Variation in soil phosphorus, sulfur, and iron pools among south Florida wetlands

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"This paper has not been submitted elsewhere in identical or similar form, nor will it be during the first three months after its submission to Hydrobiologia."

Abstract

To determine relationships between soil nutrient status and known gradients in primary production, we collected and analyzed soils from 17 LTER sampling sites along two transects through south Florida wetland ecosystems. Through upstream freshwater marsh, a middle reach including the oligohaline marsh/mangrove ecotone, and downstream estuarine habitats, we observed systematic variation in soil bulk density, organic content, and pools of phosphorus (P), inorganic sulfur, and extractable iron. Consistent with observed differences in wetland productivity known to be limited by P availability, total P averaged ~ 200 μg gdw^{-1} in soils from the eastern Taylor Slough/Panhandle and was on average three times higher in soils from the western Shark River Slough. Along both transects, the largest pool of phosphorus was the inorganic, carbonate-bound fraction, comprising 35-44% of total P. Greater than 90% of the total inorganic sulfur pool in these south Florida wetland soils was extracted as pyrite. Freshwater marsh sites typically were lower in pyrite sulfur (0.2-0.8 mg gdw^{-1}) relative to marsh/mangrove ecotone and downstream estuary sites (0.5-2.9 mg gdw^{-1}). Extractable iron in freshwater marsh soils was significantly higher from the Taylor Slough/Panhandle transect (3.2 mg gdw^{-1}) relative to the western Shark River Slough transect (1.1 mg gdw^{-1}), suggesting spatial variation in sources and/or depositional environments for iron. Further, these soil characteristics represent the collective, integrated signal of ecosystem structure, so any long-term changes in factors like water flow or water quality may be reflected in changes in bulk soil properties. Since the objective of current Everglades restoration initiatives is the enhancement and re-distribution of freshwater flows through the south Florida landscape, the antecedent soil conditions reported here provide a baseline against which future, post-restoration measurements can be compared.

Introduction

The south Florida landscape is dominated by vegetated freshwater, brackish mangrove and downstream estuarine habitats. These different wetlands exhibit variable primary production both within and between habitat types. For example, Fourqurean et al. (1992a,b) have documented the pronounced gradient in seagrass production throughout the Florida Bay estuary as a function of phosphorus availability. Nutrient availability also contributes to the greater mangrove biomass along the southwest coast of the Everglades (Chen & Twilley 1999) relative to mangrove biomass on the southeast coast (Coronado-Molina et al. 2004). Similarly, across the freshwater Everglades, Childers et al. (2003) have documented differences in vegetation and biomass related to soil phosphorus concentrations.

Given the general characteristics of phosphorus limitation in south Florida wetlands (Koch & Reddy 1992; Noe et al. 2001, 2002) coupled with a 100-year old history of changes in water flow largely driven by installation and operation of water control structures (Light & Dineen 1994; Chimney and Goforth 2001), any factors that influence the supply of phosphorus or alter the flows of water through these oligotrophic wetlands could impart dramatic changes on ecosystem structure and function (Fourqurean et al. 2003; Davis et al. 2004). To this end, the Florida Coastal Everglades Long-Term Ecological Research (LTER) program was established to examine variability in regional climate, freshwater inputs, disturbance, and perturbations affecting the coastal Everglades ecosystem. As part of the LTER program, we have initiated synoptic sampling of soils across the south Florida landscape with identical analytical methods to capture in a snapshot some of the differences and similarities in soil characteristics among wetland types.

