwater interface. The thickness of this aerobic zone can be mediated to some extent by the photosynthetic activity of periphyton at the soil and floodwater interface. Diel fluctuations in

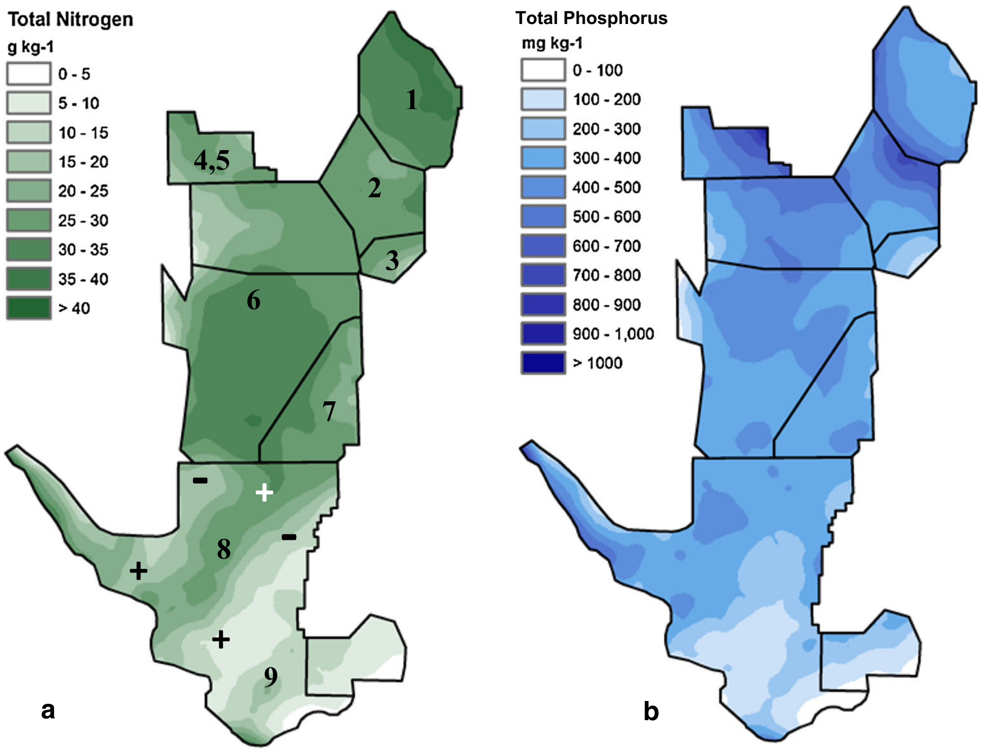

Fig. 6 Map of the Greater Everglades Ecosystem showing average **a** total nitrogen and **b** phosphorus content of 0–10 cm in soil. Baseline conditions for nitrogen or phosphorus accumulation/no change/loss in wetland soil is indicated for various areas of the ecosystem using the terminology (++, +, 0, −, −−) described in the text. Figures modified from Osborne et al. (2013). Greater Everglades Ecosystem hydrologic areas; 1-WCA1, 2-WCA2A, 3-WCA2B, 4-Rotenberger, 5-Holey Land, 6-WCA3A, 7-WCA3B, 8-Shark River Slough, 9-Taylor Slough

dissolved oxygen production and consumption in the periphyton layer can create redox gradients to support nitrification during daytime and denitrification during night time. However, these coupled reactions involving nitrification and denitrification are not quantified in the GEE wetlands. A major source of ammonium N into the surface soil layer is due to flux from underlying anaerobic soil layers, in response to sharp gradients in ammonium concentrations across aerobic–anaerobic interfaces. Increased RF can also result in increased levels of dissolved organic N (DON). Depending on RF and water movement, DON, NH_4, and NO_3 can be transported with water flow from nutrient-enriched areas into downstream. In coastal wetlands, increased salinity that accompanies sea level rise will lead to reduced denitrification and N sequestration in soil as soil organic N is mineralized to NH_4 and denitrifiers are inhibited by sulfides produced by sulfate reducing bacteria (Craft et al. 2009).

Climate Scenario Decreased Rainfall/Increased Evapotranspiration

Nitrification will likely increase due to decreased RF and development of aerobic zones in the upper soil profile. These conditions will result in increased organic N mineralization and nitrification (Fig. 6a), resulting in accumulation of nitrate N in the upper soil profile. Periphyton contribution to nitrogen fixation can decrease due to decreased RF and shorter hydroperiods. Redox gradients created due to decreased RF can support partial denitrification resulting in increased emissions of nitrous oxide. External N from surface inflows to WCAs would likely decrease due to decreased RF and shorter hydroperiods. Upon flooding of these areas, the WCAs can experience significant loads of inorganic N and DON. Many of the N cycling processes described above occur simultaneously at the interface of oxic/anoxic conditions, or at the water-table depth. Aerobic soils above the water table would likely experience more oxic conditions leading to organic N mineralization and nitrification of mineralized ammonia into nitrate. Nitrate is readily leached from soils and can accumulate in groundwater or surface waters, depending on the direction of water flow. Nitrate is produced primarily in aerobic environments, such as drained soils, which encourage heterotrophic decomposition. Conversely, nitrate is consumed in anaerobic portions of wetland soils. Nitrous oxide (N_2O), a greenhouse gas, may be produced in wetland soils during incomplete denitrification. The

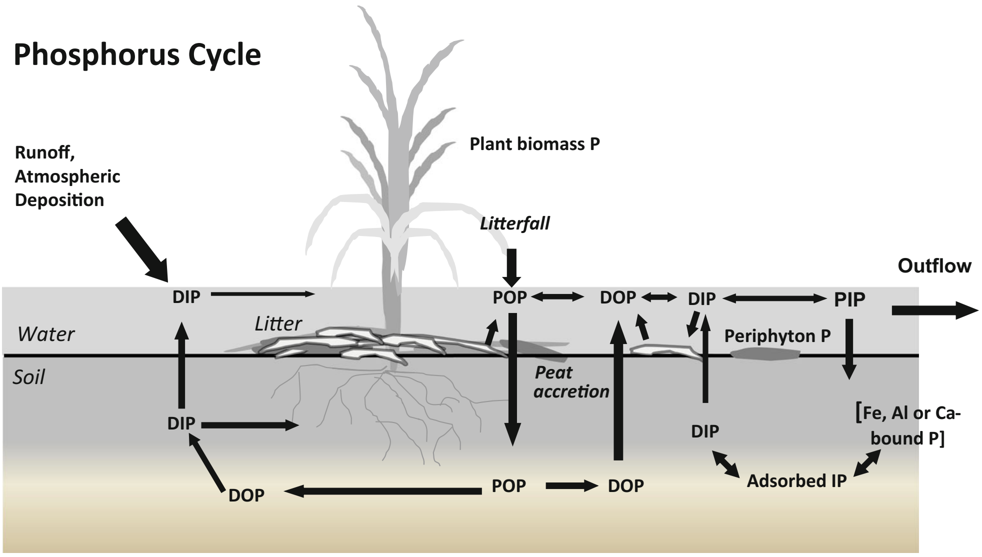

Fig. 7 The phosphorus cycle for a freshwater wetland like the Everglades (adapted from Reddy and Delaune 2008)

