

## BIOGEOCHEMICAL INDICES OF PHOSPHORUS RETENTION AND RELEASE BY WETLAND SOILS AND ADJACENT STREAM SEDIMENTS

Ed J. Dunne, Ramesh Reddy, and Mark W. Clark

*University of Florida/IFAS  
Soil and Water Science Department  
106 Newell Hall  
P.O. Box 110510  
Gainesville, Florida, USA 32611  
E-mail: ejdunne@ifas.ufl.edu*

**Abstract:** Eutrophication is still a water quality problem within many watersheds. The Lake Okeechobee Basin, Florida, USA, like many watersheds is impacted by eutrophication caused by excess phosphorus (P). To meet water quality criteria to reduce this impairment, several levels of information on P dynamics within the Basin are required. The use of biogeochemical indices to help determine P retention/release of different landscape units such as wetlands and streams provides useful information on P dynamics. The objective of our study was to determine P retention/release indices for a range of wetland soils and their adjacent stream sediments. We sampled several wetlands and adjacent streams within Okeechobee's Basin, which represented a range of P impacted systems. Regression analyses suggest that a single incubation of sediment/soil equilibrated at 1000 mg P kg<sup>-1</sup> was sufficient (> 96% of the time) to estimate maximum P sorption capacity ( $S_{max}$ ). Using this single incubation, sampled wetlands had nearly twice the P sorption capacity ( $238 \pm 21$  mg P kg<sup>-1</sup>) of stream sediments ( $146 \pm 14$  mg P kg<sup>-1</sup>). Stream sediments also had a greater P saturation ratio (PSR) than wetland soils, indicating that sediment had a greater potential to release P. Phosphorus sorption under ambient P conditions (soil equilibrated with ambient site water) covaried best with P concentrations in site surface water and, as concentrations increased, P sorption also increased. Finally, we used soil P storage capacity (SPSC) to help estimate the ability of soils and sediments to retain additional P loadings and found that wetland soils had a greater ability to retain P. Phosphorus sorption was predicted equally well (> 73%) using either ammonium oxalate or 1 M HCl extractable Fe and Al. The use of indices to quantify P dynamics of different landscape units can inform watershed management and policies aimed at reducing P loads to receiving water bodies.

**Key Words:** phosphorus, wetlands, streams, indices, sorption, retention, and release

### INTRODUCTION

Water quality is still a problem in many watersheds within the USA. Over 40% of the U.S. Environmental Protection Agency's assessed waters still do not meet water quality standards (EPA 2002). Under the 1972 Clean Water Act, States, Territories and Tribes are required to list their impaired waters, which are those waters not meeting water quality standards for a particular designated use. In addition, they are required to establish a total maximum daily load (TMDL) for those impaired waters. This is the maximum pollutant load (pollutant causing impairment) a waterbody can receive from its surrounding watershed and still meet water quality criteria. To facilitate the TMDL process and subsequent establishment of appropriate water quality criteria, a comprehensive un-

derstanding of water quality degradation in the particular watershed, is important. For example, concern about eutrophication of Lake Okeechobee, Florida initially arose back in the 1970s due to increases in water-column total phosphorus (P) concentrations (Havens et al. 2003). Phosphorus loading from the watershed to the lake is often ascribed to non-point source agricultural runoff (Reddy et al. 1995, Hiscock et al. 2003), and despite a history of implementing agricultural best management practices (BMPs) in the basin, water quality still exceeds desired criteria (Flaig and Reddy 1995). At present, the Lake Okeechobee Protection Act legislatively requires a protection plan for the lake and a component of that is a TMDL (to be achieved by 2015) of 140 metric tonnes of P per year, which is equal to an in-lake target concentration of about 40 µg P L<sup>-1</sup> (FDEP 2001).

Monitoring and managing the basin to help meet lake water quality criteria impacts land uses such as agriculture. Therefore, the use of biogeochemical indices, which can help identify impacts to water quality, such that control and mitigation management plans can be implemented, are useful. Indices that are both dynamic and have the ability to assess changes in environmental conditions are critical to environmental management plans and policies (La Peyre *et al.* 2001) so lake waters can be protected. We propose that the indices we used to determine the potential for P retention and release by wetland soils and their adjacent stream sediments help to (i) understand ecosystem processes, (ii) compare P dynamics of different landscape units, and (iii) although we determined indices using historical data, these indices are useful to the present P TMDL process in the Okeechobee Basin. Further, we believe that these indices have broad application to other watersheds, where impacts are degrading water quality. However, to be appropriate to a particular watershed, indices should be locally calibrated.

