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The Influence of Seawater and Sulfate Reduction on Phosphate Release from Tidal Wetland Soils in the St. John's River, Florida

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The influence of seawater and sulfate reduction on phosphate release from tidal wetland
soils in the St. John's River, Florida

by

Asher Williams

A thesis submitted to the Department of Biology in partial fulfillment of the requirements

for the degree of

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COLLEGE OF ARTS AND SCIENCES

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ABSTRACT

Climate change and increasing sea level elevation are predicted to increase salinity in estuarine tidal wetlands in the Southeastern United States. Since much of the ecosystem function in these areas is predicated upon salinity regimes, many fundamental changes are likely to occur as a result. The influence of salinity and SO_4^{2-} reduction on PO_4^{3-} release from tidal wetland soils was evaluated along a salinity gradient at three sites in The St. John's River, Florida using both field and laboratory-based methods. Porewater was sampled over the course of 10 months to determine ambient levels of SO_4^{2-} and PO_4^{3-} . Lab-based experiments, soils samples were subjected to seawater and SO_4^{2-} treatments in an attempt to induce PO_4^{3-} release. Salinity was lowest at Sixmile Creek ($0.45 \pm 0.1 \text{ g kg}^{-1}$) and Goodby's Creek ($2.05 \pm 2.3 \text{ g kg}^{-1}$) and much higher at Sister's Creek ($27.81 \pm 3.1 \text{ g kg}^{-1}$). The organic content of soils was highest ($82.35\% \pm 5.11$) at Sixmile Creek, intermediate at Goodby's Creek ($64.45\% \pm 7.02$) and lowest at Sister's Creek ($32.11\% \pm 9.61$). Total soil P was highest at the freshwater Sixmile Creek ($1101.64 \pm 220.2 \text{ } \mu\text{g g}^{-1}$), intermediate at the brackish Goodby's Creek ($719.61 \pm 114.3 \text{ } \mu\text{g g}^{-1}$) and lowest at the Sister's Creek saltmarsh ($475.85 \pm 110.9 \text{ } \mu\text{g g}^{-1}$). Porewater PO_4^{3-} was higher at Sixmile and Goodby's Creek sites (9.44 ± 15.6 , $8.99 \pm 14.7 \text{ } \mu\text{g L}^{-1}$, respectively) compared to Sister's Creek ($0.6 \pm 3.1 \text{ } \mu\text{g L}^{-1}$). Porewater SO_4^{2-} was lower at Sixmile ($70.73 \pm 57.58 \text{ } \mu\text{g L}^{-1}$) and Goodby's Creeks ($124.35 \pm 152.5 \text{ } \mu\text{g L}^{-1}$) compared to Sister's Creek ($1931.41 \pm 557.82 \text{ } \mu\text{g L}^{-1}$). Temporal and spatial trends indicated that SO_4^{2-} and PO_4^{3-} in porewater was likely due to floodwater content and that direct reaction between analytes in soils was unlikely. The addition of aerated seawater failed to cause PO_4^{3-} release from any sites. The incubation of soils under anaerobic conditions, in the presence of Na_2SO_4 induced SO_4^{2-} reduction, but inhibited PO_4^{3-} flux from both Sixmile and Goodby's Creek, which is attributed here to likely S^- toxicity (Roychoudhury et al., 1999). PO_4^{3-} flux from Sister's Creek increased in

association with Na_2SO_4 concentration, likely due to more Fe availability to mitigate S^{2-} toxicity. Ambient seawater additions to soils under anaerobic conditions followed a similar trend, but the results were not statistically conclusive. Overall, both field and lab-based data indicated that Tidal wetland porewater PO_4^{3-} likely originates from floodwaters and that increased salinity and SO_4^{2-} reduction did not directly enhance soil PO_4^{3-} fluxes.

INTRODUCTION

Much of the phosphate (PO_4^{3-}) available to estuaries of the Southeastern United States is released from landmasses in the surrounding basin (Sundby et al., 1992). Freshwater wetlands retain terrigenous PO_4^{3-} in soils via precipitation with metal oxides, sorption on clay particles, and accumulating organic matter (Reddy and DeLaune 2008). Under natural conditions, tidal wetland soils retain PO_4^{3-} , which has been shown to limit availability to ecology in the greater estuary (Correll 1999). The headwaters of most estuaries are generally PO_4^{3-} limited, although availability increases with salinity (Conley 2000; Blomqvist et. al 2004). Worldwide cultural eutrophication has augmented PO_4^{3-} loading to rivers and estuaries from agricultural and residential fertilizer applications (Conley et. al, 2009). The primary impact of nutrient loading in aquatic systems is increased frequency, duration, and intensity of algal blooms (Gilbert et al., 2005). Algal blooms may be directly harmful by producing toxins or reducing dissolved oxygen. These impacts degrade habitat, decrease submerged aquatic vegetative cover, and damage fisheries (Cloern 2001).

Agricultural and residential activities in the St. John's River basin (SJR), Florida have augmented PO_4^{3-} supply to a naturally PO_4^{3-} limited system (DeMort and Bowman 1985). Stratigraphic analysis indicated that nutrient loads have accumulated in wetland soils of upper SJR since the early 20th Century, paralleling human expansion in the basin

(Brenner et. al., 2001). Managing anthropogenic PO_4^{3-} loading to surface waters has been the focus of both management (Burns 2008; EPA 2010a) and research (Malecki et. al., 2004) as harmful algal blooms have persistently impacted the SJR. Eutrophication has resulted in declining SJR nekton abundance and diversity (DeMort 1991; Keller and Schell 1993), while harmful algal blooms pose specific risks to human health (Burns 2008).

Tides, seasonality, and storm events are important along the spatially dynamic saltwater-freshwater interface of Southeastern estuaries. In the SJR, Eustatic sea level rise (NOAA 2012), drought (Burkett et al., 2001), and increased municipal water demand (SJRWMD 2009) facilitate saltwater intrusion into the naturally lacustrine headwaters of the estuary. Accretion of sediments in the freshwater heads of estuaries is higher than in the downstream saline areas (Loomis and Craft 2010). When saltwater intrudes into previously fresh tidal wetland soils, soil anaerobic metabolism shifts from methanogenic to SO_4^{2-} reducing, which has been shown to increase peat mineralization rates in soils of SJR headwaters (Chambers et. al., 2011).

In freshwater soils, P release is a function of physical and chemical state. Iron (Fe) reduction releases PO_4^{3-} from strengite minerals, Calcium (Ca) bound PO_4^{3-} is released as pH is decreased during flooding, organic anions displace soil PO_4^{3-} , and phosphatase enzymes facilitate PO_4^{3-} release from organic material. Saltwater intrusion may diminish estuarine PO_4^{3-} soil retention or release, which is variable along the gradient (Pauldan and Morris 1999; Garoldinski et al., 2004; Hartzell and Jordan 2012). Salinity potentially interferes with nutrient retention in wetlands soils by directly displacing them from sorbtion sites (Megonigal and Neubauer 2009). SO_4^{2-} reduction increases decomposition of freshwater organic material and therefore potentially facilitates PO_4^{3-} release (Lamers et al., 1998). Sulfide (S^-) production disrupts the “iron curtain” that buffers PO_4^{3-} by fixing Fe into insoluble pyrite (Hartzell and Jordan 2012).

Recent droughts, slight topographic relief and low flows of the SJR expand the potential areas where saltwater is intruding into freshwater swamps (Morris 1995).

This study determined the influence of saltwater intrusion on PO_4^{3-} release from tidal wetlands soils in a coastal river. Field and experimental data were collected to address the hypothesis that PO_4^{3-} is mobilized from tidal wetland soils under saline conditions. Two aspects of saltwater intrusion were addressed, the impact of salinity on PO_4^{3-} sorption capacity and the potential for PO_4^{3-} release under SO_4^{2-} reducing conditions were investigated. The sorption hypothesis investigated during this study was that anions in saltwater would displace sorbed PO_4^{3-} from soils resulting in release. The second hypothesis investigated during this study was that SO_4^{2-} reduction would result in PO_4^{3-} release due to mineralization.

Study Area

Three study sites were selected for analysis along the freshwater-saltwater boundary of the SJR (Fig. 1). Site selection was based on likely water salinity at each site based on visual observations of vegetation. A tidal freshwater swamp, brackish marsh, and salt marsh were selected for study. Each site was classified per the Florida Natural Areas Inventory (FNAI) 2010.

A tidal freshwater swamp at Sixmile Creek (SMC) was approximately 80 km from the SJR mouth. SMC contained the most diverse canopy, including *Sabal palmetto*, *Nyssa sylvatica*, *Taxodium distichum*, *Nyssa aquatica*, *Magnolia virginiana*, and *Myrica cerifera*, with *Acrostichum danaeifolium* dominating the understory. SMC was selected for study based on the freshwater composition of the vegetative community, which appeared uninfluenced by saltwater intrusion. The upland SMC drainage basin consisted of 39% wetlands, while 22% of the total basin was impacted by human activity (EPA 2010).

The Goodby's Creek (GC) site was dominated by brackish marsh species and located approximately 50 km from the mouth of the SJR (Fig. 1). The site had clearly once been a freshwater tidal swamp, evidenced by a remnant canopy composed of stressed or dead *Fraxinus caroliniana* and *Taxodium distichum*. The understory at GC was dominated by herbaceous species including, *Typha latifolia*, *Cephalanthus occidentalis*, *Fimbristylis spathacea*, *Spartina bakerii*, and *Juncus effusus*. Groundcover was a monoculture of *Panicum spp.* The surrounding watershed was comprised of >76% urban development and <10% wetlands (FL DEP 2005).

The most saline site was Sister's Creek (SM), a salt marsh 6 km from river mouth. No visible remnant tidal forest was present at SC. The tidal marsh was predominantly *Spartina alterniflora* with intermittent clumps of *Juncus roemarianus*. The drainage at Sister's Creek is comprised of both conservation lands and diffuse residential development.