significance of the N_2O release from drained organic soils to the global greenhouse gas budget is probably even more important than that of CO_2 (Kasimir-Klemedtsson et al. 1997). Nitrous oxide is produced under suboxic conditions in soils as a byproduct of the microbiological processes of nitrification and denitrification. Nitrous oxide production and emission in organic soil depends on drainage and soil moisture content, with the highest flux at intermediate soil moisture content. There are large uncertainties in N_2O emission estimates, primarily due to the high spatial and temporal variability of N_2O fluxes from soil.

Phosphorus

Phosphorus Cycle and Biogeochemistry

Phosphorus is an essential macronutrient that is associated with fundamental building blocks (DNA, RNA), energy (ATP), and structure (membranes—phospholipids, bones—calcium phosphates) of all living organisms. Phosphorus is also found in the environment in inorganic forms. Under alkaline conditions, inorganic P is found primarily associated with calcium and magnesium compounds, while in acidic systems it is more frequently associated with iron and aluminum, either directly within the chemical structure or via adsorption. Phosphate availability is strongly influenced by pH and redox conditions. For example, under anaerobic conditions, P associated with reduced Fe^{2+} is soluble, while under oxidized conditions, the resultant Fe^{3+} phosphates are insoluble. This is in contrast to the cycling of organic P forms, which are hydrolyzed under higher energy oxidized conditions due to increased microbial activity, and tend to remain more tightly associated with organic material due to slower decomposition rates under anaerobic conditions. A simplified diagram of the wetland P biogeochemical cycle highlights the close coupling between organic and inorganic pools (Fig. 7). The majority of P in the GEE is stored in peat as organic P. In upland soils inositol phosphates, a fairly stable form of P, dominate this pool. However, at least in the northern Everglades peatlands, the organic P pool is dominated by phosphate diesters (Turner and Newman, 2005) which while a main input of organic P to soils are generally rapidly degraded (Bowman and Cole 1978). Diesters can be stabilized under strong acidic or clay soils, neither of which exist in the GEE, thus the stability of organic phosphodiesters in GEE soils is as yet unknown. While less spatially extensive, in calcareous, shorter hydroperiod areas of the ecosystem, P is associated with calcium, e.g., hydroxyapatite ($Ca_5(PO_4)_3OH$).

Typically, in freshwater ecosystems, P is often present in low concentrations and it is the limiting nutrient in bacterial, algal, and macrophyte productivity. The GEE is predominantly a P-limited ecosystem, with a tightly knit P cycle with rapid turnover and assimilation (Li et al. 2011; Noe et al. 2001, 2003). While the vast majority of the system historically had low P concentrations in the soils, it was not a homogeneous environment; small patches of highly P-enriched soil concentrations were observed in areas of high biological activity such as alligator holes and tree islands. Since the construction of the water management features and the development of the surrounding area, the ecosystem has experienced significant increased P inputs. The change in species and community composition of the ecosystem in response to nutrient enrichment is one of the most well-documented topics in the GEE ecology (Childers et al. 2003; Craft and Richardson 1993; Gaiser et al. 2005; McCormick et al. 2002). Because P is the limiting nutrient, increased P loads have resulted in higher plant and microbial productivity, dramatic increases in rates of peat accretion and decomposition (Newman et al. 2001; Reddy et al. 1993), greater production of surface detritus and, ultimately, sequestration of high P concentrations in floc and soil layers (Reddy et al. 1998). A large proportion of the total P is accounted for in organic P, indicating tight coupling between P and C accumulation in the GEE, with 0.0035 g P m^2 $year^{-1}$ per g C $m^{-2}year^{-1}$ (Reddy et al. 1993). As noted above, areas closest to inflow with greatest P enrichment have resulted in N limitation, which in turn will feedback to C cycling.

Baseline Conditions

The majority of the GEE landscape is a peatland with total P concentrations in unimpacted areas averaging <500 mg/kg (Fig. 6b). In contrast, at the southern extent of the system, the marl prairies are the most P-depauperate part of the ecosystem, with floc and surface soil total P concentrations generally averaging 140 and 300 mg/kg, respectively (Osborne et al. 2011a). A prominent characteristic of the modern GEE is zones of high total P concentrations associated with inflow structures and canals, particularly the northern part of the system (Osborne et al. 2011b; Fig. 6b). The most well-documented and spatially extensive evidence of increased P load on wetland biogeochemistry is south of the S10 structures in northeastern WCA2A, where over 4 decades of elevated P, primarily from agricultural runoff (McCormick et al. 2002; Zielinski et al. 2000), produced a P enrichment gradient extending downstream over 7 km into the marsh (Sklar et al. 2005). Highly nutrient-enriched areas such as these, with legacy P, are ecologically significant and provide an important driver of C and N cycling (Reddy et al. 2011), and in turn mediate the response of C and N to climate change.

The highest total P concentrations in the ecosystem, on a mass basis, are due to external loading; however, P has also become concentrated in the system as a result of overdrainage. Oxidation of peat soils results in the mineralization of organic C and the associated N, and when sufficiently severe, breakdown to gaseous end products which are subsequently lost to the atmosphere. Gaseous loss of P from wetlands as phosphine, while thermodynamically possible, has rarely been reported and only in trace amounts (Devai and Delaune 1995). So in contrast to C and N, P is not lost from the system in response to soil oxidation, instead it is conserved. While not always apparent as increased contents (mg/kg), P enrichment in response to organic soil mineralization becomes obvious when linked to changes in soil volume. For example, over twofold increases in volumetric total P concentrations were observed in overdrained areas such as northern and northwestern WCA3A (Bruland et al. 2006, 2007). In extreme cases, where oxidation has led to peat fires and soil loss, organic P is more comprehensively converted to inorganic P, and overall total P levels increase due to the extensive physical reduction of the soil profile (Smith et al. 2001).