Typically, P is transported from upland source areas via wetlands, streams, ditches, canals, and finally, to receiving water bodies. Our study specifically focused on wetlands and stream systems. According to the National Wetland Inventory, wetlands cover about 18% of the four priority basins (S-191, S-65D, S-154, and S-65E), which are those sub-basins within the Okeechobee Basin contributing a disproportionate amount of the P entering the lake (Flaig and Reddy 1995). Soils and sediments within wetlands and streams typically store most of the P, in comparison to other ecosystem components such as biomass both above and below ground, litter, and overlying water columns (Mitsch *et al.* 1979, Reddy *et al.* 1999). Phosphorus uptake by above-ground live biomass is typically returned to wetland water columns at the end of each growing season (Reddy *et al.* 2005). Translocating P from above-ground biomass to below-ground tissue after a growing cycle can range between 25 and 75% of P stored in above-ground-biomass (Wetzel 2001). Richardson and Marshall (1986) estimated that 35% of the above-ground P uptake by plants was returned via litterfall. Within the Okeechobee Basin, Reddy *et al.* (1996) suggested that, during a growing season, less than 20% of the P stored in above-ground biomass was retained within their studied wetlands. Phosphorus sorption by soil and P stored in organic matter are often cited as the most important long-term P-retention processes (Richardson and Marshall 1986, Reddy *et al.* 1999).

Single soil solution extractions are often undertaken to help determine P sorption capacities of soils and sediments. Parameters determined from these extractions, such as the P sorption index (PSI), are used as a proxy for P sorption capacity (Bache-Williams 1971, Simard *et al.* 1994, Axt and Walbridge 1999, Sims 2000, Bridgham *et al.* 2001, Bruland and Richardson 2005). Single extractions are relatively quick and easy to undertake relative to standard sequential P sorption isotherms (Sims 2000, Bridgham *et al.* 2001). Bridgham *et al.* (2001) used a modified Bache-Williams index to estimate P sorption potential of riverine soils. Similarly, Axt and Walbridge (1999) and Bruland and Richardson (2005) used a single incubation at saturated P conditions to measure P sorption potential of wetland and surrounding upland soils in Virginia and riparian soils in North Carolina, respectively. In contrast to using an index to determine P sorption (retention), other indices are often used to determine P release or whether a soil is P-saturated. Degree of P saturation (DPS) is often used to estimate whether terrestrial agricultural soils are P-saturated. The DPS relates P already adsorbed by a soil to its adsorption capacity (typically based on its aluminum and iron content) (Hooda *et al.* 2000, Nair *et al.* 2004). Subsequently, this index was replaced and/or an additional index is often used. Phosphorus saturation ratio (PSR) is similar to DPS; however, correction values are expressed as a ratio rather than a percentage, and no account is taken of the empirical correction factor ( $\alpha$ ) that allows for the comparison of P saturation between different soils (Sims *et al.* 2002, Nair *et al.* 2004). Little information exists on the use of either DPS or PSR as an indicator for P saturation in wetland soils and/or stream sediments.

The overall objective of this study was to determine indices of P retention and P release for a range of wetland soils and stream sediments at the landscape-scale. This could be useful to water quality managers, as they require landscape-scale nutrient dynamics data for the present TMDL process within Okeechobee Basin. Specific objectives were to (i) characterize stream sediment and wetland soils based on sediment/soil physicochemical and P characteristics; (ii) determine the robustness of a single point P sorption isotherm, relative to a sequential P sorption isotherm, to help determine P sorption capacities of wetland soils and stream sediments under varying redox conditions; (iii) investigate the use of different sediment/soil metal extraction procedures to help predict P sorption; and (iv) measure P sorption/desorption capacities of wetland soils and adjacent stream