Map Redacted. Paper copy available upon request to home institution.

Fig. 1 Location of St Johns River, Florida tidal wetlands soils selected for study.

MATERIALS AND METHODS

Soil Analysis

Soil Phosphorus. Analysis of total-P by the perchloric acid digestion procedure (Sommers and Nelson 1972) and labile phosphorus by bicarbonate extraction (Kuo 1996) was used to quantify each P fraction. Soil samples for total and labile phosphorus analysis were collected at 0-10, 11-20, and 21-30 cm depths at each porewater substation at each site, using a Dutch auger (n=27). Soil samples were collected in June 2010.

Total Organic/Loss on Ignition. Soil samples were also collected for total organic content by loss on ignition (LOI) at 400°C for 16 h (Nelson and Sommers 1996). Samples were dried at 60° C to constant mass. Dried soils were pulverized with a mortar and pestle and sieved through a 0.5 mm screen. Four homogenate samples of surface to 30 cm depth were collected from each site for LOI (n=12) in September 2010.

Total Iron, Magnesium, Manganese, and Calcium. Three individual cores were collected from the top 30 cm of soils located at the center of each site transect for metals analysis including Iron (Fe), Magnesium (Mg), Manganese (Mn), and Calcium (Ca). Individual cores were homogenized and dried at 80 °C for 48 h. Samples were pulverized with a mortar and pestle and passed through a 1 mm sieve. For each sample, 1 g of dried soil was digested in concentrated nitric acid according to EPA method 3050b in SW 846 (Edgell, 1989). Metals were quantified using flame atomic adsorption spectroscopy on a Spectrometer Analyst 800 (Perkin Elmer, USA) and reported as mass analyte to mass soil.

Porewater Collections. In-situ porewater Hesslein (1976) type-samplers, or peepers (0.63 cm thick, 15.24 cm wide and 61 cm long plexiglass daggers) were deployed from May 2010 to August 2011 for seven-day equilibration periods before being retrieved. Each peeper contained five wells at 5 cm increments from 5 to 30 cm

depth into which ions in porewater equilibrated through a dialysis membrane (Versapor, Inc.) that covered each well. Peepers were manually pushed into soils to a depth, which coincided with the soil surface. When retrieved in the field, porewater was collected through the 45 μm sampler membrane at each well depth, using a syringe and leur lock. Samples were maintained on ice during transport to the lab. Collections were made at three substations along a transect at each site. Two peepers were deployed at each substation during each collection. Substation sampling locations were distributed evenly across each transect. Peepers were deployed, 13, 14, and 11 times at SMC, GB and SC, respectively. Field salinity data were collected at each site during both deployment and retrieval using a Data Sonde (YSI, Inc.). Salinity data were collected from the bank of each creek, adjacent to each wetland.

Microcosm Studies

Three separate experiments were designed to measure potential PO_4^{3-} release from soils collected at each site, under varying salinity levels. Soil samples were collected within three days prior to experimental manipulation. Bulk composite samples were collected from 0 to 30 cm depth. Experimental treatments were full-seawater salinity (33-35 g kg^{-1}), half-seawater salinity (18 g kg^{-1}), and deionized (DI) water as a control. A culinary blender was used to prepare soil slurries, which consisted of treatment solution and a soil sample from each site. Microcosms were prepared in triplicate. Each experiment was maintained in the dark to preclude photosynthesis.

Aerobic Experiments. Sand-filtered seawater (obtained from Whitney Marine Lab, St. Augustine, FL) was used in two aerobic experiments during July 2010. Treatments levels were 18 and 35 g kg^{-1} seawater and the DI water, 0 salinity control. Seawater was diluted to 18 g kg^{-1} with DI. Each soil treatment was placed in 200 mL beaker with the mass of each sample recorded. Microcosms were sealed with a gas-permeable

membrane. Microcosms were periodically stirred to promote O_2 mixing (five to ten times daily) stirring for less than 10 sec. Stirring was conducted out of direct light. Water was sampled at 24 h intervals over the course of 8 d, by removing a 10 mL sample. Microcosms were incubated at 25°C and overlying water was collected after the soil slurry settled. Data were normalized so that reported concentrations reflected the decreased water volume as the experiment progressed.

Anaerobic Experiments. Soil slurries were prepared using 50 g soil sample in 1 L of treatment water. Homogenates, for both amendment and seawater experiments, were placed into 20 mL serum vials with the oxygen in the overlying water purged by passing N_2 through the sample water. Each vial cap was held loosely in place during the 30 sec N_2 flush (O_2 purge) and sealed with butyl stoppers held in place by aluminum crimper bands. Treatments were conducted in triplicate. Serum vials were sacrificed, to extract each sample, in triplicate every seven days. The anaerobic experiments were conducted for 6 weeks. Vials were sacrificed and discarded after a 10 mL sample was collected. The Na_2SO_4 amendment experiment was conducted January 2011 and the seawater experiment was conducted in January 2012.

SO_4^{2-} amendments were prepared using Na_2SO_4 solutions prepared individually in DI water and reflected the level of SO_4^{2-} in 35 and 17.5 g kg^{-1} seawater (3.579 and 1.79g/L Na_2SO_4) and a 0 salinity (DI) water control. Homogenates consisted of 200 mL treatment solution and 50 g wet weight soil mass. Seawater, collected from Talbot Island State Park, FL, was applied to soil samples and followed the same protocol as the Na_2SO_4 amendment experiment. Homogenates were prepared at salinities (33 and 18 g kg^{-1}) similar to the amendment experiment.

Cl⁻, SO_4^{2-} , PO_4^{3-} Analysis. Analyte concentrations of porewater and experimental samples were determined chromatographically via anion exchange (Dionex® 2100, Sunnyvale CA.) per US EPA Methods 300.0 (A) and 300.1. The instrument was

calibrated using three standards relative to dissolved F^- , Cl^- , NO_2^- , Br^- , NO_3^- , PO_4^{3-} , and SO_4^{2-} . Porewater samples were passed through 45 μM glass-fiber filters to limit analytical column contamination.

Statistical Analysis

Analyte interactions and association with depth were tested with Pearson's product moment correlation. Correlations among variables were assessed within individual sites. Yates-adjusted Chi Square was calculated to determine any difference between the expected ratio of Cl^- to SO_4^{2-} in seawater (19.35 : 2.71, Pilson 1998) and the observed porewater ratio at 30 cm depth for each site. Chi Square calculations were conducted on Excel (Microsoft Corp.). LOI, total-P, labile-P, porewater- PO_4^{3-} , porewater- SO_4^{2-} , and metals (Fe, Mg, Mn, Ca) were tested with One-Way ANOVA between study sites, with site as the independent variable. Tukey's HSD post-hoc test was used for means separation of significant results. Porewater SO_4^{2-} and PO_4^{3-} data were compared between seasons (April-October and January-March) with an independent samples t-test. PO_4^{3-} data from the anaerobic experiments were analyzed using two-way ANOVA, with treatment (three levels) and study site (three levels) as independent variables. When main effects of treatment or site were significant, Tukey's HSD post hoc was used. A One-way ANOVA was also used to identify significant differences between PO_4^{3-} and SO_4^{2-} concentrations during the six-week experiment. Correlations, ANOVA, and t-tests were performed using SPSS (IBM). Significance for all statistical analysis was set at $\alpha=0.05$. Data are reported as mean \pm standard deviation.

RESULTS

Field Data and Soil Properties

Soil Properties. Soils at all sites were histosols, however, SC soil contained only 32% organic material (LOI), near the limit of that classification. Both SMC and GC Soils were organic peats with an O Horizon that extended beyond 1 m. SC Soils consisted of a gleyed matrix with abundant pyrite formations, distributed uniformly through the top 1 m. Percent organic based on LOI was significantly different at each site and decreased along the downstream axis. SMC contained more organic matter LOI ($82.35 \pm 5.11\%$) than GC ($64.45 \pm 7.02\%$), which was higher than SC soils ($32.11 \pm 9.61\%$).

There was a significant total-P trend along the downstream axis in soils at the three sites (mean = 1101, 719 & 475 $\mu\text{g/g}$ of soil for SMC, GC, and SC, respectively). Labile P fractions in soils were similar for the two upstream sites (5.27 and 5.51 $\mu\text{g/g}$, SMC and GC, respectively) with significantly lower concentrations at SC (2.36 $\mu\text{g/g}$). There was no significant difference in either total or labile phosphorus fractions between 0-10, 11-20, and 21-30 cm depths at any of the study sites.

Fe content at SMC soils ($3.4 \pm 0.92 \text{ mg g}^{-1}$) was significantly lower than either GC ($6.7 \pm 0.62 \text{ mg g}^{-1}$) or SC ($6.7 \pm 2.05 \text{ mg g}^{-1}$). A significant trend was observed between sites for soil Mg content. Mg was higher at SC ($8.12 \pm 2.05 \text{ mg g}^{-1}$) than GC ($4.39 \pm 0.38 \text{ mg g}^{-1}$) and lowest at SMC ($1.42 \pm 0.26 \text{ mg g}^{-1}$). Mn and Ca content of soils did not vary significantly between any of the three study sites. Mean Mn content at SMC, GC, and SC was 24.51 ± 1.67 , 45.25 ± 11.497 , and $35.96 \pm 14.7 \mu\text{g g}^{-1}$ respectively. Mean Ca content at SMC, GC, and SC was 22.57 ± 6.89 , 28.97 ± 36.30 , and $1.44 \pm 0.75 \text{ mg g}^{-1}$ respectively.

Porewater. At all sites, Cl^- and SO_4^{2-} were positively correlated ($r = 0.940$, $P < 0.01$). A weak negative correlation was found between SO_4^{2-} and PO_4^{3-} at SMC ($r = -0.198$, $P = 0.05$) and GC ($r = -0.319$, $P = 0.05$), but no significant interaction was observed at SC.