Climate Scenario Increased Rainfall

The effect of most concern under the increased RF scenario is the expectation of greater quantities of fertilizer and particulates due to higher run off from the Everglades Agricultural Area (EAA) and urban areas, resulting in increased P discharge through water control structures. The relative ability of the stormwater treatment areas (STAs—marshes constructed along the EAA-Everglades border for P removal) to settle and assimilate this additional P will dictate whether increased RF will exacerbate eutrophication downstream. While some downstream areas are already P-enriched, additional P loading will cause nutrient enrichment gradients to extend further downstream into areas that are currently unenriched.

Independent of external P sources, the P content of rain collected from the GEE is low, thus spatially distributed increased RF is not likely to cause a change in P concentrations throughout the ecosystem. However, indirectly, increased RF may cause internal changes due to increased flows and greater inundation. Assuming RF increases are sufficient to cause greater mass movement of water this will result in increased rates of P supply which may cause local nutrient loading stimulating primary productivity. If RF increases are sufficient to increase marsh flows causing sediment entrainment, then redistribution of floc and its associated nutrients will occur across the landscape, helping maintain or redevelop the ridge and slough landscape. In cases where increased RF causes excessive inundation, the associated decrease in pH in neutral to alkaline soils may cause the breakdown of more stable pools, such as calcium phosphates, resulting in the release of readily available P.

In the modeling scenarios provided, increased RF resulted in a wetter and slightly extended wet season. If the RF were to cover more of the dry season, the increased RF would have the benefit of counteracting seasonal organic soil oxidation following dry out of the marshes. Similarly, in the southern coastal GEE, increased RF during the dry season would be particularly beneficial in minimizing the seasonal increases in surface water P that occur following mobilization of P from limestone bedrock by high-salinity ground water (Koch et al. 2012; Price et al. 2010).

Climate Scenario Decreased Rainfall/Increased Evapotranspiration

Because the majority of P stored in the GEE is in organic forms, changes that have significant effects on C cycling will have a concomitant influence on P. Of the various scenarios, decreased RF and increased ET will have the most catastrophic impact on peat soils in the landscape. Laboratory studies show GEE soils are capable of producing trace amounts of phosphine gas, and this pathway is increased under elevated P concentrations and in the presence of labile organic C (Devai and Delaune 1995). Increased decomposition of organic C under oxidized conditions may stimulate P loss via phosphine gas in enriched areas. However, these trace amounts will be overwhelmed by the primary effect of overdrainage on P cycling in organic soils; the conversion of organic P to inorganic forms, which will cause internal eutrophication and conditions amenable to cattail invasion (Newman et al. 1998). As noted previously, severe cases of decreased RF and increased ET resulting in peat fires cause immediate localized P enrichment and the creation of a highly bioavailable P pool (Smith et al. 2001; Smith and Schindler 2009). In addition, upstream of the GEE, decreased RF, and increased ET will increase soil loss in the organic soils of the EAA and in upland areas, thus producing greater external P loads.

Sulfur

Sulfur Biogeochemistry

Sulfur is an important element in wetland biogeochemistry, primarily because of its role as a metabolic terminal electron acceptor in microbial sulfate reduction. Sulfate-reducing bacteria reduce sulfate to sulfide during the degradation (oxidation) of OM under anoxic conditions (Rheinheimer 1994); in wetlands this typically occurs in saturated soils. Microbial sulfate reduction is also important in the recycling of nutrient elements (C, N, P), regulation of redox conditions, and control of many metal ion concentrations through formation of insoluble metal sulfides and redox control of metal solubility. High levels of sulfate loading to freshwater wetlands may lead to excessive release of nutrients from the soil, a process often referred to as internal eutrophication (Lamers et al. 1998). Release of phosphate and ammonium from peat soil at sulfate levels of 50–100 mg/L has been demonstrated in the GEE from mesocosm experiments (Axelrad et al. 2007). Sulfate is also a plant nutrient required in about the same amounts as P (Hawkesford and DeKok 2007), but rarely limiting with sulfate levels 100–1,000 fold higher than P (Orem et al. 2011). An important environmental impact of microbial sulfate reduction is the methylation of inorganic mercury to methylmercury (Fig. 8), a highly bioaccumulative neurotoxin and endocrine disruptor discussed in “Sulfur” section of this paper.

In the biogeochemical cycle of S in the freshwater Everglades (Fig. 8), S enters the ecosystem as sulfate in rainwater, groundwater, and discharge of canal water. For much of the ecosystem, sulfate from the discharge of canal water is the main source of S and drives S biogeochemistry. At least 60 % of Everglades marshes have sulfate levels above the maximum background level of 1 mg/L due to sulfate loading from canal discharge (Scheidt and Kalla 2007). It is likely that the pre-development GEE was a low sulfate wetland (sulfate levels of $\ll$1 mg/L), and the dominant soil microbial processes were fermentation and methanogenesis. Sulfate in canal discharge likely originates from sulfur use in agriculture (Ye et al. 2000), and soil oxidation in the EAA (Corrales et al. 2011). Sulfate in Everglades surface water diffuses into the anoxic soil and overlying flocculant layer where microbial sulfate reduction occurs (Fig. 8). Sulfide from microbial sulfate reduction may accumulate in soil porewater and diffuse back to surface water, where oxidation to sulfate by sulfur oxidizing bacteria occurs. Sulfide is highly reactive with organic matter in soils to form organic S, or with metals to form insoluble metal sulfides (e.g., pyrite). This sequesters a fraction of the sulfur entering the ecosystem, with organic S as the major sink for S in the GEE peat soil (Bates et al. 1998). Sequestered organic S and metal sulfides may be oxidized back to sulfate by drought or fire, and the sulfate remobilized after rewetting of the marsh.

The S cycle in the marine portion of the GEE is generally similar to that described above, but the major source of S in the coastal and marine environment is sulfate in seawater (Fig. 8).

Baseline Conditions

Sulfur distributions and biogeochemistry in the freshwater GEE are dominated by sulfate in canal discharge at the northern end of the ecosystem (Orem et al. 2011), which also impacts soil sulfur levels (Fig. 9a). The highest average surface water sulfate concentrations in the freshwater GEE are found in canal water in the EAA. STAs generally receive high sulfate loads from EAA canals, and have elevated surface water sulfate concentrations (e.g., 20–60 mg/L in STA 1 W, and 70–100 mg/L in STA 2; Scheidt and Kalla 2007; Garrett and Ivanoff 2008). Sulfate loading to the GEE has been linked to increas microbial sulfate reduction, mercury methylation (Orem et al. 2011), and excessive ammonium and phosphorus release from wetland soils via internal eutrophication (Axelrad et al. 2007).