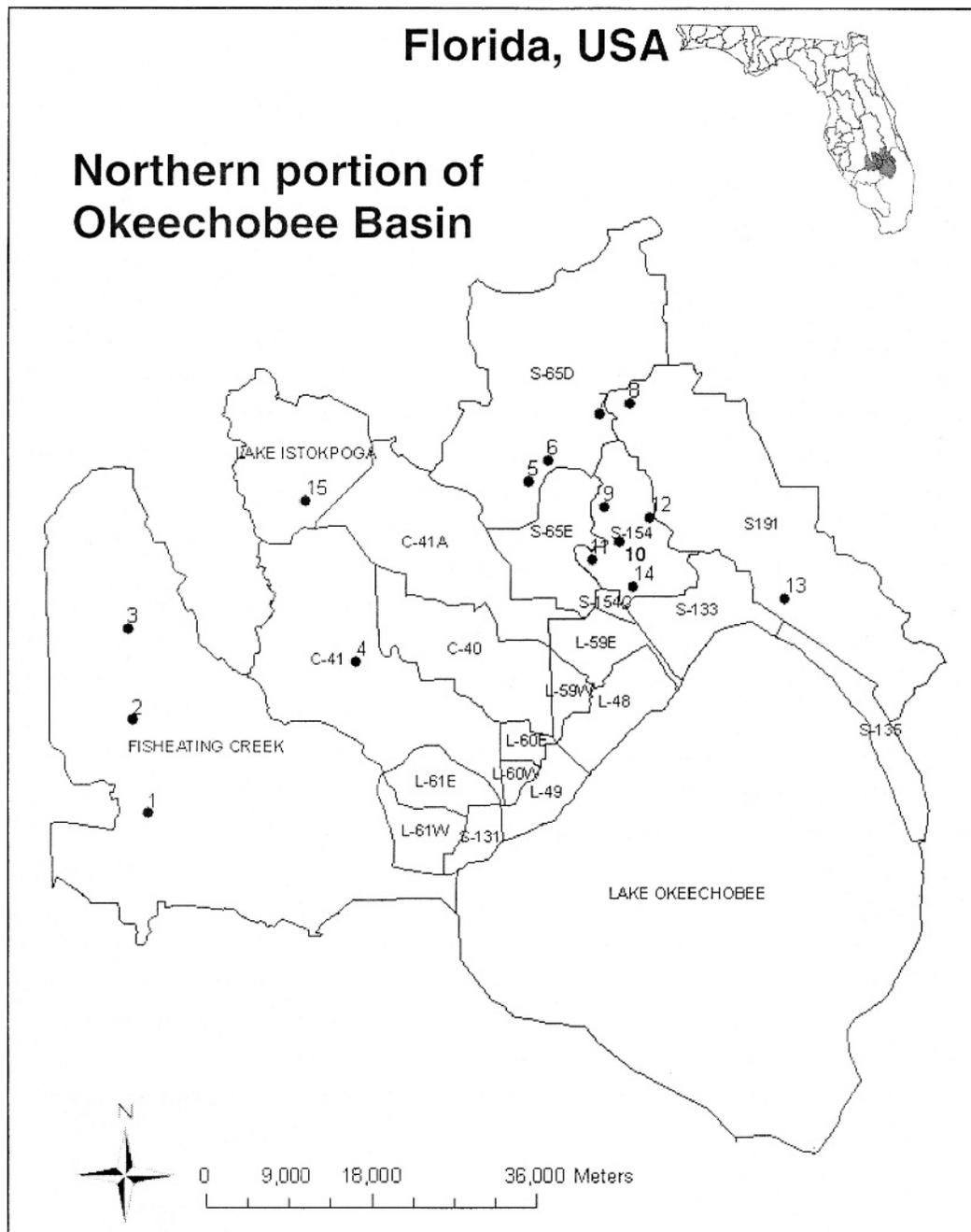


Figure 1. Wetland soil and stream sediment sampling sites within the northern portion of Okeechobee Basin, Florida. Sites 1, 2, and 3 = Fisheating Creek; 4 = Archbold Sawgrass; 5 = Chandler Slough; 6 = Cypress Slough; 7 = Fish Slough; 8 = McArthur # 5; 9 = Larson Dixie; 10 = Turkey Slough; 11 = Yates marsh; 12; Pelaez; 13 = Nubbin Slough; 14 = Popash Slough; and 15 = Istokpoga marsh.

sediments under ambient and saturated P conditions.