Soil properties can be viewed as the integrated outcome of processes occurring over extended time scales, much in the same way that climate is a description of aggregate weather conditions for a region. In this study we present the aggregate soil properties along two transects, with a focus on forms of phosphorus, sulfur and iron. Phosphorus is a limiting nutrient in these oligotrophic wetlands and has been used to characterize ecological community types in other Florida habitats (Schwandes et al. 2001). Reduced inorganic sulfur is the by-product of the principle anaerobic respiratory process in marine and estuarine soils (sulfate reduction); soil sulfide exerts some control on mercury speciation (Benoit et al. 1999) and can also be used to track sulfate sources (Bates et al. 2002). In turn, both the phosphorus and sulfur cycles in soils are influenced by the availability of reactive iron in carbonate soils (Sherman et al. 1998). Our objective was to quantify the pools of sulfur, iron and phosphorus in different wetland soils and establish a baseline for tracking long-term changes in the coastal Everglades ecosystem.

Methods

Study Site

The south Florida landscape is dominated by sub-tropical wetland environments where hydrology—in terms of water volume, source, and residence time—plays a major factor in ecosystem structure (e.g., Ross et al. 2003). As part of the Florida Coastal Everglades LTER, two transects along separate freshwater drainage networks in the Everglades have been established (Figure 1). In the western Everglades, six sampling sites are located in the Shark

River Slough (SRS) basin, extending from freshwater marsh (SRS sites 1 and 2), through the oligohaline marsh/mangrove forest ecotone (SRS sites 3 and 4), and out through coastal estuarine mangroves (SRS sites 5 and 6). Eight sampling sites are located in the eastern Taylor Slough/Panhandle basin, extending from freshwater marsh (TS/Ph sites 1, 2, and 4), through a region including the oligohaline marsh/mangrove forest ecotone (TS/Ph sites 3, 5, 6, 7, and 8), and out to the seagrass-dominated Florida Bay estuary (TS/Ph sites 9-11).

Relative to the TS/Ph drainage, SRS is characterized during the wet season by larger inflows of freshwater from canal discharge at SRS 1 and greater tidal exchange of coastal ocean water at SRS 6. Additionally, soils in the SRS basin tend to be peaty, whereas soils in the TS/Ph basin have less peat and more marl deposits (Childers et al. 2003). Florida Bay sediments are almost exclusively comprised of marine carbonates.

Soil Collection and Analysis

Soils for determination of organic content were collected in August 2002; soils for all other analyses were collected during August 2003. From each of the 17 sampling sites, three 60-ml syringe cores were pushed into the soil surface to a depth a 10 cm. The syringe barrels were capped with butyl rubber stoppers and stored on ice for transport to the laboratory, then cores were refrigerated prior to analysis. Cores were extruded, and subsamples from each core were obtained at depths from 0-2.5 cm, 2.5-5.0 cm, and 5.0-10 cm.

Soils from all 17 sampling sites were treated identically. Soil samples for bulk density, % organic matter, total phosphorus and extractable iron analyses were placed in tared vials, dried at

80°C and weighed to determine bulk density, then ashed at 450°C for four hours to determine weight loss on ignition. The ashed soils were then resuspended in 1N HCl to hydrolyze phosphates, and colorimetric analyses for total phosphorus using the ascorbate method and extractable iron (Fe_{HCl}) using the ferrozine method (Stookey 1970) were completed.

A four-step sequential extraction scheme based on a method used by Jensen et al. (1998) and Koch et al. (2001) was completed to determine selected inorganic and organic pools of phosphorus in carbonate sediment. First, extraction with 1N magnesium chloride released loosely sorbed inorganic phosphate (P_{MgCl2}). Next, extraction with a buffered dithionite solution released inorganic phosphate considered sorbed to metal oxides (principally iron and manganese compounds)(P_{BD}). Third, extraction with 1N HCl dissolved the carbonate minerals in the soil and released inorganic phosphate sorbed to or in mineral phase with calcium carbonate (P_{HCl}). Finally, subsequent ashing and 1N HCl acid extraction was used to release recalcitrant phosphate, operationally defined as the residual organic phosphorus fraction (P_{Org}). Less resistant organic phosphates associated with the first three extraction steps were not analyzed, but have been shown to account for 10-30% of the total sediment phosphorus in Florida Bay seagrass beds (Koch et al. 2001).