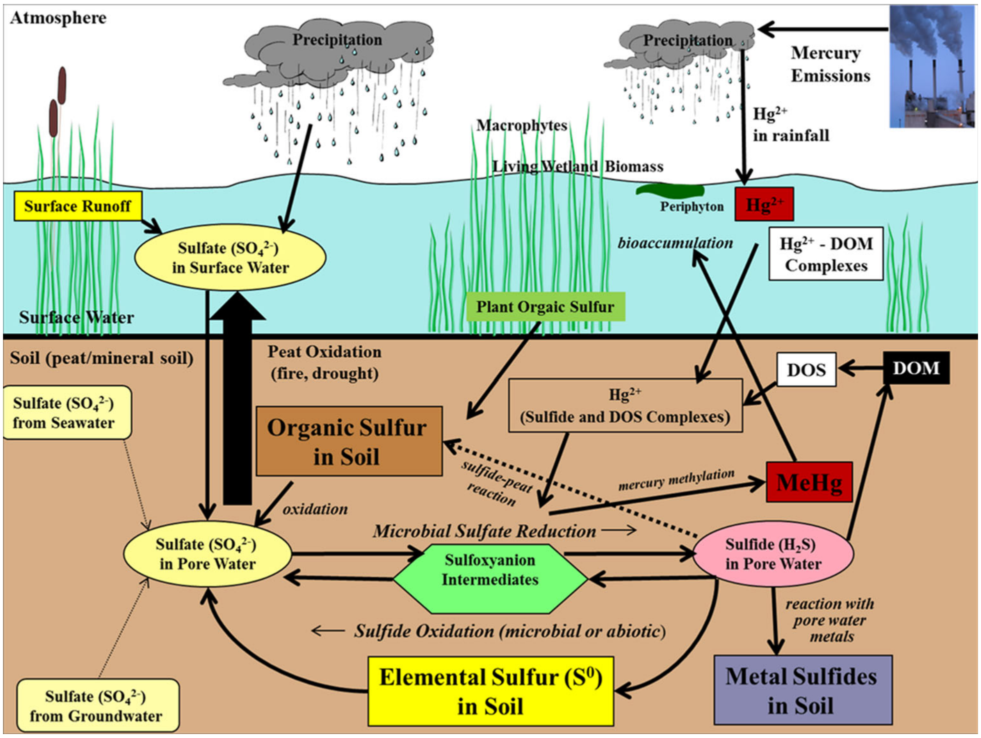

Fig. 8 The sulfur and mercury cycle for a freshwater wetland like the Everglades; sulfur and mercury cycles are closely linked

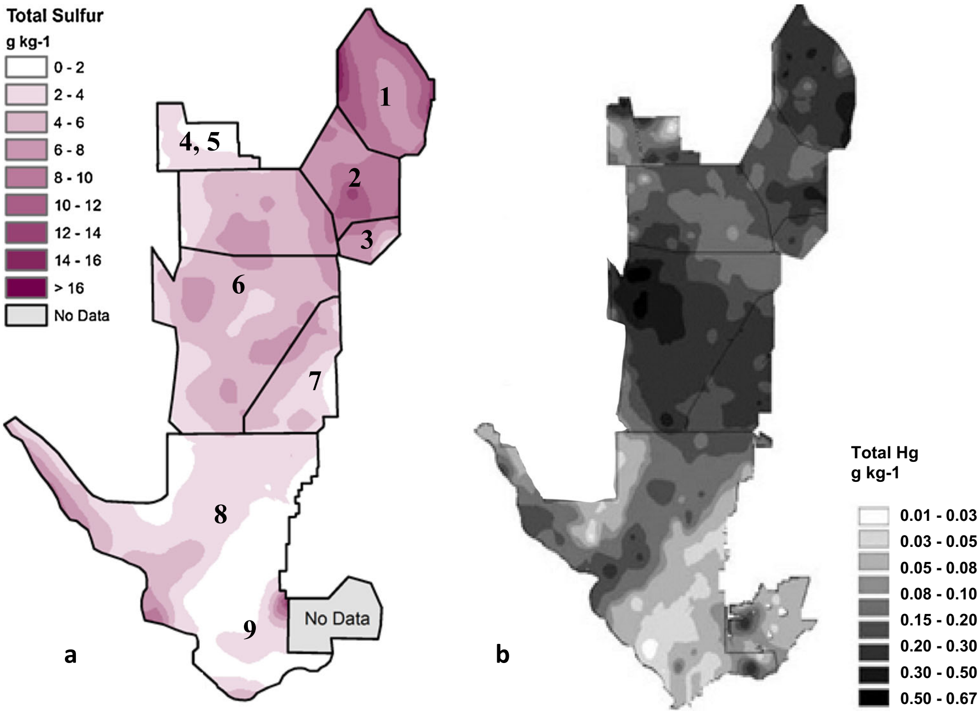

Fig. 9 Map of the Greater Everglades Ecosystem showing average **a** total sulfur and **b** mercury content of 0–10 cm in soil. Figure a modified from Osborne et al. (2013), figure b from Cohen et al. 2009. Greater Everglades Ecosystem hydrologic areas; 1-WCA1, 2-WCA2A, 3-WCA2B, 4-Rotenberger, 5-Holeyland, 6-WCA3A, 7-WCA3B, 8-Shark River Slough, 9-Taylor Slough

Sulfate concentrations in GEE marshes currently range from <0.05 mg/L in areas distant or protected from canal discharge, to 100 mg/L near canal or STA discharges (Payne et al. 2009; Orem et al. 2011). There is an overall gradient in sulfate concentration from north (higher) to south (lower) in the GEE, reflecting the presence of the EAA at the northern end of the ecosystem. However, elevated sulfate concentrations occur near major canals throughout the ecosystem. The most S-enriched marshes are in WCA2A, and northern WCA3A (Scheidt et al. 2000;

Orem et al. 2011). Surface water sulfate concentrations across the GEE tend to be highest during the wet season due to the pumping of stormwater from the EAA into the GEE for flood control. Concentrations of sulfate in EAA canals and points of discharge into the ecosystem can exceed 100 mg/L in the wet season, but are typically <30 mg/L in the dry season (Scheidt and Kalla, 2007).

In freshwater ENP, sulfate concentrations in surface water are generally <1 mg/L, except for sites near canal discharge in the north. Regional Environmental Monitoring and Assessment Program (REMAP—a USEPA Program to examine GEE chemistry) data from the 1995, 1996, 1999, and 2005 wet seasons indicate elevated sulfate levels (5–10 mg/L) penetrating into the Shark Slough marsh near the L-67 canal terminus within ENP (Stober et al. 2001; Scheidt and Kalla 2007). Sulfate concentrations in marsh surface waters exhibit substantial temporal variability due to changes in RF and canal discharge, seasonal drying and rewetting cycles, and perhaps the timing of additions of agricultural chemicals to soils in the EAA. Longer-term temporal trends are superimposed on this shorter-term variability, and result from structural changes in water flow to the ecosystem. For example, the opening of STA 2 has resulted in increased loading of sulfate to the northwest portion of WCA2A, while surface water sulfate concentrations at marsh sites in eastern WCA2A have shown significant downward trends over time due to rerouting of canal water through STA 2 (Garrett and Ivanoff 2008; Orem et al. 2011). The temporal variability of sulfate concentrations in different parts of the ecosystem highlights the many factors that influence sulfate levels, most importantly the discharge and movement of sulfate-enriched canal water.