## MATERIALS AND METHODS

### Wetland and Stream Site Locations

The Okeechobee Basin, Florida surrounds Lake Okeechobee, which is a shallow subtropical lake

having a surface area of about 1,700 km<sup>2</sup> (SFWMD 1993). Wetlands and adjacent stream sites were located within several sub-basins of the northern portion of Okeechobee Basin (Figure 1). The majority of our sampling sites were located in the four priority basins (S-65D, S-65E, S-154, and S-191). Streams and wetlands were selected to represent a range of P-impacted wetlands and

streams in the northern portion of the basin. Most of the wetlands sampled were riparian emergent marsh wetlands; however, we did sample some riparian forested systems including Popash Slough, Cypress Slough, Turkey Slough, Nubbin Slough, and Chandler Slough. We also sampled a non-riparian emergent marsh wetland (Istokpoga Marsh). In total, we sampled 13 wetlands and 10 streams.

The main land use within the northern part of the basin were in agriculture (beef cattle ranching and dairy). Improved pasture accounted for 37%, while unimproved pasture and dairy sites accounted for 13 and 4% of the land area, respectively. Rangelands and wetlands each covered about 16% of the land area, forests about 10%. Other major land uses included citrus, sod, urban, and rural residential (Boggess *et al.* 1995). In general, soils in the Okeechobee Basin are predominantly (> 80%) classified as Spodosols (Anderson *et al.* 1995).

### Sample Collection

Intact soil and sediment cores were randomly collected from various wetland and adjacent stream ecosystems located in the basin (Figure 1). At each site, a polyvinyl chloride pipe (10 cm internal diameter) with one end sharpened was hammered down into the sediment/soil to a depth of about 25 cm (Reddy *et al.* 1998). The pipe was then capped with a rubber stopper; both pipe and adhered sediment/soil sample were extracted from substrate. Sediment/soil samples were extruded from pipe using a plunger and ramrod. Samples were sectioned at 10-cm depth if there was no transition present. If a transition was present, we sectioned according to horizon breaks. Sectioned samples were then placed on ice and stored at 4°C. For physiochemical soil sediment characterization and sorption/desorption at ambient and saturated P conditions, we used samples from 10 streams and nine wetland sites. In addition to these sites, we previously sampled four other wetland sites for P-sorption isotherm studies under varying redox conditions. Those four sites were Chandler Slough, Cypress Slough, Fisheating Creek, and Istokpoga Marsh (Figure 1). These sites were sampled during May 1992, whereas the other wetlands and their adjacent stream sites were sampled in March 1993.

Water samples were also collected at the time of sampling at each wetland and stream site, when open water was present. When surface waters were collected, a subsample was filtered onsite through a 0.45- $\mu\text{m}$  disc filter, and both filtered and unfiltered samples were stored at 4°C until analyses.

### Initial Characterization and Analytical Methods

Prior to experiments, soil/sediments and water samples were analyzed for selected physicochemical properties. Water samples were analyzed for pH, electrical conductivity (EC), soluble reactive P (SRP), total P (TP), total Kjeldahl N (TKN), total organic C (TOC), and metals (Ca, Mg, K, Fe, and Na) (APHA 1989). Unfiltered samples were analyzed for EC, TP, TKN, and TOC. Filtered samples were analyzed for SRP and metals. For each soil/sediment depth increment, samples were analyzed for bulk density, pH, water content, organic matter, total P, and extractable cations. Bulk density was determined on a dry mass per volume basis. Soil pH was measured in a 1:1 soil-to-water ratio. Organic matter was determined by loss on ignition and TP was measured on an ignited (550°C for three hours) one-gram oven-dry sample. The ash residue was then dissolved in 6 M HCl (Andersen 1974) and total P was analyzed colorimetrically (Method 365.1, USEPA 1993) using a Technicon Autoanalyzer. Air-dry sediment/soil samples were extracted (1:50 soil/sediment to solution ratio) with 0.2 M oxalic acid + 0.175 M ammonium oxalate (adjusted to pH 3.5) (McKeague and Day 1966, Khalid *et al.* 1977) and filtered solutions were analyzed for P, Fe, and Al using atomic absorption spectroscopy (AAS). Field moist samples were extracted with either 1 M KCl (Loeppert and Inskeep 1996) or 1M HCl (Reddy *et al.* 1998a) (soil/sediment to solution ratio of 1:50). Filtered solutions were analyzed for extractable Ca, Mg, Fe, and Al using AAS. As part of laboratory quality assurance/quality control, we repeated 5% of samples, included a blank and an internal and external quality control standard during all analyses.