Field salinity data showed a significant difference between the upstream sites and SC. Mean salinity was lower at SMC ($0.45 \pm 0.1 \text{ g kg}^{-1}$) and GC ($2.05 \pm 2.3 \text{ g kg}^{-1}$) compared to SC ($27.81 \pm 3.1 \text{ g kg}^{-1}$) (Table 1).

PO_4^{3-} data was significantly different between the upstream study sites and SC. Porewater PO_4^{3-} was higher at SMC and GC (9.44 ± 15.6 , $8.99 \pm 14.7 \text{ } \mu\text{g L}^{-1}$, respectively) compared to SC ($0.6 \pm 3.1 \text{ } \mu\text{g L}^{-1}$) (Fig. 2). PO_4^{3-} content in porewater did not vary with depth at any of the study sites (Fig. 3), but porewater PO_4^{3-} was always higher at the 30cm depth compared to 5cm at all sites. Seasonally, PO_4^{3-} content in porewater varied significantly ($P=0.05$), comparing the growing season of April-October ($9.8 \pm 27.12 \text{ } \mu\text{g L}^{-1}$) with the cooler January-March season ($2.98 \pm 5.01 \text{ } \mu\text{g L}^{-1}$) (Fig. 4).

SO_4^{2-} content of porewater was significantly lower at SMC and GC (70.73 ± 57.58 and $124.35 \pm 152.5 \text{ } \mu\text{g L}^{-1}$, respectively) compared to SC ($1931.41 \pm 557.82 \text{ } \mu\text{g L}^{-1}$) (Fig. 2). SO_4^{2-} concentration was significantly lower at 20 to 30 cm soil depth (Fig 3) at SMC and GC. Mean SO_4^{2-} content in porewater at SMC was $84.45 \text{ } \mu\text{g L}^{-1}$ between 5 to 15 cm depth and significantly less ($56.86 \text{ } \mu\text{g L}^{-1}$) at the 20 to 30 cm depth (Fig. 3). At GC, mean SO_4^{2-} concentrations decreased significantly from $161.6 \text{ } \mu\text{g L}^{-1}$ at 5 to 15 cm depth to $79.51 \text{ } \mu\text{g L}^{-1}$ 20 to 30 cm soil deep. SC mean porewater SO_4^{2-} was $1931.41 \text{ } \mu\text{g L}^{-1}$ with no significant decrease with depth (Fig. 3). Seasonal comparisons of porewater SO_4^{2-} collected in April-October ($711.75 \pm 971.56 \text{ } \mu\text{g L}^{-1}$) and January-March ($726.40 \pm 808.70 \text{ } \mu\text{g L}^{-1}$) were not significantly different.

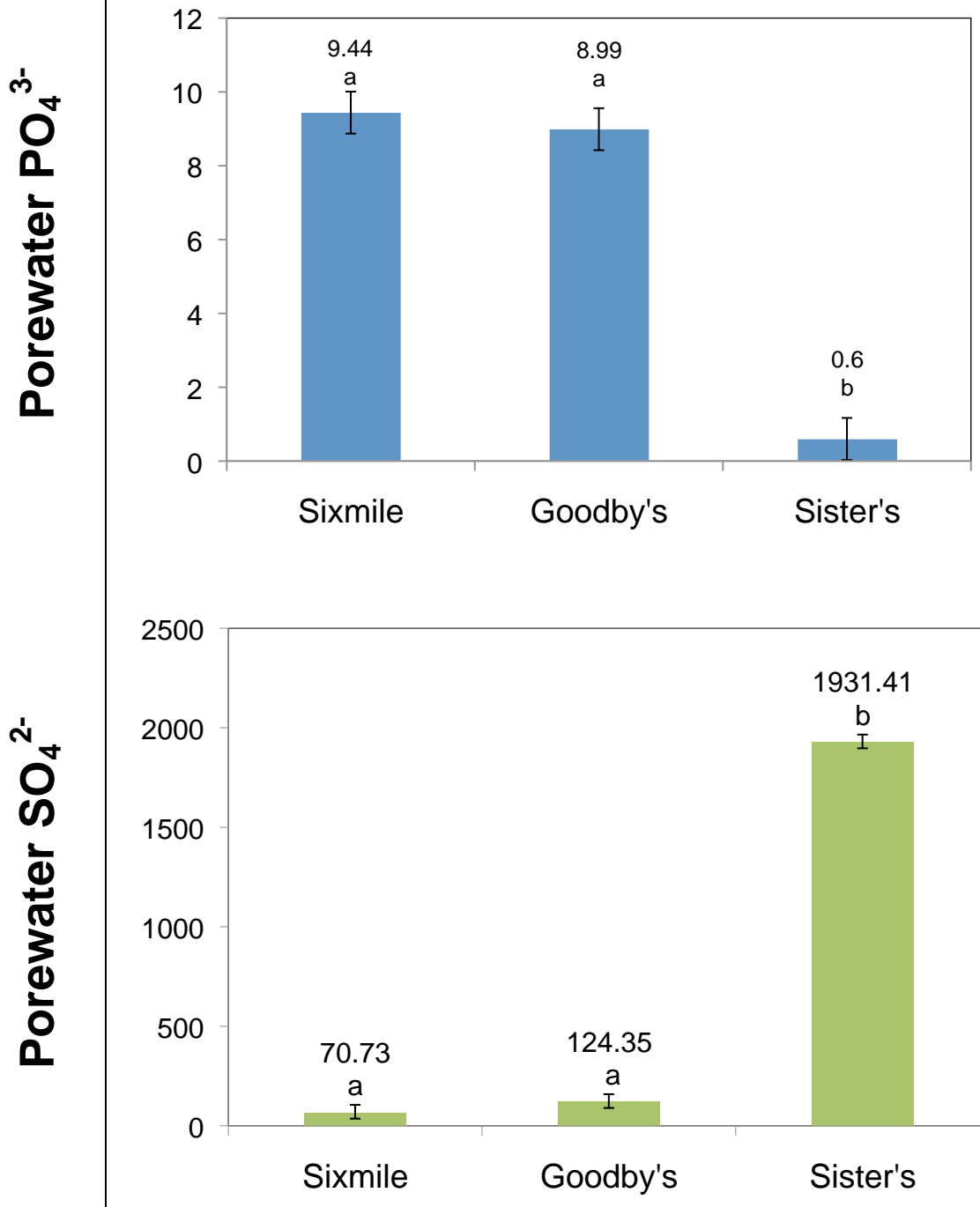


Fig. 2. Mean porewater content of PO_4^{3-} and SO_4^{2-} from soils at three study sites. Error bars represent SEM ($\text{PO}_4^{3-} = 0.569$, $\text{SO}_4^{2-} = 34.55$). Letters indicate significant differences ($\alpha=0.05$).

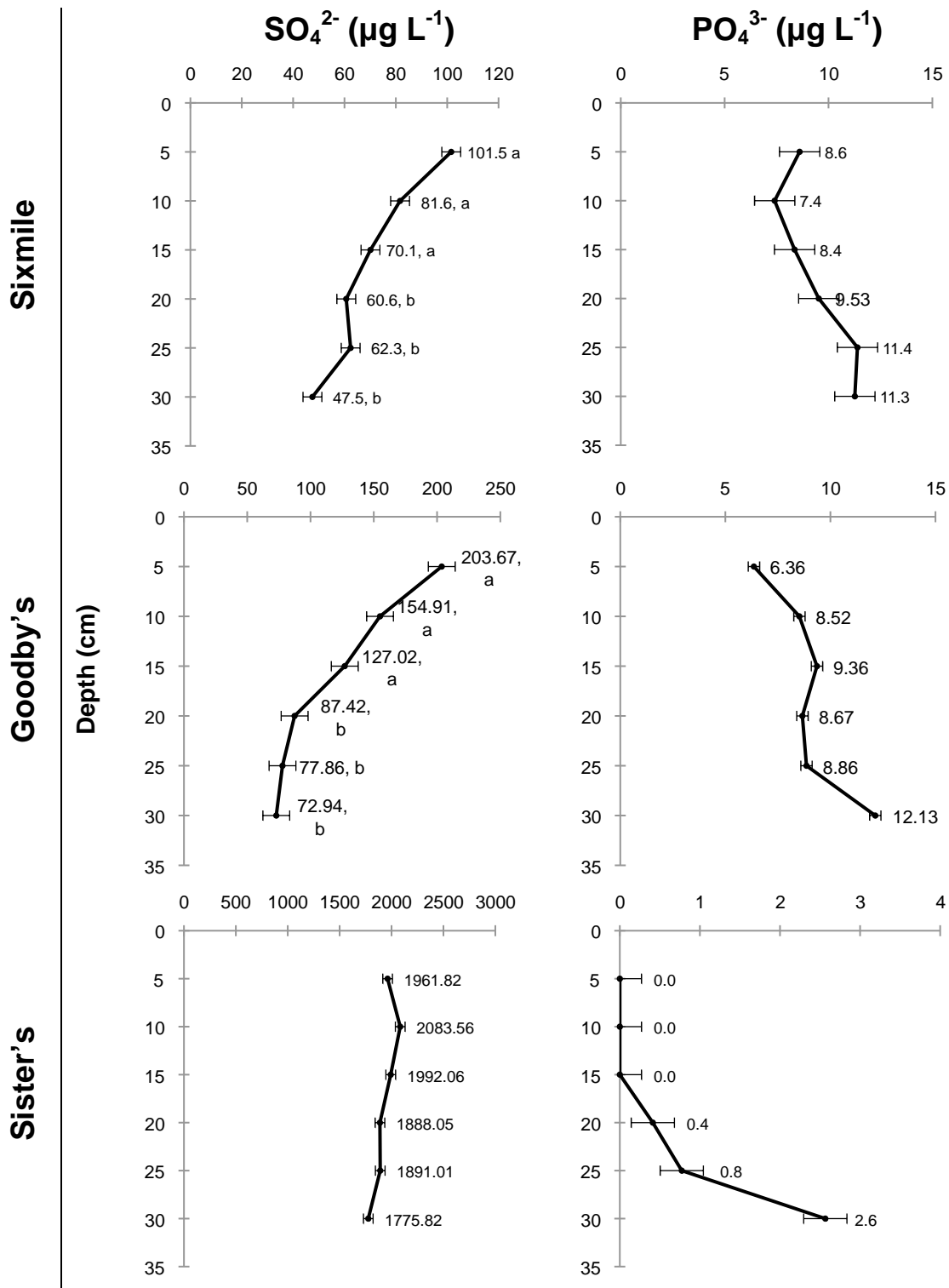
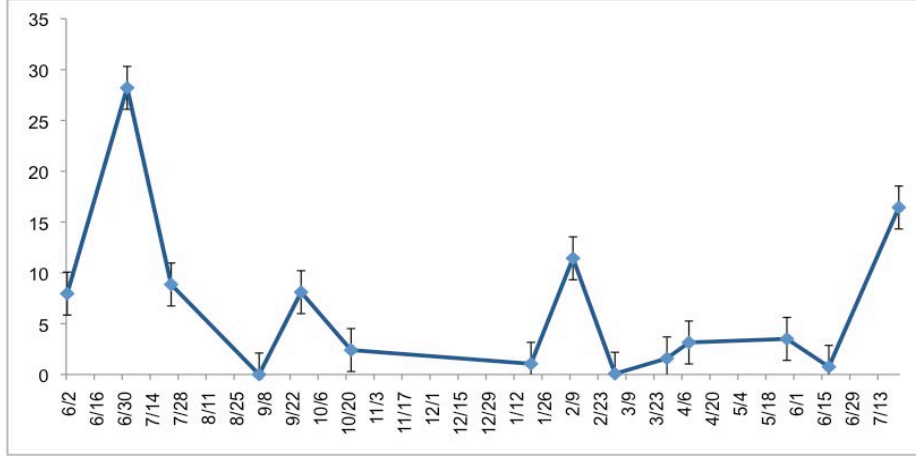