Drought and fire are natural environmental factors in the GEE (Gunderson and Snyder 1994; Lodge 2004). Fire and drought degrade organic soil, releasing reduced S sequestered in the soil as organic S or metal sulfides, and oxidizing the released sulfur to sulfate (Fig. 8). This sulfate may be remobilized by later rewetting of the wetland surface when RF returns. Anthropogenic changes to the ecosystem, especially water demands of urban and agricultural areas and water management practices, have resulted in more severe drought and fire cycles within the ecosystem compared to pre-development periods (Wu et al. 1996; Lockwood et al. 2003). Climate change is also very likely to impact fire and drought cycles within the GEE (Beckage et al. 2003; Pearlstine et al. 2009).

Climate Scenario Increased Rainfall

Sulfate in canal water discharge dominating the S biogeochemistry of the freshwater GEE originates within the EAA from the use of S in agriculture, and the oxidation of aerated organic agricultural soils. In the aerobic agricultural soils, S added or present in different forms is oxidized to highly soluble sulfate. This sulfate is mobilized during rain events and flows into small farm canals, and then into larger canals, and is eventually discharged into the GEE. While the canal water is often moved through STAs to remove P, little change in sulfate concentration occurs. Under an increased RF climate scenario, sulfate loading to the ecosystem is likely to increase due to increased runoff of sulfate from the EAA (increased runoff of other elements like P and some metals is also likely). Agricultural fields are pumped dry as needed to maintain aerobic soil conditions, so it is unlikely that increased RF will change soil oxidation patterns within the EAA. The amount of additional sulfate loading to the ecosystem from increased RF is unknown, and is an area for future research. Future land use changes in the EAA resulting from effects of climate change on agriculture (e.g., residential or business development replacing agriculture) could result in increased soil oxidation and sulfate release during rain events as the water table is lowered for these other land use options.

Increased RF may also increase the S loading to the ecosystem from wet deposition, as more atmospheric S could be washed out. Currently, rainwater from the northern GEE has sulfate concentrations ranging from <1 to 2.5 mg/L (Bates et al. 2002; McCormick et al. 2011), and rainwater from ENP has an annual volume-weighted mean of 0.5–0.7 mg/L sulfate (NADP 2008). The additional sulfate in RF, however, is likely to be far less than that from canal discharge. In addition, increases in sulfate in RF may be offset by drops in dry deposition of sulfur. Data on dry deposition of sulfate and total S in south Florida are not readily available. Data from other areas of North America show that dry deposition of sulfate and total S is always less than or equal to wet deposition (USEPA 2006).

Of particular concern is a scenario of overall increased RF, but with extreme seasonality. This could represent the worst case scenario causing (1) increased oxidation during the dry period of both EAA and marsh soil sulfur to sulfate, and (2) increased RF and sulfur loading during the wet season. An example of the magnitude of sulfate release from oxidation of peats occurred in May/June 1999 when drought and fire affected most of northern WCA3A. Prior to the drought and burn surface water sulfate concentrations in this area averaged about 7 mg/L (Orem, unpublished data), but surface water sulfate levels in June 1999 at 14 sites in northern WCA3A averaged 58 mg/L, with some sites in the 100’s of mg/L sulfate (Gilmour et al. 2004). A year later (September 2000), sulfate levels at these 14 sites averaged 5 mg/L, similar to preburn levels. Soil oxidation may also lead to C loss from peat oxidation, and release of phosphate and nitrogen from the peat soil, as mentioned earlier.

The modeling scenarios for increased RF indicate a wetter and slightly extended wet season for the GEE. A reduction in the length of the dry season and overall increased RF in the wet season should provide enough water to mitigate seasonal organic soil oxidation following dry out of the marshes, exacerbated by agricultural and urban demands for water and water management practices. This would minimize sulfur release from soil.

Climate Scenario Decreased Rainfall/Increased Evapotranspiration

Under a decreased RF scenario runoff from the EAA would likely decline, resulting in some decrease in sulfate loading to the ecosystem. A decrease in RF would also produce a decline in sulfate loading from wet deposition. Sulfate loading from RF, however, is small compared to that from canal discharge, and the decline in RF-derived sulfate would only have a small impact on overall sulfate loading. If decreased RF results in greater reliance on water stored in aquifers (aquifer storage and recovery or ASR) then this picture could change. ASR water contains significant sulfate acquired from mixing with connate seawater and dissolution of sulfur-containing minerals. Models needed to determine the overall balance of reduced sulfate loading from EAA runoff versus increased ASR discharge of sulfate-enriched water under this scenario are not currently available.

As discussed previously, the reduced RF scenario would be expected to result in more frequent drought and fire. The resulting oxidation-induced S release from the soil would result in sulfate pulses following rewet. This could represent a significant sulfate source especially during the end of the dry season (March to June). Significant sulfate loading in northern WCA3A was observed following the 1999 drought and fire, with sulfate concentrations averaging <10 mg/L before and a year after the drought event, but averaging nearly 60 mg/L immediately after the drought and rewet (Orem, unpublished data). Laboratory soil oxidations also result in significant sulfate releases from soil (Gilmour et al. 2004).

Mercury

Mercury Cycle and Biogeochemistry

Mercury in fish and other wildlife is a serious issue impacting many wetlands worldwide. The GEE has one of the more severe Hg in fish problems in the USA. Elevated levels (>0.05 μg/g) of Hg in fish and wildlife caught from the GEE were first observed in 1989, and prompted the issuance of consumption advisories (Ware et al. 1990). Methylmercury (MeHg), the major form of Hg in biota, is highly bioaccumulative, and adversely affects reproductive, physiological, and neurological systems in humans and wildlife. In humans, fetuses and young children with developing neurological systems (especially the brain) are especially vulnerable, and consumption advisories for pregnant women are generally more stringent, Recent work has shown that MeHg may adversely affect the reproductive success of fish-eating wading birds (Frederick and Jayasena 2010; Frederick et al. 2011). At least one Florida panther was reported to have died from elevated MeHg (Barron et al. 2004).