### Phosphorus Characterization Methods

We characterized P parameters of sediments and soils using several methods. The first was the P sorption index originally proposed by Bache and Williams (1971), where P sorption was measured at a fixed concentration (1000 mg P kg<sup>-1</sup>):

$$\text{PSI} = S/\log C_t$$

where PSI is the sorption index, S is the P sorbed after a 24 hr equilibration period and  $C_t$  is the concentration in solution after this period. The second index we used was P saturation ratio (PSR). We calculated the PSR as

$$\text{PSR} = P_{\text{ox}}/(Fe_{\text{ox}} + Al_{\text{ox}})$$

where PSR is the P saturation ratio, expressed as a ratio;  $P_{\text{ox}}$ ,  $Fe_{\text{ox}}$ ,  $Al_{\text{ox}}$  is the molar mass of

ammonium oxalate P, Fe and Al in sediment/soil,  $\text{mmol kg}^{-1}$ . This is similar to the approach adopted by Nair et al. (2004); however, they used a Mehlich 1 as their soil extract.

The final P index we used was soil P storage capacity (SPSC). This index is used as an indicator of a soils ability to sorb additional P before exceeding a threshold P concentration, at which point, P levels are of environmental concern (Nair and Harris 2004). This index is similar the degree P saturation (DPS), which uses a correction factor and values are expressed as a percentage. Nair and Harris (2004) estimated SPSC as

$$\text{SPSC} = (0.15 - \text{PSR}) \times (\text{M1Al} + \text{M1Fe})$$

where 0.15 is an estimate of a critical PSR that contributes to eutrophication (Nair et al. 2004); M1Al and M1Fe are soil Al and Fe content as extracted with Mehlich 1. We used an ammonium oxalate extract to help estimate sediment soil P sorption capacity. Reddy et al. (1998) suggested that sediment soil P sorption could be predicted well (> 75%) using Al and Fe as extracted with ammonium oxalate. They sampled two wetland/stream sites that were impacted by dairy effluent within the Okeechobee Basin.

#### Sequential and Single Point Phosphorus Sorption Isotherms under Varying Redox Conditions

Sequential aerobic P sorption isotherms were also carried out. Two grams of field-moist soil (1 g dry wt. equivalent) were placed in 50-mL centrifuge tubes and treated with 20 mL of 0.01 M KCl. This KCl solution contained several P concentrations (0, 0.05, 0.2, 1.0, 2.5, 5.0, and 50  $\text{mg P L}^{-1}$ ). Samples were equilibrated, centrifuged, and filtered to 0.45  $\mu\text{m}$ . Soluble reactive P was measured in filtered extract as described previously. We used a linear version of the Langmuir equation to derive P sorption parameters (Reddy et al. 1998). For the single point P sorption isotherms, soils (1 g dry wt. equivalent) were equilibrated at saturated P conditions (1000  $\text{mg P kg}^{-1}$ ) also under aerobic conditions.

Under anaerobic conditions, sediment/soil samples (1 g dry wt. equivalent) were flooded with 10 mL deionized water and purged with a mixture of  $\text{N}_2+\text{CO}_2$  (300 ppm  $\text{CO}_2$  v/v) to help create anaerobic conditions within the tube. Tubes were then incubated in the dark at 25°C for four weeks. At the end of each week, tubes were purged with a gas mixture. After four weeks, samples were spiked with 10 mL of 0.02 M KCl containing various P concentrations to get a final concentration of 0, 0.05,

0.2, 1.0, 2.5, 5.0, and 50  $\text{mg P L}^{-1}$  (sequential P isotherm) or 10 mL of 0.02 M KCl to obtain a final P concentration of 50  $\text{mg P L}^{-1}$  (single point P sorption isotherm; 1000  $\text{mg P kg}^{-1}$ ). All suspensions were centrifuged, filtered, and analyzed for SRP.

#### Phosphorus Sorption/Desorption at Ambient Phosphorus Conditions

Homogenized, field-moist sediment/soil samples were used in phosphate sorption and desorption experiments. To determine P sorption, two grams of field-moist samples were placed into 50-mL centrifuge tubes and equilibrated for 24 hours with 20 mL of filtered (0.45  $\mu\text{m}$ ) ambient site water (Ambient P conditions) obtained from each respective site. In instances where there was no site surface water present, we used Kissimmee River water. After sediment/soil suspensions were equilibrated, samples were centrifuged at 5000 rpm for 10 minutes, and the supernatant was filtered through a 0.45- $\mu\text{m}$  membrane filter paper. Filtered solutions were colorimetrically analyzed for SRP using Technicon Autoanalyzer (APHA 1989). Phosphorus not recovered in solution was assumed retained by the sediment or soil.