Soil samples for mineral sulfide extraction were first suspended in 1N zinc acetate to precipitate any free sulfide in solution. Then, the soils were subjected to a two-step sulfur extraction sequence following the method used by Chambers et al. (1994). Acid-volatile sulfide (AVS) was extracted using a 1N HCl solution, then sequestered in an NaOH trap. Chromium-reducible sulfide (CRS) was extracted using a boiling solution of concentrated HCl and reduced chromium, then sequestered in an NaOH trap. The trapped AVS and CRS fractions were fixed using Cline's reagent and analyzed colorimetrically (Cline 1969). The CRS fraction was assumed to be pyrite (FeS_2).

Total phosphorus concentrations were calculated both by soil weight and by volume to allow for comparison with other published values. All other nutrient concentrations were calculated per weight of soil and compared among transect locations (i.e., freshwater marsh, oligohaline marsh/mangrove forest, downstream estuary). One way ANOVAs were used to compare means among transect locations, and LSD post hoc comparisons were completed using SPSS Version 10.0 (SPSS 1999). Percent organic values were log-transformed to normalize the data prior to statistical analysis.

Results and Discussion

Total P concentration typically was higher along the Shark River Slough transect relative to the Taylor Slough/Panhandle transect (Table 1). Expressed by soil weight, total P was fairly constant from SRS 2 through SRS 6; per soil volume, however, total P increased down the transect. Plant roots respond to changes in nutrient density, and the pattern of downstream soil P enrichment is consistent with an observed gradient in mangrove productivity along the SRS transect (Chen and Twilley 1999). Along the TS/Ph transect, however, total P concentration decreased from the most northern freshwater marsh sites before rising at TS/Ph 7 and 8 to values similar to those measured at SRS 4-6. The profound difference in mangrove production between SRS and TS/Ph transects (Coronado-Molina et al. 2004) despite similar total P concentration in the soil demonstrates that other factors in addition to soil P content influence wetland productivity.

We expected to see a gradient of decreasing total P in sediment from west-to-east across Florida Bay, concomitant with prior research demonstrating a bay-wide gradient in P availability and seagrass production (Fourqurean et al. 1992a,b). We found, however, that sediment P was unusually high in the eastern portion of Florida Bay (TS/Ph 9; Table 1). This site is located adjacent to Duck Key where a heron rookery was recently established, so our measured high P value at TS/Ph 9 may be a result of localized P enrichment from bird guano.

All soils in the current study were calcareous, but soil bulk density was significantly lower in freshwater marsh environments and along the SRS transect (Table 2). The most dense soils were located in Florida Bay. Concomitant with high bulk density in Florida Bay seagrass meadows was low percent organic matter, averaging about 7%. In contrast, the emergent freshwater marshes and mangrove forest soils had much higher organic content, and organic content was significantly higher along the Shark River Slough transect. The implication from these data is that marly soils are more consolidated or compacted along the Taylor Slough/Panhandle transect, with higher water content in soils along the SRS transect.

As found in a prior study of sulfur in Everglades soils (Bates et al. 1998), the acid-volatile component of the extracted soil sulfur pool was always less than 10% (Table 2). The concentration of AVS, which includes free sulfide (HS^-) plus iron monosulfide (FeS), was significantly higher in the marsh/mangrove ecotone of both transects. Most inorganic sulfide, however, was extracted in the CRS fraction. As expected, the CRS concentration was highest in the wetland habitats influenced by saltwater, the largest source of sulfate for bacterial sulfate reduction to sulfide and subsequent pyrite formation. Between marsh, ecotone, and estuarine wetland types, CRS was significantly higher along the SRS transect, relative to the TS/Ph transect.