Major factors contributing to high levels of MeHg in organisms include (1) high rates of inorganic Hg deposition, and (2) environmental and biogeochemical conditions facilitating microbial production of MeHg, and (3) food web dynamics allowing for effective transfer and bioaccumulation of MeHg (Liu et al. 2008; Fig. 8). Anaerobic microorganisms (sulfate reducing bacteria, iron reducing bacteria, methanogens) are known to methylate inorganic Hg. Thus, wetlands with saturated and anoxic soils provide suitable conditions for these microorganisms. Sulfate-reducing bacteria in particular are known to be important in MeHg production (Fig. 8), and sulfate is an important control on MeHg production in aquatic ecosystems (Gilmour et al. 1992, 1998; Heyes et al. 1998), including the GEE (Orem et al. 2011). Dissolved iron levels in the GEE are low, and methanogenesis is subordinated energetically as a process to sulfate reduction. As shown earlier, sulfate enters the GEE in high concentration in canal discharge. As a result, S is a major driver of MeHg production in the ecosystem (Gilmour et al. 1998, 2007). It should be noted that sulfate-reducing bacteria (and other microorganisms) also demethylate mercury (Robinson and Tuovinen 1984; Oremland et al. 1991). Studies indicate, however, that for all locations studied in the GEE methylation always exceeds demethylation (Marvin-DiPasquale and Oremland 1998).

The relationship between S geochemistry and MeHg production and accumulation in wetland environments is complex. In earlier work, Gilmour et al. (1992) showed that the relationship between sulfate concentration and MeHg production is probably non-linear. In this study, increasing sulfate concentration in sediments initially increases MeHg production to a maximum beyond which further sulfate addition actually diminishes MeHg production. The decline in MeHg production at higher sulfate concentrations was hypothesized to result from the buildup of sulfide and/or organic sulfur species in soil porewater. Subsequent work suggested that sulfide and dissolved organic S strongly bind inorganic Hg, thereby impacting its bioavailability for methylation (Benoit et al. 2001, 2003; Heyes et al. 1998; Fig. 8). Thus, if this biogeochemical theory holds true under the environmental variations in south Florida marshes, then changes in S loading or distribution with climate change have the potential to impact mercury methylation through stimulation by sulfate and inhibition by sulfide. Currently available work (Gabriel et al. 2014) suggests there may be some relationship between sulfate concentration and MeHg levels in three different trophic level fish from the GEE. However, unexplained variability in these data indicates that other factors besides sulfate (e.g., demethylation and photodegradation rates, differences in food sources for fish across the ecosystem, trophic transfer, MeHg exposure pathway) might also be determinants of mercury levels in GEE fish.

Other factors, besides sulfate levels, also impact MeHg production and distributions within an ecosystem, including: inorganic Hg inputs and bioavailability, redox conditions, pH, and DOC (Miskimmin et al. 1992). All of these factors, especially the high rate of Hg deposition in south Florida, are factors in the high levels of MeHg production and bioaccumulation in the GEE (Gilmour et al. 1998, 2007). In many respects, the south Florida ecosystem represents an ideal environment for MeHg production: (1) large wetland area with anoxic conditions in organic-rich soils, (2) high deposition of Hg^{2+} in abundant RF, (3) high DOC for binding and transport of Hg^{2+} to sites where methylation occurs, (4) circumneutral pH, and (5) high sulfate loads to drive microbial sulfate reduction and mercury methylation.

Baseline Conditions

Mercury differs from the other elements discussed in this report in several ways: (1) it is not a nutrient for biota, (2) its primary role in the ecosystem is as a contaminant that negatively impacts biota, and (3) its primary form of concern (MeHg) is produced by bacteria as a byproduct of metabolism. As mentioned earlier, many factors influence the levels of total Hg and MeHg in the ecosystem. Deposition of Hg is one key factor, with deposited inorganic mercury accumulating in soils where production of MeHg occurs (Fig. 9b).

Mercury enters the ecosystem as both wet and dry deposition, with wet-deposition dominant. Wet deposition of total Hg to the GEE consistently ranks among the highest in the continental United States (rates of about 15–25 $\mu g/m^2$), ranking highest nationally at mercury deposition network (MDN) sites for most years between 1997 and 2010. Deposition rates appear to be mostly uniform across the GEE and have not changed significantly over the past 15 years despite massive reductions in local emissions. This suggests that long-range transport processes and reemissions from the landscape are the primary sources of atmospheric mercury deposited on the GEE in RF. The large wet-deposition Hg fluxes in south Florida reflect the combination of high Hg concentrations in RF, coupled with high RF totals characteristic of south Florida (Guentzel et al. 2001). Guentzel et al. (2001) suggested that the tall convective storms characteristic of south Florida during the summer can access and scavenge comparatively high concentrations of mercury in the free troposphere where levels are high, producing summertime rain Hg concentrations that are high. Furthermore, the presence of high concentrations of key mercury oxidants (e.g., OH^-, O_3) derived from the marine boundary layer may also be involved in the high mercury levels in RF on the GEE (Selin and Jacobs 2008; Holmes et al. 2010).

While mercury deposition is a major driver of high levels of MeHg in the GEE, it is S and the biogeochemistry of Hg methylation that drives the distribution of MeHg within the ecosystem. The opposing effects of sulfate stimulation and sulfide inhibition on MeHg production, coupled with the north to south gradient in sulfate concentrations in the GEE, provide geographic context to MeHg distributions and Hg methylation rates (Orem et al. 2011). Areas of the ecosystem with sulfate levels <1 mg/L exhibit low levels of MeHg due to sulfate limitation of microbial sulfate reduction, while areas heavily contaminated with sulfate from canal discharge (>20 mg/L sulfate) exhibit sulfide inhibition of MeHg production. Areas with intermediate concentrations of sulfate exhibit the highest MeHg production. Recently published data on sulfate concentration and MeHg levels in fish show similar nonlinear trends (Gabriel et al. 2014), although with variability in the data that could reflect other factors such as food source or trophic transfer. During the mid to late 1990s, the highest MeHg concentrations in sediment (Gilmour et al. 1998), fish (Stober et al. 1996, 2001), and wading birds (Frederick et al. 1997) in the GEE were observed near the center of WCA3A. Sulfate concentrations in surface water in central WCA3A during this time ranged from 2 to 10 mg/L, and porewater sulfide concentrations were low enough (5–150 ppb) to prevent significant inhibition of Hg methylation (Orem et al. 1997; Stober et al. 1996, 2001). Thus, areas at the downgrade edge of the sulfate contamination plume in the GEE have sulfate and sulfide levels in the correct balance to promote maximum MeHg production. Sulfate levels in central WCA3A declined beginning about 1998 or 1999 from the 2–10 mg/L range to current values of <0.1 mg/L. The decline in sulfate is strongly correlated with a drop in MeHg levels in sediments in central WCA3A since the late 1990s (Gilmour et al. 2007; Axelrad et al. 2008). The drop in sulfate levels in central WCA3A may be linked to changes in water distribution patterns accompanying Everglades restoration. Restoration activities are rerouting water to ENP to increase water levels there.