To measure desorption of P from soil and sediment, residual material (sediment/soil left after sorption study) was equilibrated for 24 hours in 20 mL of 0.01 M KCl that contained no P. Similarly, sediment/soil suspensions were centrifuged, filtered, and analyzed for SRP.

#### Phosphorus Sorption/Desorption at Saturated Phosphorus Conditions

Homogenized, field-moist soil and sediment samples were placed into centrifuge tubes with 0.01 M KCl containing 50  $\text{mg P L}^{-1}$  as  $\text{KH}_2\text{PO}_4$  (Saturated P conditions; 1000  $\text{mg P kg}^{-1}$ ) and equilibrated for 24 hours. After sediment/soil suspensions were equilibrated, samples were centrifuged, filtered, and analyzed as above. Sediment/soil P desorption was also determined post incubating samples at saturated conditions by incubating samples for 24 hours in 0.01 M KCl containing no P. Soluble reactive P was measured in filtrates after samples were centrifuged and filtered.

#### Statistical Methods

Data distributions were tested for normality. If data were not normally distributed, they were log-transformed. Statistical analyses (Student t-test and

Table 1. Initial chemical characteristics of site surface waters used in P sorption experiments of selected stream sediments and wetland soils from Okeechobee Basin.

Sampling sites	pH	EC $\mu\text{S cm}^{-1}$	SRP	TKN	TP	TOC	Metals				
							Ca	Mg	K	Fe	Na
							$\text{mg L}^{-1}$				
Archbold Sawgrass	6.14	170	0.89	3.59	1.27	76.8	15.9	7.4	4.6	2.18	17.6
Fish Slough	6.76	175	0.05	1.48	0.07	29.5	23.9	3.8	1.5	0.32	18.8
Fisheating Creek†	7.01	208	0.05	2.44	0.07	36.8	17.6	7.8	1.6	0.45	23.7
Fisheating Creek†	6.15	205	0.25	1.84	0.27	27.6	13.6	6.4	2.4	0.76	20.7
Istokpoga Marsh†	7.12	98	0.18	0.92	0.18	11.9	12.8	3.6	1.8	0.21	4.9
Kissimmee River†	7.45	145	0.03	1.17	0.03	18.6	16.0	4.0	1.9	0.04	10.3
Larson Dixie	6.51	256	0.75	1.89	0.77	33.6	29.3	6.4	8.1	0.39	24.6
McArthur # 5	6.71	220	0.78	1.59	0.83	38.9	13.4	4.7	23.6	0.33	22.1
Nubbin Slough	6.18	185	0.64	4.11	0.71	32.2	12.1	3.2	15.8	0.22	16.9
Pelaez	6.51	450	0.51	3.00	0.75	61.1	28.4	13.9	9.7	1.26	62.8
Popash Slough	6.99	300	0.76	2.16	0.98	42.4	21.6	7.1	15.6	0.27	36.9
Turkey Slough	6.89	285	1.22	3.42	1.45	57.8	25.3	7.3	10.8	0.63	33.7
Yates Marsh	6.42	365	0.07	1.87	0.10	30.5	19.1	11	5.3	0.23	50.7

† Water samples were collected in May 1992. Rest of water samples were collected in March 1993.

analysis of variance) were conducted on transformed data. Statistically significant differences were determined at the  $p < 0.05$ ,  $p < 0.01$ , and  $p < 0.001$ . We compared P indices between wetlands and streams. We compared least squared means using Student t-tests and analysis of variance (ANOVA). Linear correlations we report in the text and in tables were determined using the Pearson product-moment correlation on transformed data. In regression analyses between metal extractions and P sorption parameters, we used the standard least squares fit model. We also used stepwise regression. All statistical analyses were performed using the JMP software program (SAS Institute Inc., Cary, North Carolina).