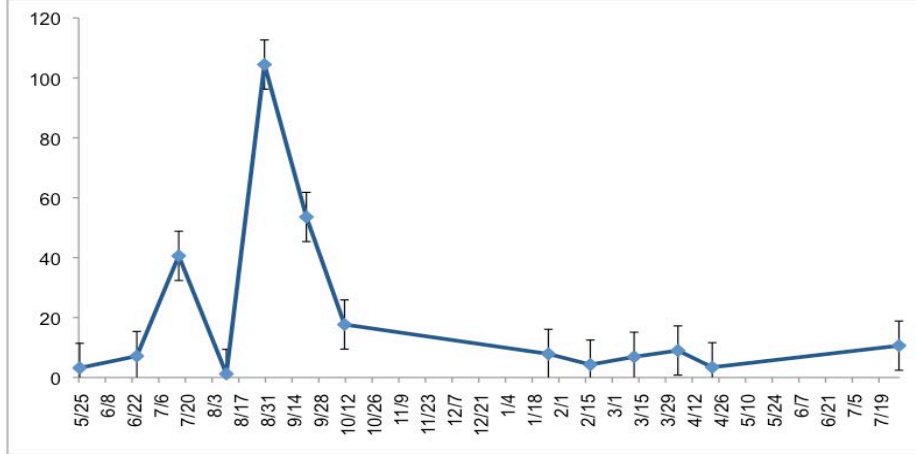
Fig. 3. Mean SO_4^{2-} and PO_4^{3-} soil profiles. Error bars represent SEM. Letters indicate significant differences ($\alpha=0.05$) between depths.

PO_4^{3-} ($\mu\text{g L}^{-1}$)

Sixmile Creek



Goodby's Creek



Sister's Creek

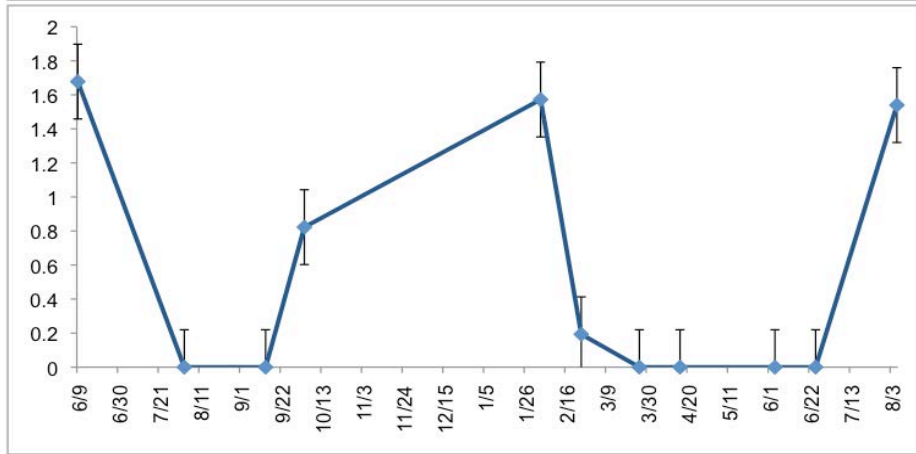


Fig. 4. Temporal PO_4^{3-} trends for Sixmile, Goodby's, and Sister's Creeks.

Table 1. Bulk Soil and field properties collected from three tidal wetland study sites.

Site and Soil Characteristics	Sixmile Ck.	Goodby's Ck.	Sister's Ck.
Salinity (g kg ⁻¹)	0.45 ± 0.1 ^a	2.05 ± 2.3 ^a	27.81 ± 3.1 ^b
Total-P (µg g ⁻¹)	1101.64 ± 220.2 ^a	719.61 ± 114.3 ^b	475.85 ± 110.9 ^c
Labile-P (µg g ⁻¹)	5.27 ± 1.78 ^a	5.51 ± 2.73 ^b	2.36 ± 0.90 ^a
LOI (%)	82.35 ± 5.11 ^a	64.45 ± 7.02 ^b	32.11 ± 9.61 ^c
Total-Fe (mg g ⁻¹)	3.4 ± 0.92 ^a	6.7 ± 0.62 ^b	8.12 ± 2.05 ^b
Total-Mg (mg g ⁻¹)	1.42 ± 0.26 ^a	4.39 ± 0.38 ^b	8.11 ± 0.98 ^c
Total-Mn (µg g ⁻¹)	24.51 ± 1.67	45.25 ± 11.497	35.96 ± 14.7
Total-Ca (mg g ⁻¹)	22.57 ± 6.89	28.97 ± 36.30	1.44 ± 0.75

Means ± standard deviations for each parameter, followed by letters, are significantly different ($\alpha=0.05$).

Microcosm Studies

Aerated soil slurries treated with filtered seawater did not result in detectable PO₄³⁻ flux from soils into overlying water at any point during the two experiments, which were conducted independently for 8 d. The PO₄³⁻ contents in water from aerated microcosms was below detection level regardless of soil site or salinity treatment level.

PO₄³⁻ was released into the overlying water in experimental microcosms prepared with Na₂SO₄ amendments. There were several significant trends, shown in Table 2. SMC Creek soils exposed to DI water released significantly more PO₄³⁻ to the overlying water (0.5 ± 1.03 µg L⁻¹) than either SO₄²⁻ treatment, both of which were below detection. GC microcosm PO₄³⁻ data were also significantly higher under reference (2.76 ± 1.71 µg L⁻¹) and intermediate (0.59 ± 1.14 µg L⁻¹) treatments, as the highest treatment

SO_4^{2-} level was below detection for PO_4^{3-} . A significant trend was also observed for soils from GC. Microcosm PO_4^{3-} content was higher under treatment with DI water ($2.76 \pm 1.71 \mu\text{g L}^{-1}$) compared to the intermediate treatment regime ($0.59 \pm 1.14 \mu\text{g L}^{-1}$) and was below detection at the highest treatment level. Samples collected from the Salt marsh at SC showed a significant positive trend associated with reference, intermediate, and high Na_2SO_4 treatment levels. The DI reference microcosm PO_4^{3-} content was the lowest $2.36 \pm 1.79 \mu\text{g L}^{-1}$. The $1.79 \text{ g L}^{-1} \text{ Na}_2\text{SO}_4$ treatment was lower ($6.52 \pm 4.79 \mu\text{g L}^{-1}$) than the 3.58 g L^{-1} ($10.76 \pm 5.19 \mu\text{g L}^{-1}$) treatment. PO_4^{3-} content in SMC and GC microcosms (0.17 ± 0.63 , $1.17 \pm 1.67 \mu\text{g L}^{-1}$ respectively) was significantly less than SC ($6.52 \pm 5.36 \mu\text{g L}^{-1}$) (Fig. 5). During the six-week timeframe of the Na_2SO_4 experiment, PO_4^{3-} content did not vary significantly.

SO_4^{2-} content in the microcosms did not change significantly ($p = 0.05$) between weeks of the Na_2SO_4 experiment. Mean SO_4^{2-} content in SMC microcosms increased $39.41 \mu\text{g L}^{-1}$ in the control treatment, decreased $237.86 \mu\text{g L}^{-1}$ in the 1.79 g L^{-1} treatment, and decreased $515.04 \mu\text{g L}^{-1}$ in the 3.58 g L^{-1} treatment. Mean SO_4^{2-} content in GC microcosms increased $12.62 \mu\text{g L}^{-1}$ in the control treatment, decreased $190.79 \mu\text{g L}^{-1}$ in the 1.79 g L^{-1} treatment, and decreased $525.21 \mu\text{g L}^{-1}$ in the 3.58 g L^{-1} treatment. Mean SO_4^{2-} content in SC microcosms increased $219.21 \mu\text{g L}^{-1}$ in the control treatment, decreased $191.16 \mu\text{g L}^{-1}$ in the 1.79 g L^{-1} treatment, and decreased $374.15 \mu\text{g L}^{-1}$ in the 3.58 g L^{-1} treatment.