The decline in MeHg levels in the central WCAs does not mean that the mercury problem is solved; rather it has moved elsewhere. Indeed, there is evidence that MeHg production and levels of MeHg in biota are currently increasing in ENP (Lange 2006; Rumbold et al. 2007).

Climate Scenario Increased Rainfall

The climate scenario involving increased RF is likely to increase overall MeHg production and levels in biota for two main reasons: (1) increased wet deposition of Hg^{2+} in RF on the ecosystem, and (2) increased flux of sulfate in canal discharge. Higher RF totals mean more tropospheric scavenging of inorganic Hg from the atmosphere by the high clouds. More deposition means more Hg^{2+} available for methylation. Higher RF will also keep more of the ecosystem inundated for longer periods (especially with longer wet seasons as indicated by the model), increasing the area of anoxic sediments suitable for MeHg production by sulfate-reducing bacteria.

Higher RF also means greater runoff of SO_4^{2-} from the EAA into the ecosystem. The increased sulfate loading will increase overall microbial sulfate reduction and mercury methylation in the ecosystem as a whole, especially when coupled with increased areas and duration of inundated marsh under this scenario. However, the increased sulfate loading may actually decrease MeHg production in some areas due to the resulting buildup of sulfide and the inhibition of mercury methylation from the sulfide. This inhibition would be most likely to occur in the northern part of the ecosystem closest to the EAA source of the sulfate, and near STA and canal discharge sites throughout the ecosystem.

Climate Scenario Decreased Rainfall/Increased Evapotranspiration

Under the decreased RF scenario, overall effects are expected to be a decrease in MeHg production across the ecosystem, but isolated instances of very high MeHg production may occur. Overall lower rates of MeHg production will result from (1) lower Hg^{2+} deposition on the GEE with lower RF and shorter wet seasons, (2) lower runoff of SO_4^{2-} from EAA with resulting lower rates of sulfate reduction and mercury methylation, and (3) a smaller area submerged for shorter periods of time.

Lower RF amounts and a shorter wet season may result in more frequent drying events, peat oxidation, and fires. The peat oxidation and fires will release bound S and Hg^{2+} from the organic soils which would stimulate microbial sulfate reduction and mercury methylation upon rewet and produce large plumes of MeHg. Large inventories of total Hg are present in organic soils in the GEE (Liu et al. 2011) and may produce episodic periods of Hg^{2+} release following peat oxidation events. However, the MeHg plumes resulting from peat oxidation are typically short duration events (Rumbold and Fink 2006). Thus, we expect the overall lower Hg^{2+} deposition and lower sulfate loading to the ecosystem to result in lower overall MeHg production under this scenario. Drying events under this scenario will likely produce episodic plumes of MeHg superimposed on overall lower MeHg production. Additional model scenarios that accommodate these various factors would be useful in better quantifying the ecosystem MeHg response to lower RF.

Increased Temperature

The general increase in temperature associated with climate change could have some impact on biogeochemical cycling of C across the GEE. Microbial activity and thus decomposition/OM oxidation is known to be very sensitive to temperature (Inglett et al. 2012; Fierer et al. 2005; Segers 1998) with rates doubling with every 10 °C increase in temperature. Increased temperature combined with increased microbial activity may result in significant increases in peat oxidation. Increased temperature is also anticipated to increase plant growth rates for similar reasons. This could ameliorate some of the temperature-induced increase in microbial activity. However, in areas not impacted by nutrient enrichment, unless the increased microbial activity increases organic P turnover, P limitation may be a regulator of plant production (Newman et al. 1996). Potential increased CO_2 and CH_4 production (Inglett et al. 2012; Scanlon and Moore, 2000; Moore and Dalva 1993) due to elevated temperature and microbial activity is an issue of concern not limited to the GEE, as both gases exacerbate climate change. Methane production with higher temperature, however, may be limited by increased sulfate loading and microbial sulfate reduction under higher RF conditions, and by peat oxidation (absence of anaerobic conditions needed for methanogenesis) under the lower RF scenario.

Microbial activity is generally positively correlated with temperature (up to a point). The temperature increase postulated for the GEE in the climate model used here will likely increase overall microbial activity including microbial sulfate reduction rates. Higher rates of mercury methylation are typically seen during the warmer wet season in south Florida. Higher temperatures may also increase cloud coverage and atmospheric radicals that would increase Hg^{2+} deposition on ecosystem. These effects would tend to increase levels of MeHg in the ecosystem, especially under the higher RF scenario with increased sulfate loading driving microbial sulfate reduction and mercury methylation.

However, in general, under the modeling scenario of a 1.5 °C change in temperature, specific effects are expected to causes minimal biogeochemical changes in this subtropical ecosystem where temperatures are generally conducive to microbial activity. RF patterns driving peat oxidation or buildup, and driving changes in chemical loading to the ecosystem, are likely to have much larger biogeochemical implications than the modeled temperature increase.

Sea Level Rise

Projections of sea level rise associated with climate change have significant implications for the southern GEE, specifically, ENP, and are primarily addressed elsewhere in this special issue (Koch et al. this issue). With soil elevation of approximately 1 m above mean sea level in the northern portions of ENP, significant portions of freshwater organic soils in SRS, Taylor Slough and wet prairies to the west are at risk for loss. Loss can occur from erosional processes (via increased tidal pumping), increased decomposition rates (Chambers et al. 2013) or through a process termed peat collapse in which increased salt water transgression causes freshwater plant mortality and a subsequent loss of soil cohesion. While the phenomenon of peat collapse in the GEE has been observed by many researchers, it is not well documented in the literature. Other factors such as increased storm surge incursion and physical dispersion of organic matter by high salt content waters may contribute to the breakdown of soil structure and mass loss of organic soil by erosion. Decomposition rates have been found to increase during periodic exposure of freshwater marsh soils to moderate and high-salinity waters (Chambers et al. 2013). The combination of these processes is anticipated to produce a gradient of impact, from upstream areas where periodic salt water incursions occur to downstream areas where peat collapse and erosion will embody the potential effects from sea level rise.

Significant uncertainty exists in whether the rate of mangrove and salt marsh accretion will withstand any of the ranges of sea level rise projections. Even if the extensive mangrove communities now present in southern ENP can keep pace with sea level rise, the risk of rapid loss of organic soils from peat collapse and resulting deeper water may impede mangrove colonization, resulting in open water replacing current marsh habitats. Increased major storm activity from climate change (hurricanes) may greatly exacerbate the impacts of sea level rise with periodic catastrophic storm surge resulting in extensive peat soil erosion (Michener et al. 1997).