## RESULTS

### Physicochemical Properties of Site Waters, Sediments, and Soils

Initial chemical properties of ambient site surface water used in P sorption experiments are presented in Table 1. Water pH values from wetland and stream sites were slightly acidic to circumneutral; they ranged between 6.1 and 7.5. Turkey Slough had the highest concentrations of TKN, SRP, and TP, while Kissimmee River had lowest concentrations. Soluble reactive P from all site waters ranged between 0.03 and 1.22 mg P L<sup>-1</sup>, which was probably a result of surrounding land uses. When wetland soils and adjacent stream sediments were incubated with ambient site surface water to determine P sorption at ambient P conditions, site water characteristics such as SRP, TP, TOC, K, Fe,

TKN, and soil sediment physicochemical characteristics (TP, organic matter and bulk density) covaried significantly with P sorption (Table 2). The TP content of sediment or soil and concentrations of SRP and TP in site surface water seemed to influence P sorption the most under ambient P conditions.

Physicochemical properties measured in wetland soils and stream sediments of the different sites were variable both within (as a function of depth) and between sampling locations (Table 3). Sediment/soil pH varied from being acidic, about 4.8 pH units to circumneutral (about 7.7 pH units). Generally, soil pH, and bulk density were greater in stream sediments relative to wetland soils, while organic matter in wetland soils was greater than in stream sediments. Total P (mg kg<sup>-1</sup>) was highest in wetland soils (F ratio = 5.7; df = 48;  $p = 0.02$ ;  $n = 50$ ). Wetland soil total P was variable, ranging greater than ten-fold, from a low of 104 mg P kg<sup>-1</sup> at Fisheating Creek to a high of 1642 mg P kg<sup>-1</sup> at McArthur #5 site. McArthur #5 was a wetland within a dairy in the four priority basins of the Okeechobee Basin. Total P of stream sediments ranged from as low as 29 mg P kg<sup>-1</sup> to 703 mg P kg<sup>-1</sup>. In terms of TP storage, where sediment/soil TP values were normalized for bulk density and sampling depth (g m<sup>-2</sup>), wetland soils stored greater TP than stream sediments (F ratio = 7.5; df = 48;  $p = 0.009$ ;  $n = 50$ ; Table 3).

We found that wetlands, on average, had nearly a two-fold greater P sorption capacity (PSI) ( $167 \pm 18 \text{ L kg}^{-1}$ ) than stream sediments ( $95 \pm 10 \text{ L kg}^{-1}$ ) (F ratio = 14.1; df = 47;  $p < 0.001$ ;  $n = 49$ ). In

Table 2. Pearson product-moment correlations between sediments/soil initial physicochemical characteristics and of stream sediments and site surface waters characteristics under ambient P conditions ( $n = 50$ ).

Sediment/Soil	Sediment/Soil										Site Water									
	P sorbed	pH	Bulk density	Organic matter	TP	SRP	TP	pH	EC	TKN	TOC	Ca	Mg	K	Fe					
pH	-0.109																			
Bulk density	-0.606***†	0.038																		
Organic matter	0.619***	0.080	0.880***																	
TP	0.707***	-0.144	-0.761***	0.861***																
SRP	0.671***	-0.007	-0.118	0.204	0.276															
TP	0.667***	-0.017	-0.135	0.238	0.277	0.995***														
pH	-0.230	0.725***	0.303	-0.305*	-0.323*	0.041	0.033													
EC	0.161	0.251	-0.429*	0.330*	0.143	-0.125	-0.108	0.242												
TKN	0.379**	-0.575***	-0.366*	0.400**	0.456**	0.341*	0.368*	-0.287	-0.052											
TOC	0.454**	-0.334	-0.355*	0.518***	0.335*	0.536**	0.602**	-0.139	-0.006	0.693**										
Ca	0.246	0.023	-0.419**	0.241	0.176	0.071	0.056	0.274	0.624**	0.122	0.167									
Mg	0.091	-0.143	-0.469**	0.456**	0.183	-0.259	-0.207	-0.037	0.771**	0.186	0.352*	0.573**								
K	0.423**	0.418*	0.042	0.022	0.070	0.690***	0.678***	0.209	0.158	-0.147	-0.008	-0.198	-0.312							
Fe	0.384*	-0.510**	-0.447**	0.551	0.357*	0.309	0.370*	-0.395*	-0.086	0.614**	0.900***	0.192	0.398*	-0.290						
Na	0.080	0.225	-0.400**	0.327*	0.108	-0.208	-0.179	0.251	0.984***	-0.012	0.048	0.588**	0.824***	0.058	-0.042					

† \*\*\*, \*\*, \* are significant at the  $p < 0.001$ ,  $p < 0.001$ , and  $p < 0.05$  probability levels, respectively.