Extractable iron concentration was typically very low throughout all habitats sampled, but higher along the eastern TS/Ph transect (Table 2). Still, the average concentration of Fe_{HCl} from the TS/Ph mangrove sites (~1.7 mg gdw^{-1}) was roughly six times lower than the total soil iron measured in a prior study sampling the mangrove fringe in the Taylor Slough drainage (Koch et al. 2001). Because pyrite authigenesis relies on the availability of reactive iron and sulfide, either species could limit its formation. Further, sulfate reduction only occurs in anaerobic soils where labile organic matter is available for microbial decomposition. Relative to soils in mangrove and seagrass habitats, freshwater marsh soils are exposed to lower concentrations of sulfate, they experience oxidation during seasonal drawdowns of water, and microbial decomposition of organic matter can be limited by phosphorus availability (Amador and Jones 1993). Together, these features are consistent with less net mineral sulfide formation in freshwater marsh environments and more generally along the TS/Ph transect.

Though different in magnitude between transects, the patterns in pool sizes of total phosphorus and total inorganic sulfur were fairly similar among transect locations (Figure 2). Brown & Cohen (1995) completed a sediment survey along a transect line running from Florida Bay, through the mangrove fringe and into freshwater marsh habitat near Whitewater Bay. They found a pattern in mineral sulfide accumulation that was highest in the mangrove fringe, lowest in the freshwater marsh, and intermediate in Florida Bay. Not only is the coastal ocean the primary source of sulfate for eventual sulfide production and mineral sulfide formation; the coastal ocean is also the source of much of the phosphorus enrichment observed in both Florida Bay and saltwater mangrove habitats along both SRS and TS/Ph transects (Figure 2). Fourqurean et al. (1992a,b) have demonstrated the longitudinal decrease in phosphorus deposition in Florida Bay from west to east, effectively showing the primary source of P in the bay is the Gulf of Mexico. Similarly, Chen and Twilley (1999) have documented that soil phosphorus concentration in mangrove forests along the SRS transect decreases with distance upstream from the Gulf of Mexico. The pattern of P enrichment in the coastal zone is smaller along the Taylor Slough transect (Figure 2), but consistent with the documented decrease in total phosphorus concentration in the eastern portion of Florida Bay (Boyer et al. 1997).

Our sequential extraction scheme identified the three principal inorganic soil phosphorus pools and what has been measured as the major organic phosphorus pool in organic carbonate sediments (Koch et al. 2001) (Table 3). The easily desorbed P_{MgCl2} pool was usually less than 10% of total extracted P. The size of the P_{BD} pool was approximately 25% of the total extracted P, whereas Koch et al. (2001) found the P_{BD} fraction typically was below detection in organic carbonate soils. We have not resolved this difference but note that the similar, large size of the P_{BD} pool across wetland types (Table 2) suggests we may have extracted other forms of P not associated with metal oxides in this fraction. Collectively, the average of the summed P fractions (124 µg gdw^{-1} ± 21 s.e.) was not significantly different from the independent measurement of total P in Table 1 (129 µg gdw^{-1} ± 33 s.e.) (paired t-test, $t = 0.437$, $p = 0.33$), but we do not know whether any of the unmeasured organic fractions could have been detected spectrophotometrically without prior ashing of the extract.

P_{HCl}, the fraction considered bound to calcium carbonate minerals, made up between 34 and 44% of extracted P and was consistently the largest P fraction.(Table 3). The carbonate-bound P pool has great potential to vary among these wetland soils because the bulk density (and thus mineral density) among sites varies by a factor of 4 (Table 2). Together, bulk density and the size of the P_{HCl} pool highlight the potential importance of carbonate-bound P to observed variability in productivity within freshwater marsh (Childers et al. 2003), mangrove (Chen and Twilley 1999) and estuarine seagrass (Fourqurean et al. 1992b) habitats in the south Florida landscape. Although the sources and amounts of deposited P can be different for different habitats (e.g., P sources from coastal ocean water, terrestrial runoff and groundwater, atmospheric deposition), much of the variation in soil storage of phosphorus is due to variation in the carbonate-bound P pool (Zhang et al. 2004), even though short-term P storage occurs in organic plant and periphyton pools (McCormick et al. 1996; Dodds 2003; Noe et al. 2003).