Table 2. PO₄³⁻ content in microcosms subjected to treatment with Na₂SO₄

Treatment	Sixmile Ck.	Goodby's Ck.	Sisters Ck.
Na ₂ SO ₄ g L ⁻¹	PO ₄ ³⁻ μg L ⁻¹		
0	0.5 ± 1.03 ^a	2.76 ± 1.71 ^a	2.36 ± 1.79 ^a
1.79	BD ^b	0.59 ± 1.14 ^b	6.52 ± 4.79 ^b
3.58	BD ^b	BD ^b	10.76 ± 5.19 ^c
Mean (n=54)	0.17 ± 0.63	1.17 ± 1.67	6.52 ± 5.364*

Means ± standard deviations followed by letters are significantly different ($\alpha=0.05$), comparing treatments. BD, below detection limit. *Site PO₄³⁻ content means are significantly different at ($\alpha=0.05$).

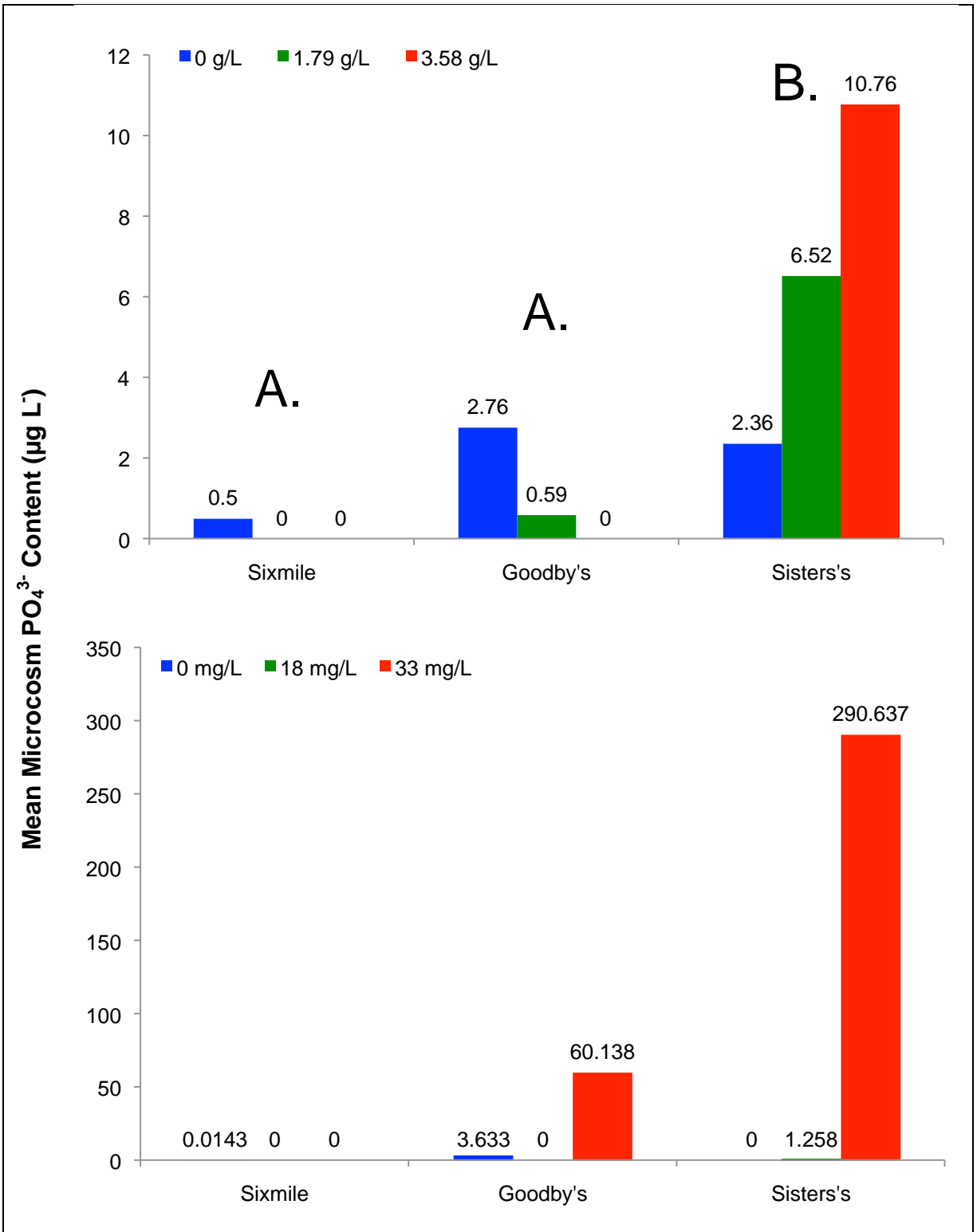


Fig. 5. Mean PO_4^{3-} content by treatment during the six-week microcosm experiments.

Seawater Treatments. Treatment of soils sampled from each site with ambient seawater, collected from the terminus of the SJR, showed no significant difference between site or treatment level. The water applied to each soil was analyzed prior to the experimental run and was highly P-limited (BD). While not significant, several notable trends occurred during the six-week experiment (Table 3). SMC soil microcosms contained higher PO_4^{3-} content at the reference treatment level, i.e. zero salinity, and were below detectable levels at both 18 and 33 g kg^{-1} treatments. GC seawater microcosms had the highest PO_4^{3-} at the 33 g kg^{-1} treatment level ($60.138 \pm 255.145 \mu\text{g L}^{-1}$), and the DI treatment was lower ($3.633 \pm 10.594 \mu\text{g L}^{-1}$). PO_4^{3-} was observed at SC in the 18 and 33 g kg^{-1} treatments and remained below detection in the DI reference. PO_4^{3-} release was negligible from all sites and highly variable ($39.43 \pm 334 \mu\text{g L}^{-1}$), however, it is notable that water from SMC microcosms had less PO_4^{3-} ($0.005 \pm 0.026 \mu\text{g L}^{-1}$), while GC microcosms were intermediate ($21.275 \pm 147.274 \mu\text{g L}^{-1}$) and SC had considerably more ($97.028 \pm 558.623 \mu\text{g L}^{-1}$). Saltwater microcosms showed no temporal variability in PO_4^{3-} composition.

SO_4^{2-} concentration of ambient seawater (at 33 g kg^{-1}) was $2859 \mu\text{g L}^{-1}$ and $1689.05 \mu\text{g L}^{-1}$ in the 18 g kg^{-1} treatment. SO_4^{2-} content in the microcosms did not change significantly between weeks of the seawater experiment. Mean SO_4^{2-} content in SMC microcosms increased $36.38 \mu\text{g L}^{-1}$ in the control treatment, decreased $602.81 \mu\text{g L}^{-1}$ in the 18 g kg^{-1} treatment, and decreased $725.65 \mu\text{g L}^{-1}$ in the 33 g kg^{-1} treatment. Mean SO_4^{2-} content in GC microcosms increased $6.74 \mu\text{g L}^{-1}$ in the control treatment, decreased $587.47 \mu\text{g L}^{-1}$ in the 18 g kg^{-1} treatment, and decreased $762.33 \mu\text{g L}^{-1}$ in the 33 g kg^{-1} treatment. Mean SO_4^{2-} content in SC microcosms increased $202.52 \mu\text{g L}^{-1}$ in the control treatment, decreased $382.76 \mu\text{g L}^{-1}$ in the 18 g kg^{-1} treatment, and decreased $566.28 \mu\text{g L}^{-1}$ in the 33 g kg^{-1} treatment.

Table 3. PO₄³⁻ content in microcosms subjected to treatment with Seawater

Treatment	Sixmile Ck.	Goodby's Ck.	Sisters Ck.
Seawater mg L ⁻¹	PO ₄ ³⁻ µg L ⁻¹		
0	0.0143 ± 0.448	3.633 ± 10.594	BD
18	BD	BD	1.258 ± 1.364
33	BD	60.138 ± 255.145	290.637 ± 955.6964
Mean (n=54)	0.005 ± 0.026	21.275 ± 147.274	97.028 ± 558.623

DISCUSSION**Field Data and Soil Properties**

Along the salinity continuum of the SJR, several parameters relevant to PO₄³⁻ chemistry varied. LOI is an effective means of quantifying the organic fraction of a soil and therefore serves as a proxy for P storage, as well (Sundareshwar and Morris 1999). LOI was significantly decreased between each site in accordance with the increasing saltwater access to each site (Table 1). Total soil P decreased in accordance with LOI, along SJR saltwater gradient (Table 1), a common observation of soil contents compared along tidal estuaries (Sundareshwar and Morris 1999; Craft 2007; Loomis and Craft 2010). Increased total P accumulation associated with human expansion in SJR basin was confirmed by Brenner et al., (2001), who found a pronounced decrease in total P below 0 - 20 cm in the wetland soils at headwaters of the river. In that study, the fertilized strata of soils contained nearly three times more P than SMC, four times more P than GC, and six times more than SC, indicating that significant soil P storage hasn't occurred in the areas of SJR that were analyzed in this study. Because the samples collected in the field during this analysis were both uniform at depth and comparable to similar tidal rivers (Loomis and Craft 2010), it is unlikely that augmented P loads in SJR

have resulted in exceptional P accumulation in the studied soils. The labile fraction of P was higher at SMC ($5.27 \mu\text{g g}^{-1}$) and GC ($5.51 \mu\text{g g}^{-1}$) than SC ($2.36 \mu\text{g g}^{-1}$) (Table 1). The labile P contents trend paralleled the porewater PO_4^{3-} collected at each site (Fig 2), which appeared more influenced by drainage activities than saltwater influence.