Increased sea level rise and the associated penetration of high-salinity, high sulfate water into the marsh interior will, as noted previously, result in the mobilization of P from calcium bound forms.

Overall Conclusions and Future Research

Organic soils cover much of the GEE, which prior to development constituted the largest single body of organic soils in the world, covering over 8,000 km^2 (Stephens 1956). However, development in and around the ecosystem has caused significant loss of organic soil, primarily due to drainage for agriculture and urbanization, demand for water (especially during the dry season), and water management practices. Nowhere is this more evident than in the EAA, which has long been drained for agriculture (primarily sugarcane production). Oxidation of the original peat soil here, once up to 4 m in thickness, is pronounced with a long-term average rate of subsidence of 2.5–3 cm/year (Stephens and Johnson 1951; Stephens 1974; Shih et al. 1979; Stephens et al. 1984). Today, much of the EAA is covered by less than 0.3 m of soil, and the original organic soil over a large area is highly mineralized. Because of this, prospects for long-term agriculture in the EAA are limited. Land subsidence in the EAA from organic soil loss is pronounced and highly significant in a landscape where the maximum elevation above sea level is only 6 m. The oxidation of EAA organic soil has also impacted wetlands to the south through release of elements that affect water quality.

Organic soil subsidence potential in the GEE is less well understood compared to that in the EAA, but is one of the most significant landscape-scale issues with respect to climate change that ecosystem managers will need to plan for. The process of soil oxidation is much more rapid than soil accretion, and soil oxidation has great impact on the surrounding landscape in many ways. Research directed toward understanding the rates of oxidative C loss from soils in different regions of the GEE, and minimum moisture levels needed to limit oxidative loss of peat soil are needed. While higher temperature plays some role in increasing biodegradation of organic soil, hydrologic factors are considered to be a much more important determinant of C accretion or loss as organic soils. Under current baseline conditions some areas of the GEE experience a degree of peat oxidation, especially in dry years. This is especially true of northern WCA1, much of WCA2A, northern WCA3A, and areas in ENP outside of the major sloughs.

The 10 % increased RF scenario is expected to have beneficial impacts on C accretion as organic soils in most areas, although peat soil oxidation will continue during dry years in areas currently experiencing peat loss. Ponding currently occurring in southern WCA3A might expand under the higher RF scenario, although the restoration plans (Comprehensive Everglades Restoration Plans or CERP) to open flow under the Tamiami Trail may alleviate this. In ENP, the increased RF scenario is expected to result in expansion of both Shark River and Taylor Sloughs, and resulting peat accretion in areas adjacent to the sloughs which currently have thin or absent organic soil cover. Greater flow down Shark River and Taylor Sloughs may mitigate sea level rise to some degree, reduce hypersaline conditions in Florida Bay, and promote mangrove growth leading to reduced impacts from cyclonic storms.

The 10 % reduced RF scenario has much more devastating impacts on the GEE. Under this scenario, a normal year will look like a dry year under current conditions. Peat oxidation in the areas currently seeing peat loss in dry years only will become more frequent. The length of the dry season may also expand, further exacerbating peat soil loss. Dry years under the reduced RF scenario will produce much more extensive peat oxidation and a high probability of fire that could further destroy peat soil and rooted vegetation. In ENP, both Shark River and Taylor Sloughs would be expected to narrow, with areas outside of the major slough channels drying out. Marl soil deposition in ENP may also be impacted, and large areas of ENP may become essentially rock covered and devoid of soil. Lower freshwater flow down Shark River and Taylor Sloughs will lead to increased hypersalinity in Florida Bay, and make the coastal areas of ENP more subject to erosion from sea level rise.

Loss of organic soil through oxidation is closely tied to the biogeochemistry of other key elements, and has great potential to increase the release of N, P, and S. The release of nutrients and contaminants stored in the organic soil may exacerbate eutrophication and contamination downstream. For example, spatial patterns of S and Hg suggest extensive accumulation of both of these elements in wetland soil south of the most severe areas of current soil subsidence. Thus, the 10 % reduced RF scenario may lead to increased flux of N, P, and S from areas where peat oxidation occurs to downflow areas. For example, flux of N, P, and S from northern to central WCA1 may cause increased eutrophication in central WCA1, which is currently highly oligotrophic. However, under the 10 % increased RF scenario the flux of P and S may increase due to increased flux of P and S contaminated runoff from the EAA. This could lead to additional eutrophication and MeHg production (due to both increased sulfate loading and Hg^{2+} deposition in increased RF) in parts of the ecosystem.

Assessing the biogeochemical responses to the modeled climate change scenarios highlighted many knowledge gaps, two key areas of uncertainty are (1) will increased RF actually produce increased loading, either through atmospheric or terrestrial sources?, and (2) what hydrologic conditions cause oxidation of surface soils, and does that vary dependent on antecedent conditions? To address the first uncertainty greater evaluations of atmospheric and land sources of pollutants are essential. For example, will a 10 % increase in RF scrub greater quantities of Hg from the atmosphere, or is this already at a maximum under current RF conditions? Similarly, will increased RF result in greater solubilization of pollutants in the EAA and urban areas, or does existing RF already deplete these pools sufficiently that additional RF will not result in increased loading of pollutants to the downstream ecosystem?

However, by far the greatest uncertainty that needs to be answered is how to control the mineralization of organic soils. As noted above, reversing soil oxidation is the key to conservation and restoration. During drought conditions, peat fire risk is part of the assessment criteria when making water management decisions (Smith et al. 2003); however, prior to such a catastrophic condition, soil oxidation is a significant concern. Future research should examine how much water, both depth below ground surface and duration of dry out, is required to minimize peat loss, and what hydrologic conditions are necessary to optimize peat accumulation. At the northern-most overdrained areas, e.g., WCA3AN, it is likely that antecedent conditions have changed the capillarity of the soil, such that OM oxidation may be more sensitive to water loss during dry outs; however, this is unknown. In contrast, at the southern-most extent of the system, elimination of OM oxidation is critical and continuous peat accumulation is essential for the ecosystem to keep up with sea level rise. Finally, water management will play a key role in minimizing the impacts of peat soil loss. Effective use of the limited water resources will be essential, especially under the reduced RF scenario and given the increasing demands of the ecosystem, urban area, and agriculture. The use of approaches such as aquifer storage of excess water during the wet season for reuse during the dry season, despite the water quality issues associated with this approach, may be essential to prevent extensive peat loss. Additional research and the development of models will be needed to provide the necessary information for effectively managing the anticipated climate impacts.

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