Bioavailability of carbonate-bound P has not been demonstrated clearly but is suggested from other studies. In subtropical environments where primary production is enhanced by P enrichment or fertilization (DeBusk et al. 2001; Ferdie & Fourqurean 2004), soil accumulation of P could be a direct consequence of organic matter deposition and decomposition (Romero et al. 2005), leading to P storage in carbonates. The stored P could then contribute to enhanced production when soil processes such as sulfate reduction solubilize the calcium carbonate matrix (Ku et al. 1999) and release inorganic phosphorus for plant uptake. Since sulfate reduction is greatest in marine and estuarine wetland soils (but see Bates et al. 2002), a dynamic system of inorganic P storage and P release ultimately may control whether carbonate-bound phosphorus operates as a sink or a source in freshwater, brackish, and marine wetland soils. A number of possible feedbacks involving carbonate saturation, wetland hydroperiod, organic matter and sulfate supply would influence soil phosphorus dynamics in the south Florida wetland environments.

The Florida Coastal Everglades LTER program is designed to study the structure and function of subtropical aquatic ecosystems and determine how different forces contribute to long-term stasis or ecosystem change. As part of that effort we measured soil characteristics across south Florida habitats distinguished by hydrology and wetland type. Along transects through upstream freshwater marsh, a middle reach including the oligohaline marsh/mangrove ecotone, and downstream estuarine habitats we observed systematic variation in soil bulk density, organic content, extractable iron, and pools of phosphorus and inorganic sulfur. Many of these soil characteristics represent a collective, integrated signal of ecosystem structure, so any long-term changes in factors like water flow or water quality may be reflected in changes in bulk soil properties. Since the objective of current Everglades restoration initiatives is the enhancement and re-distribution of freshwater flows through the south Florida landscape (Chimney and Goforth 2001; Perry 2004), the antecedent soil conditions reported here are part of a five-year time series to provide a baseline against which future, post-restoration measurements can be compared.

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Table 1. Total phosphorus concentration in soils from the Shark River Slough (SRS) and Taylor Slough/Panhandle (TS/Ph) transects in south Florida. For comparison, average concentrations (standard error, N=9) are expressed by soil weight and by soil volume.

Sampling Site	Total P μg gdw^{-1}	Total P μg cm^{-3}	Sampling Site	Total P μg gdw^{-1}	Total P μg cm^{-3}
SRS 1	501 (100)	106 (10)	TS/Ph 1	266 (33)	140 (14)
SRS 2	488 (29)	88 (5.9)	TS/Ph 2	210 (19)	83 (6.8)
SRS 3	876 (28)	97 (4.0)	TS/Ph 3	96 (5.3)	33 (2.5)
SRS 4	860 (60)	167 (7.4)	TS/Ph 4	153 (16)	54 (4.7)
SRS 5	813 (17)	203 (9.3)	TS/Ph 5	129 (49)	40 (1.6)
SRS 6	533 (77)	297 (6.5)	TS/Ph 6	59 (3.7)	45 (2.2)
			TS/Ph 7	362 (32)	171 (5.3)
			TS/Ph 8	454 (24)	160 (11)
			TS/Ph 9	228 (35)	141 (21)
			TS/Ph 10	71 (9.6)	60 (2.2)
			TS/Ph 11	296 (31)	199 (13)

Table 2. Summary of soil characteristics by drainage basin and habitat location along each transect. Values are grand means ± standard error. For each variable, letter superscripts show the results of post hoc comparisons among locations ($p<0.05$).