Karstic springs provide point source groundwater discharge, which contributes to the overall SJR flow (Demort 1991). Pore water at the three sites used in this study, however, received surface water from tides and not from groundwater, evidenced by the close correlation between Cl^- and SO_4^{2-} ($r = 0.94$, $P < 0.01$). The inverse relationship between PO_4^{3-} and SO_4^{2-} at both SMC and GC ($r = -0.198$ and -0.319 , $P = 0.05$, respectively) was moderate, suggesting that PO_4^{3-} wasn't directly displaced by SO_4^{2-} due to decreased sorption or SO_4^{2-} reduction, rather that porewaters are simply infiltrated by overlying water. The Salinity of water adjacent to the study sites was much lower at SMC and GC (0.45 and 2.05 g kg^{-1} , respectively) compared to the SC salt marsh (27.81 g kg^{-1}) (Table 1). The salinity differences between sites were reflected in the porewater analysis of SO_4^{2-} concentration at each site, which were transient at SMC and GC. The mortality and stress exhibited in *Taxodium distichum* and *Fraxinus caroliniana* at GC infer a long period of fresh conditions persisted at that site prior to this study. The salinity recorded at GC was apparently toxic to the freshwater community that previously persisted there, a phenomenon widely recorded in tidal swamps (Williams et al., 1999; Saha 2011).

At all study sites, PO_4^{3-} content in porewater was relatively low, ranging from $9.44 \mu\text{g L}^{-1}$ at SMC and $8.99 \mu\text{g L}^{-1}$ at GC to $0.6 \mu\text{g L}^{-1}$ at SC (Fig. 2), similar to the detailed analysis provided in Paludan and Morris (1999). Malecki et al., (2004), found that PO_4^{3-} released at the soil-water interface was 37 times greater under anaerobic conditions in the SJR. This study supports previous studies, which conclude that porewater PO_4^{3-}

depletion is due in part to oxic state (Gunnars and Blomqvist 1997; Pant and Reddy 2001).

For all data combined, mean porewater PO_4^{3-} was $6.34 \mu\text{g L}^{-1}$ however; the upstream SMC and GC were over ten times higher than the SC salt marsh. Porewater PO_4^{3-} content was significantly higher at SMC and GC (Fig. 2), which can be attributed to source water condition, also found by Yang et al., 2010. The SMC catchment was predominantly agrarian (EPA 2010b) and consisted of row cropping systems, which utilize PO_4^{3-} to support industrial farming practices. GC PO_4^{3-} was enriched due to the surrounding urbanized landscape, which included dense residential and commercial development (FL DEP 2005). PO_4^{3-} at SC was significantly lower than either upstream site (Table 1), which supports the conclusion that porewater fertilization is associated primarily with human activities in SJR catchment. SC drainage is comprised of conservation areas to the north and is subject to inundation with water from the Atlantic Ocean, where fertilizer impact is dilute. SC porewater is also subject to higher turnover and flushing, due to higher tidal amplitude at the mouth of SJR (NOAA 2012). The significant temporal porewater PO_4^{3-} differences described during this study compared the growing season of April-October ($9.8 \mu\text{g L}^{-1}$) with the cooler January-March season ($2.98 \mu\text{g L}^{-1}$), when both residential and agricultural fertilization is potentially less (Fig. 4). There were no significant differences between PO_4^{3-} contents compared between sampling depths at any site (Fig. 3) although there were significant seasonal differences, because PO_4^{3-} presence in porewaters was owed to water column fertilization at any given time. The data collected during the field efforts of this study reveal that porewater PO_4^{3-} contents are more likely associated with floodwater condition rather than potential interactions with saltwater constituents.

SO_4^{2-} content varied significantly between the upstream SMC ($70.73 \mu\text{g L}^{-1}$) and GC ($124.35 \mu\text{g L}^{-1}$) wetlands compared to SC ($1931.41 \mu\text{g L}^{-1}$) consistent with site

distance from the ocean. Hackney et al. (2007) reported that SO_4^{2-} reduction in tidal wetlands was sustained at levels as low as $100 \mu\text{g L}^{-1}$. These levels of SO_4^{2-} persisted intermittently at SMC and GC during the current study. GC soil SO_4^{2-} porewater exceeded the SO_4^{2-} reduction threshold more frequently than SMC and was likely subject to reduction more frequently than SMC. At SC, SO_4^{2-} supply was nearly 20 times that of upstream and constantly available to SO_4^{2-} reducers. SO_4^{2-} content was significantly depleted between the shallow (5 to 15 cm) and deep (20 to 30 cm) sampling depths at SMC and GC, indicating that reduction was occurring, but limited at those sites by the SO_4^{2-} oxidant, which only moved that far upriver during episodic saltwater intrusion. SC SO_4^{2-} content did not vary significantly with soil depth because soils at SC contained less organic material and reduction was not limited through the salt marsh soil profile.

There was no significant difference in soil SO_4^{2-} (Fig. 5) between April-October ($711.75 \mu\text{g L}^{-1}$) and January-March ($726.4 \mu\text{g L}^{-1}$) seasons (growing versus non-growing). Throughout sampling, SO_4^{2-} concentration in the SJR was likely dictated by tidal amplitudes and unassociated with season. SO_4^{2-} reduction was not subject to the thermal seasonality found in wetlands from much colder climates (Howarth and Teal 1979; Rooney-Varga et al., 1997).

Comparison of Fe content in wetland soils revealed an increasing trend from SMC to the downstream sites. Sundareshwar and Morris 1999 described the implications of this trend for PO_4^{3-} cycling varies based on salinity. The data collected in this study was similar and indicated that Fe content is proportionally less abundant in the freshwater extent of SJR estuary due to more abundant organic contents. The surface area interaction between soil organics and Fe decreases PO_4^{3-} precipitation from porewater due to proportionally decreased Fe availability. An important factor specific to GC soils is that oligohaline conditions facilitate Fe oxide and FePO_4 flocculation and, therefore, precipitation to soils (Sundareshwar and Morris 1999). Since the highest

content of Fe was observed at the SC system, while the lowest porewater PO_4^{3-} was recorded there, it is most likely that PO_4^{3-} retention is decreased in the soils at that site due to S^- production and pyrite precipitation, as described by Luther et al 1992 and that the constant flooding of the soils with marine waters readily removes dissolved PO_4^{3-} .

Microcosm Studies

The aerobic experiments outline the importance of oxic state in soil PO_4^{3-} retention capacity, a phenomenon widely recognized in wetland soils for both the SJR (Malecki et al., 2004) and elsewhere (Pomeroy et al., 1965; Reddy et al., 1999; Pant and Reddy 2001). During both 8 d studies, the variable salinity treatments did not result in different PO_4^{3-} fluxes from any of the assessed tidal wetland soils. Aerating samples maintained the PO_4^{3-} in each soil and did not change based on ion content as some studies have reported (Barrow et al., 1980; Garoldinski et al., 2004).

Na_2SO_4 was applied in varying treatment level to soils from each site to isolate the influence of SO_4^{2-} reduction on PO_4^{3-} mobilization from each wetland soil studies during field efforts. SO_4^{2-} reduction was verified by depleted microcosm contents compared to initial treatments, during the experiment. SO_4^{2-} content decreased in microcosms most rapidly during the first week of the incubation study. Similar rates of SO_4^{2-} depletion were recorded during this study as by Chambers et al., 2011. SO_4^{2-} depletion in amended treatments is commonly considered a result of dissimilatory reduction in a variety of soil types (Scheid, et al, 2003; Vile et al., 2003; etc). SO_4^{2-} reduction in SMC microcosms depleted 18 and 19% in the 1.79 and 3.58 g L⁻¹ Na_2SO_4 treatment, respectively. Amended GC soils were depleted of 14 and 19% of SO_4^{2-} in the respective 1.79 and 3.58 g L⁻¹ Na_2SO_4 treatments. SC microcosms treated with 1.79 and 3.58 g L⁻¹ Na_2SO_4 , were depleted by 14 and 13% respectively. The temporal trends in SO_4^{2-} concentration described reduction rates increasing in the 0-1 week, which is most likely a response to terminal electron acceptor availability, including acetate and lactate,

which are rapidly utilized by SO_4^{2-} reducing bacteria. In control treatments, SO_4^{2-} increased during the course of the experiment due to residual SO_4^{2-} contents of soil samples. According to the Hackney et al., 2007 threshold, only the SC control treatment retained sufficient enough SO_4^{2-} to support reduction.

Soils at both SMC and GC released significantly more PO_4^{3-} under the DI control. Since SO_4^{2-} reduction was recorded for treatment microcosms, the PO_4^{3-} released from these soils was likely as a result of alternative oxidation pathways such as Fe reduction, which has been previously described as highly influential on PO_4^{3-} release from SJR sediments (Malecki et al 2004). At SMC and GC, SO_4^{2-} amendments had an inhibitory effect on PO_4^{3-} mobilization (Table 2), despite being higher in all assessed fractions of P (Table 1). Dierberg et al., 2011 conducted a similar experimental effort, while treatment levels were much lower than was assessed during this study, and similarly concluded some inhibition of PO_4^{3-} mobilization under SO_4^{2-} amendments. The likely explanation for this phenomena is that the available PO_4^{3-} at SMC and GC was utilized biotically, considering P is a commonly limiting nutrient (Reddy and DeLaune 2008). Also, SO_4^{2-} reduction acts on specific electron donors (Liamleam and Annachhatre 2007; Sutton-Grier 2011), none of which are directly associated with P. S^- production may have inhibited microbial activity in treatment microcosms (Dierberg et al., 2011) particularly the proportionally less Fe-abundant SMC and GC soils. The results recorded at SMC and GC support recent assertions that diagenetic state may not enhance reactive PO_4^{3-} flux into overlying water (Southwell et al., 2011). Furthermore, is the data collected in the freshwater extent of the SJR show that the more abundant soil P content is not bioavailable (Pauldan and Morris 1999) and that porewater PO_4^{3-} is primarily a result of hydrologic factors. Clearly, however, PO_4^{3-} mobilization is not enhanced by SO_4^{2-} reducing conditions at SMC or GC soils.