Drainage Basin	Location	N	Bulk Density g cm^{-3}	% Organic	Fe_{HCl} mg gdw^{-1}	AVS mg gdw^{-1}	CRS mg gdw^{-1}
Shark River Slough	Freshwater Marsh	18	0.220 ± 0.024^{a}	81.6 ± 0.9^{d}	1.14 ± 0.17^{a}	0.06 ± 0.01^{a}	0.78 ± 0.19^{b}
	Marsh/Mangrove Ecotone	18	0.156 ± 0.013^{a}	83.7 ± 0.9^{d}	1.22 ± 0.21^{a}	0.07 ± 0.01^{ab}	1.85 ± 0.31^{c}
	Downstream Estuary	18	0.450 ± 0.080^{b}	47.1 ± 13.5^{c}	0.83 ± 0.10^{a}	0.05 ± 0.01^{a}	2.85 ± 0.49^{d}
Taylor Slough/Panhandle	Freshwater Marsh	27	0.443 ± 0.025^{b}	14.4 ± 1.7^{b}	3.16 ± 0.37^{b}	0.04 ± 0.01^{a}	0.24 ± 0.04^{a}
	Marsh/Mangrove Ecotone	45	0.491 ± 0.030^{b}	35.8 ± 7.1^{c}	1.67 ± 0.15^{ab}	0.10 ± 0.01^{b}	0.95 ± 0.15^{b}
	Downstream Estuary	15	0.677 ± 0.082^{c}	6.6 ± 0.3^{a}	1.04 ± 0.48^{a}	0.06 ± 0.03^{a}	0.49 ± 0.06^{ab}

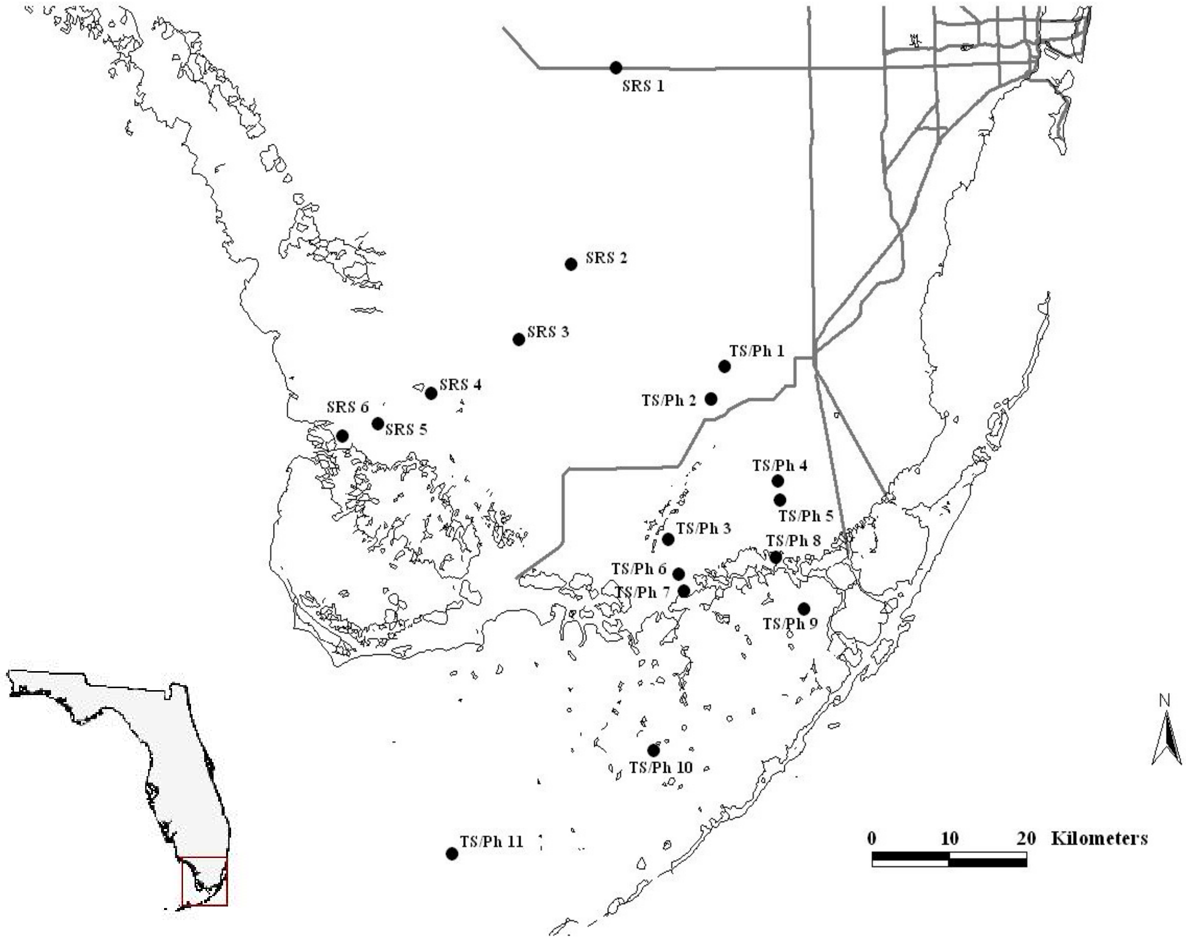
Table 3. Summary of soil phosphorus fractions by drainage basin and habitat location along transect, expressed by soil weight. Values are grand mean concentrations ± standard error, with the average percent of total P in parentheses. Operational definitions: P_{MgCl2} = loosely sorbed inorganic P; P_{BD} = inorganic P associated with metal oxides; P_{HCl} = carbonate-bound inorganic P; P_{Org} = residual organic P.

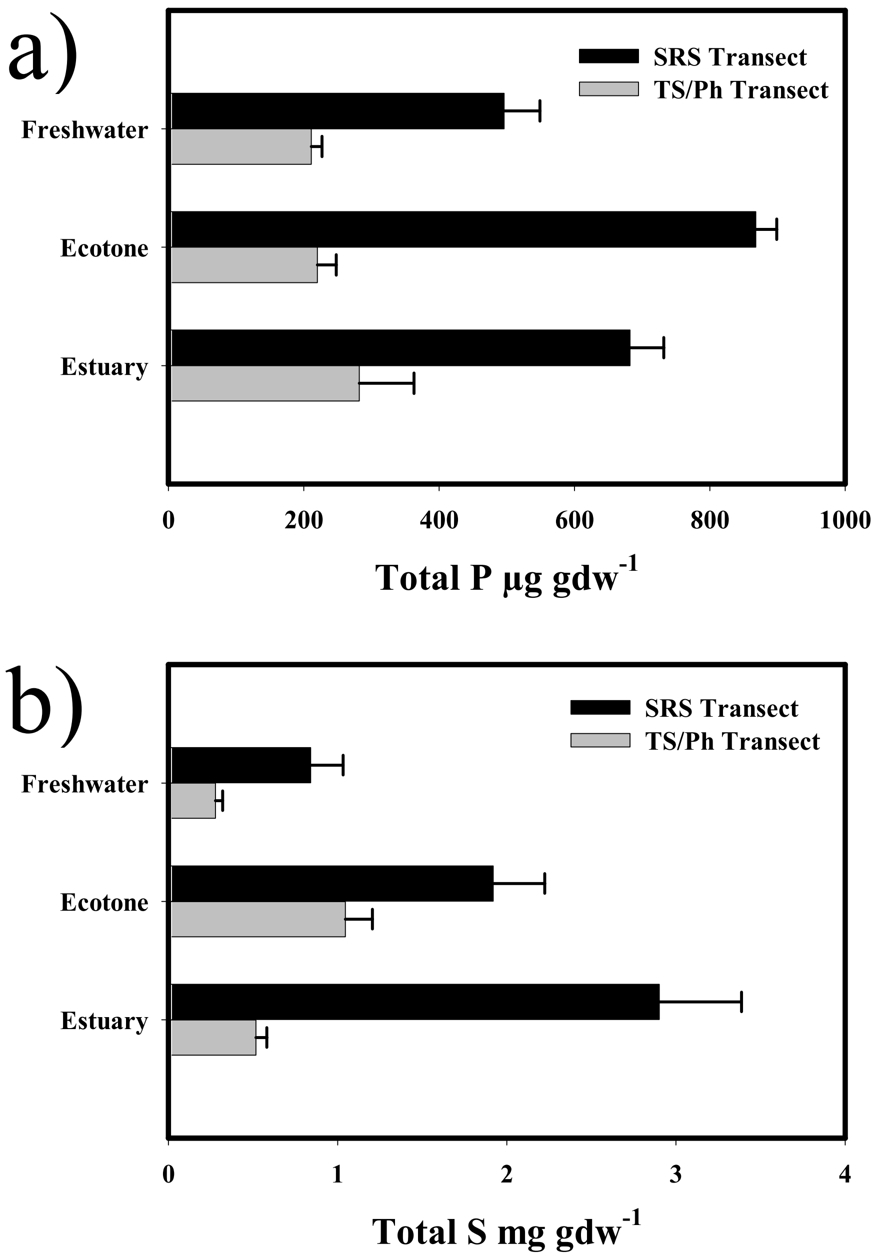
Drainage Basin	Location	N	P_{MgCl2} µg gdw^{-1}	P_{BD} µg gdw^{-1}	P_{HCl} µg gdw^{-1}	P_{Org} µg gdw^{-1}
Shark River Slough	Freshwater Marsh	18	49 ± 8.7 (7.6)	179 ± 32 (27.9)	225 ± 22 (35.1)	189 ± 22 (29.5)
	Marsh/Mangrove Ecotone	18	94 ± 6.5 (9.5)	296 ± 32 (30.1)	332 ± 31 (33.8)	261 ± 13 (26.6)
	Downstream Estuary	18	41 ± 6.5 (6.8)	104 ± 14 (17.1)	267 ± 20 (43.9)	196 ± 21 (32.2)
Taylor Slough/ Panhandle	Freshwater Marsh	27	32 ± 4.3 (10.0)	83 ± 13 (26.1)	126 ± 16 (39.2)	79 ± 9.0 (24.7)
	Marsh/Mangrove Ecotone	45	20 ± 3.4 (6.8)	82 ± 9.0 (27.9)	107 ± 8.7 (36.6)	84 ± 9.0 (28.6)
	Downstream Estuary	15	21 ± 8.7 (6.9)	87 ± 35 (29.5)	104 ± 23 (35.2)	84 ± 32 (28.4)