The DI reference treatment at SC soils resulted in measurable PO_4^{3-} flux, however SO_4^{2-} reduction likely occurred during the experiment, as residual SO_4^{2-} was present in sufficient enough quantities to support reduction. SO_4^{2-} treatments on soils at SC did not inhibit microbial activity, rather SO_4^{2-} reduction stimulated PO_4^{3-} flux (Table 2). The most plausible explanation for the observed relationship is that the Fe content recorded at SC is partially available to fix S^- , which limited toxicity, and that the PO_4^{3-} was displaced from FePO_4 , a reaction most recently reiterated by Hartzell and Jordan 2011. SC was the most P depleted wetland during the field sampling efforts (Table 1). Such conclusions support previous studies, which reveal pyrite formation as the mechanism of increased PO_4^{3-} availability in salt marsh ecosystems (Sundareshwar et al., 2003). The conclusion by Lamers et al., (1998) that PO_4^{3-} eutrophication is directly induced by SO_4^{2-} reduction examined porewater interactions using a flow through design. During the timeframe in which PO_4^{3-} mobility was enhanced in the Lamers et al, (1998) study systems, S^- increased at a commensurate rate to Fe depletion in porewaters. If soil P is characterized as more recalcitrant, as is proposed in this study and elsewhere (Pauldan and Morris 1999), the PO_4^{3-} releases may be a direct result of Fe precipitation to pyrite, which thereby limits the retention capacity of waterlogged soils by disrupting the “iron curtain” described by Chambers and Odum (1989). The experimental amendments indicate that the field data were the result of a limited capacity to retain P indirectly due to SO_4^{2-} reduction and support the finding that hydrologic export plays a significant role in the paucity of porewater PO_4^{3-} at all sites (Megonigal and Neubauer 2009).

Ambient seawater was applied in varying treatment levels to soils from each site to experimentally determine how natural conditions, including SO_4^{2-} reduction, would affect PO_4^{3-} mobility. Similar trends were noted to the Na_2SO_4 experiment, however data were not conclusive and highly variable. SO_4^{2-} depletion during the experiment was

interpreted as a result of reduction and data were similar to amended microcosms reported in previous studies (Chambers et al., 2011). SO_4^{2-} reduction in SMC microcosms depleted 11 and 25% in the 18 and 33 g kg^{-1} microcosms, respectively. GC soil microcosms were depleted of 34 and 26% of SO_4^{2-} in the 18 and 33 g kg^{-1} microcosms, respectively. 18 and 33 g kg^{-1} microcosm treatments applied to SC soils were reduced 22 and 20%, respectively, in SO_4^{2-} concentration. In DI reference treatments, SO_4^{2-} increased during the course of the experiment due to residual SO_4^{2-} contents of soil samples. Again, similar to the amendment experiment, only the SC control treatment retained sufficient SO_4^{2-} concentrations to support reduction (Hackney et al., 2007).

Notably, SMC PO_4^{3-} mobilization only occurred during exposure to DI water, which also indicates that S^- production may have inhibited microbial activity and PO_4^{3-} flux, as reported by Dierberg et al., (2011) and that the total P content recorded at that site is less bioavailable (Paludan and Morris 1999). GC soils were variable in response to seawater treatment concentration. DI reference treatment resulted in PO_4^{3-} content delivery to microcosm water, most likely as a result of Fe reduction and associated PO_4^{3-} release (Malecki et al. 2004; Hartzell and Jordan 2012). Treatments with 33 g kg^{-1} seawater resulted in higher PO_4^{3-} flux than the 18 g kg^{-1} (Table 3) or the analogous amended treatment (Table 2). The 18 and 33 g kg^{-1} treatments may reflect the influence of salinity on a freshwater microbial pool as recorded by Pattnaik et al., (2000) and Wong et al., (2008). The intermediate ion content in the 18 g kg^{-1} treatment may have inhibited freshwater microbial activity while not exceeding the osmotic threshold of the microbial population present. The ionic content in the 33 g kg^{-1} treatment may represent an exceedance of freshwater microbial pool salinity tolerance causing plasmolysis and nutrient release. At SC, PO_4^{3-} mobility increased with treatment concentration, similar to the amendment experiment, though the data were not determined to be significant.

Applying ambient seawater to soils increased the potential variability in recorded PO_4^{3-} flux, by likely introducing osmotic stress gradients, alternative oxidants (NO_3^- , Fe, and Mn), and potentially contamination. The variability in the seawater treatments precluded specific interpretation of the data set, importantly however, a generalized trend similar to the amendment experiment and revealed that PO_4^{3-} fluxes are not the direct result of seawater amendment or SO_4^{2-} reduction.

References

- Barrow, N.J., J.W. Bowden, A.M. Posner, J.P. Quirk. 1980. Describing the effects of electrolyte on adsorption of phosphate by a variable charge surface. *Australian Journal of Soil Research* 18: 395-404.
- Blomqvist, S., A. Gunnars, R. Elmgren. 2004. Why the limiting nutrient differs between temperate coastal seas and freshwater lakes: A matter of salt. *Limnology and Oceanography* 49: 2236-2241.
- Brenner M., C.L. Schelske, L.W. Keenan. 2001. Historical rates of sediment and nutrient accumulation in marshes of the Upper St. Johns River Basin, Florida, USA. *Journal of Paleolimnology* 26: 241-257.
- Burkett, V., R. Ritschard, S. McNulty, J.J. O'Brien, J.J., Abt, R., Jones, J., Hatch, U., Murray, B., Jagtop, S., Cruise, J., 2001. Potential consequences of climate change variability and change for the southeastern United States. In: *Climate Change Impacts on the United States: The Potential Consequences of Climate Variability and Change*. Cambridge University Press, Cambridge, pp. 137–164.
- Burns, J. 2008. EPA International Symposium on Cyanobacterial Harmful Algal Blooms: Cyanobacterial Harmful Algal Blooms: State of the Science and Research Needs. Chapter 5: Toxic Cyanobacteria in Florida Waters pp. 128-137. Springer.
- Chambers, L.G., K.R. Reddy and T.Z Osborne. 2011. Short-term pulses of carbon cycling to salinity pulses to salinity pulses in a freshwater wetland. *Journal of The Soil Science Society America* 75: 2000-2007.
- Cloern, J. E. 2001. Our evolving conceptual model of the coastal eutrophication problem. *Marine Ecology Progress Series* 210: 223-253.
- Conley, D., 2000. Biogeochemical nutrient cycles and nutrient management strategies. *Hydrobiologia* 410: 87-96.

- Conley, D., H.W. Paerl, R.W. Howarth, D.F. Boesch, S.P. Seitzinger, K.E. Havens, C. Lancelot, G.E. Likens. 2009. Controlling Eutrophication: Nitrogen and Phosphorus Science 323: 1014-1015.
- Correll D.L. 1999. Phosphorus: A Rate Limiting Nutrient in Surface Waters. Poultry Science 78: 674-682.
- Craft, C. 2007. Freshwater input structures soil properties, vertical accretion, and nutrient accumulation of Georgia and U.S. tidal marshes. Limnology Oceanography 52: 1220-1230.
- DeMort, C. 1991. The Rivers of Florida. Volume 83. Chapter. 7 - The St. Johns River system. Springer-Verlag, New York, NY. pp. 97- 120.
- DeMort, C., R.D. Bowman. 1985. Seasonal Cycles of Phytoplankton Populations and Total Chlorophyll of the Lower St. Johns River Estuary, Florida. Biological Sciences 48: 96-107.
- Dierberg, F., T. A. DeBusk, N.R. Larson, M.D. Kharbanda, N. Chan, M.C. Gabriel. 2011. Effects of sulfate amendments on mineralization and phosphorus release from South Florida (USA) wetland soils under anaerobic conditions. Soil Biology and Biochemistry 43: 31- 45.
- Edgell, K. 1989. US EPA Method Study 37 SW-846 Method 3050 Acid Digestion Of Sediments, Sludges, and Soils.
- EPA (United States Environmental Protection Agency), Region 4. 2010b. Proposed Total Maximum Daily Loads for the Sixmile Creek WBID 2411 Dissolved Oxygen.
- EPA (United States Environmental Protection Agency). 2010a. 40 CFR 131. Part II Water Quality Standards for the State of Florida's Lakes and Flowing Waters. Federal Register 75: 75762-75807.
- FL-DEP (Florida Department of Environmental Protection). 2005. TMDL Report Fecal Coliform TMDL for Goodby's Creek (WBID 2326). Technical Report.