Figure Legends

Figure 1. Map of south Florida, showing the location of the 17 LTER sampling sites arranged along Shark River Slough (SRS) and Taylor Slough/Panhandle (TS/Ph) transects. SRS 1, 2 and TS/Ph 1, 2, 4 are located in upstream freshwater marsh habitat, SRS 3, 4 and TS/Ph 3, 5, 6, 7, 8 are located in a mid-transect region including the marsh/mangrove ecotone, and SRS 5, 6 and TS/Ph 9, 10, 11 are located in the downstream estuary.

Figure 2. Average concentration and standard error of a) total phosphorus and b) total inorganic sulfide in soils from the upstream freshwater marsh, the mid-transect region including the marsh/mangrove ecotone and the downstream estuary along SRS and TS/Ph transects.


SRS 1
SRS 2
SRS 3
SRS 4
SRS 5
SRS 6
TS/Ph 1
TS/Ph 2
TS/Ph 3
TS/Ph 4
TS/Ph 5
TS/Ph 6
TS/Ph 7
TS/Ph 8
TS/Ph 9
TS/Ph 10
TS/Ph 11
N
0 10 20 Kilometers


a)
SRS Transect
TS/Ph Transect
Freshwater
Ecotone
Estuary
0
200
400
600
800
1000
Total P µg gdw-1
b)
SRS Transect
TS/Ph Transect
Freshwater
Ecotone
Estuary
0
1
2
3
4
Total S mg gdw-1