- Florida Natural Areas Inventory (FNAI). 2010. Guide to the natural communities of Florida: 2010 edition. Florida Natural Areas Inventory, Tallahassee, FL.
- Gardolinski, P., P.J. Worsfold, I.D. McKelvie. 2004. Seawater induced release and transformation of organic and inorganic phosphorus from river sediments. *Water Research* 38: 688–692.
- Glibert, P.M., D. Anderson, P. Gentien, E. Granéli, K. Sellner. 2005. The global, complex phenomena of harmful algal blooms. *Oceanography* 18: 136–147.
- Gunnars A., S. Blomqvist. 1997. Phosphate exchange across the sediment-water interface when shifting from anoxic to oxic conditions – an experimental comparison of freshwater and brackish-marine systems *Biogeochemistry* 37: 203–226.
- Hackney, C., G. Avery, L. Leonard, M. Posey, T. Alphin. 2007. Ecology of Tidal Freshwater Forested Wetlands of the Southeastern United States: Chapter 8 - Biological, Chemical, and Physical Characteristics of Tidal Freshwater Swamp Forests of the Lower Cape Fear River/Estuary, North Carolina. Springer, New York, NY. pp. 183-221.
- Hartzell, J., T.E. Jordan. 2012. Shifts in the relative availability of phosphorus and nitrogen along estuarine salinity gradients. *Biogeochemistry* 107: 489–500.
- Hesslein, R.H. 1976. An in-situ sampler for close interval porewater studies. *Limnology and Oceanography* 21: 912-914.
- Howarth, R., J.M. Teal. 1979. Sulfate Reduction in a New England Salt Marsh. *Limnology and Oceanography* 24: 999-1013.
- Keller AE, JD Schell. 1993. St. Johns River Basin Reconnaissance: Sediment Characteristics and Quality. Volume 5. St. Johns River Water Management District Technical Publication SJ93-6.

- Kuo, S., 1996. Phosphorus. In: Sparks, D.L., et al. (Eds.), *Methods of Soil Analysis Part 3: Chemical Methods*. SSSA Book Series 5. American Society of Agronomy, Madison, WI, pp. 869–920.
- Lamers, L., H. Tomassen, J.G.M. Roelfs. 1998. Sulfate-Induced Eutrophication and Phytotoxicity in Freshwater Wetlands. *Environmental Science and Technology* 32: 199-205.
- Liamleam W., A. P. Annachatre. 2007. Electron donors for biological sulfate reduction. *Biotechnology Advances* 25: 452-463.
- Loomis, M.J., C.B. Craft. 2010. Carbon sequestration and nutrient (nitrogen, phosphorus) accumulation in river-dominated, tidal marshes, Georgia, USA. *Soil Science Society America* 74: 1028-1036.
- Luther, G.W., J.E. Kostka, T.M. Churcha, B. Sulzberger, W. Stumm. 1992. Seasonal iron cycling in the salt-marsh sedimentary environment: the importance of ligand complexes with Fe(II) and Fe(III) in the dissolution of Fe(III) minerals and pyrite, respectively. *Marine Chemistry* 40: 81-103.
- Malecki L., J. White, K. Reddy. 2004. Nitrogen and Phosphorus Flux Rates from Sediment in the Lower St. Johns River Estuary. *Journal of Environmental Quality* 33: 1545–1555.
- Megonigal, P., S. Neubauer. 2009. Biogeochemistry of Tidal Freshwater Wetlands. In: Gerardo M. E. Perillo, Eric Wolanski, Donald R. Cahoon, Mark M. Brinson, editors, *Coastal Wetlands: An Integrated Ecosystem Approach*. Elsevier Amsterdam, Netherlands. p. 535-562.
- Morris, F. 1995. Volume 3 of the Lower St. John's River Reconnaissance, Hydrodynamics and Salinity of Surface Water. St. John's River Water Management District Technical Report SJ95-9.

- National Oceanic and Atmospheric Administration. 2012. Mean Sea Level Trend 8720218 Mayport, Florida. Accessed at: http://tidesandcurrents.noaa.gov/sltrends/sltrends_station.shtml?stnid=8720218
- National Oceanic and Atmospheric Administration. 2012. Tide Predictions for Mayport, Florida Station ID 8720211. Accessed at: <http://tidesandcurrents.noaa.gov/noaatidepredictions/NOAATidesFacade.jsp?Stationid=8720211>
- Nelson, M.L., L.E. Sommers. 1996. Total carbon, organic carbon, and organic matter: Loss-on-ignition method. p. 1004–1005. In D.L. Sparks (ed.) Methods of soil analysis. Part 3. Chemical methods. SSSA Book Ser. 5. SSSA, Madison, WI.
- Paludan, C., J. Morris. 1999. Distribution and speciation of phosphorus along a salinity gradient in intertidal marsh sediments. *Biogeochemistry* 45: 197-221.
- Pant, H. K., K.R. Reddy. 2001. Phosphorus Sorption Characteristics of Estuarine Sediments under Different Redox Conditions. *Journal of Environmental Quality* 30: 1474-1480.
- Pattnaik, P., S.R. Mishra, K. Bharati, S.R. Mohanty, N. Sethunathan, T.K. Adhya. 2000. Influence of salinity on methanogenesis and associated microflora in tropical rice soils. *Microbiology Research* 155: 215-220.
- Pomeroy L., E. Smith, C. Grant. 1965. The Exchange of Phosphorus between Estuarine Waters and Sediments. *Limnology and Oceanography* 10: 167-172.
- Reddy, K. R., R. H. Kadlec, E. Flaig, P.M. Gale. 1999. Phosphorus Retention in Streams and Wetlands: A Review, *Critical Reviews in Environmental Science and Technology* 29: 83-146.
- Reddy, K.R, R. DeLaune, 2008. *Biogeochemistry of Wetlands - Ch. 9: Phosphorus*. CRC Press. Boca Raton FL. pp. 325-403.

- Reddy, K.R. R.H Kadlec, E. Flaig, P.M. Gale. 1999. Phosphorus Retention in Streams and Wetlands: A Review. *Critical Reviews in Environmental Science and Technology* 29: 82-146.
- Rooney-Varga J.N., R. Deveraux, R.S. Evans, M. Hines. 1997. Seasonal changes in the relative abundance of uncultivated sulfate-reducing bacteria in a salt marsh sediment and in the rhizosphere of *Spartina alterniflora*. *Applied and Environmental Microbiology* 63: 3895-3901.
- Roychoudhury, A.K., P. Van Capellen, J. Kostka, E. Voillier. 2003. Kinetics of microbially mediated reactions: dissimilatory sulfate reduction in saltmarsh sediments (Sapelo Island, Georgia, USA). *Estuarine, Coastal, and Shelf Science* 56: 1001-1010
- Saha, A.K., S. Saha, J. Sadle, J. Jiang, M.S. Ross, R.M. Price, L.S. Sternberg, K.S. Wendelberger. 2011 Sea level rise and South Florida coastal forests. *Climate Change* 107: 81-108.
- Scheid, D., S. Stubner, R. Conrad. 2003. Effects of nitrate and sulfate amendment on the methanogenic populations in rice root incubations. *Microbiology Ecology* 43: 309-315.
- Smolders AJP, L. Lamers, M. Moonen, K. Zwaga, J. Roelofs. 2001. Controlling phosphate release from phosphate-enriched sediments by adding various iron compounds. *Biogeochemistry* 54: 219-228.
- Sommers, L.E., D.W. Nelson. 1972. Determination of total phosphorus in soils: a rapid perchloric acid digestion procedure. *Soil Science Society of America Proceedings* 36 902-904.
- Southwell, M.W., R.N. Mead, C.M. Luguire, A. Barbera, G.B. Avery, R.J. Kieber, S.A. Skrabal. 2011. Influence of organic matter source and diagenic state on

- photochemical release of dissolved organic matter and nutrients from resuspended estuarine sediments. *Marine Chemistry* 126:114-119.
- St. John's River Water Management District. 2009. News Release: Governing Board Approves Seminole County Withdrawal Permit. Accessed at: <http://webapub.sjrwmd.com/agws/newsrelease/index.aspx?year=2009>
- Sundareshwar P. V., J. T. Morris, E. K. Koepfler, B. Fornwalt. 2003. Phosphorus limitation of coastal ecosystem processes. *Science*. 299: 563-565.
- Sundareshwar, P., J. Morris. 1999. Phosphorus Sorption Characteristics of Intertidal Marsh Sediments along an Estuarine Salinity Gradient. *Limnology and Oceanography* 44: 1693-1701.
- Sundby, B., C. Gobeil, N. Silverberg, A. Mucci. 1992. The phosphorus cycle in coastal marine sediments. *Limnology and Oceanography* 37: 1129-1145.
- Sutton-Grier, A.E., J.K. Keller, R. Koch, C. Gilmour, J. Megonigal, 2011 Electron donors and acceptors influence anaerobic soil organic matter mineralization in tidal marshes. *Soil Biology & Biochemistry* 43: 1576-1583.
- Vile, M.A., S.D. Bridgham, K. Weider. 2003. Response of Anaerobic Carbon Mineralization Rates to Sulfate Amendments in a Boreal Peatland. *Ecological Applications* 13: 720-734.
- Williams, K., K.C. Ewel, R.P Stumpf, F.E. Putz, T.W. Workman. 1999. Sea-level rise and coastal forest retreat on the west coast of Florida, USA. *Ecology* 80: 2045-2063
- Wong, V.N.L., R.C. Dalal, R. Greene. 2008. Salinity and sodicity effects on respiration and microbial biomass of soil. *Biology of Fertilized Soils* 44:943–953.
- Yang, Y.G., Z.L. He, Y. Lin, P.J. Stoffella. 2010. Phosphorus availability in sediments from a tidal river receiving runoff water from agricultural fields. *Agricultural Water Management* 97: 1722–1730.

VITA

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From 2005-2007, Mr. Williams was an employee of the Aquatic Ecology Laboratory at The Center for Marine Science in Wilmington, North Carolina. As a research technician in The Aquatic Ecology Laboratory, his primary responsibilities were field data collection and analysis of water quality throughout several estuarine basins in Southeastern North Carolina. Also during 2007, Mr. Williams was an employee of the Wetlands Ecology Laboratory at The University of North Carolina at Wilmington. His primary duties were to deploy and retrieve field instruments in tributaries of The Cape Fear River. From 2008-2010 Mr. Williams worked for TEC. Inc, an environmental consulting firm. As an analyst for TEC, he conducted ambient surface water quality analysis on military installations and ground proofed wetlands delineations for base personnel.

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