Table 3. Depth specific physicochemical and phosphorus index characteristics of stream sediments and wetland soils on a site-specific basis ( $n = 10$  sampled streams; and  $n = 9$  sampled wetlands).

Site	Depth cm	pH	Organic matter %	Bulk density $\text{g cm}^{-3}$	Total phosphorus		PSR†	SPSC‡		PSI¶
					$\text{mg kg}^{-1}$	$\text{g m}^{-2}$		$\text{mg kg}^{-1}$	$\text{g m}^{-2}$	
<b>Streams</b>										
Archbold Sawgrass	0–10	5.54	18.8	0.534	387	20.7	0.10	125	6.6	205
Fish Slough	0–10	6.76	1.7	0.957	65	6.2	0.10	23	2.2	66
Fisheating Creek	0–10	6.3	0.8	1.472	58	8.5	0.12	7	1.0	51
Larson Dixie	0–13	6.54	11.3	0.452	321	14.5	0.15	2	0.1	95
McArthur #5	0–10	6.71	2.0	1.348	59	7.9	0.16	-4	-0.5	39
McArthur #5	10–20	6.89	3.2	1.392	58	8.1	0.13	7	0.9	41
Nubbin Slough	0–10	6.23	4.6	1.089	257	28.0	0.25	-99	-10.7	77
Nubbin Slough	10–20	5.98	8.9	0.896	531	47.6	0.24	-175	-15.7	156
Palaez	10–20.5	5.89	22.8	0.403	434	17.5	0.11	160	2.2	139
Pelaez	0–10	6.49	31.8	0.138	703	9.7	0.09	143	5.8	183
Popash Slough	0–10	6.8	0.7	1.424	46	6.5	0.28	-10	-1.5	32
Popash Slough	10–20	6.51	4.8	1.227	266	32.6	0.14	7	0.8	127
Turkey Slough	0–10	6.64	21.4	0.382	467	17.8	0.11	80	3.0	83
Turkey Slough	10–20	6.57	17.3	0.771	458	35.3	0.13	30	2.3	140
Yates Marsh	0–10	6.3	1.4	1.202	29	3.49	0.13	2	0.3	36
<b>Wetlands</b>										
Archbold Sawgrass	0–10	4.82	20.0	0.782	338	26.4	0.08	139	10.8	137
Fish Slough	0–10	6.02	17.0	0.589	579	34.1	0.07	390	23.0	283
Fisheating Creek	0–10	6.37	3.5	1.176	104	12.2	0.12	10	1.2	62
Larson Dixie	0–10	5.58	11.6	0.753	311	23.4	0.11	83	6.2	152
McArthur #5	0–16	7.72	29.1	0.445	1642	73.1	0.18	-287	-12.7	330
Nubbin Slough	0–12.5	5.5	9.4	0.686	515	35.3	0.17	-47	-3.2	206
Popash Slough	0–10	6.96	91.2	0.738	152	11.2	0.10	38	2.7	94
Turkey Slough	0–10	6.22	76.7	0.503	550	27.7	0.12	79	4.0	184
Yates Marsh	0–10	6.27	78.9	0.410	377	15.5	0.09	153	6.3	114
Yates Marsh	10–20	6.1	90.1	1.018	143	14.6	0.05	137	14.0	114

† PSR = Phosphorus sorption ratio.

‡ SPSC = Soil phosphorus sorption capacity.

¶ PSI = Phosphorus sorption index.

contrast, the PSR, which can indicate a soils potential to release P was greater for stream sediments ( $0.15 \pm 0.01$ ) in comparison to wetland soils ( $0.11 \pm 0.01$ ) (F ratio = 7.6; df = 47;  $p = 0.008$ ;  $n = 49$ ). On a site-specific basis, Popash Slough stream sediments had the highest PSR; whereas wetlands soils of Yates Marsh had the lowest (Table 3). The SPSC, which estimates the amount of additional P a soil can receive, before added P becomes an environmental risk (Nair and Harris, 2004), was greater for wetland soils ( $69.6 \pm 26 \text{ mg kg}^{-1}$ ) relative to stream sediments ( $15.7 \pm 11 \text{ mg kg}^{-1}$ ) (F ratio = 4.3; df = 47;  $p = 0.04$ ;  $n = 49$ ; Table 3). Positive values indicate that soils or sediments have the ability to retain additional amounts of P, whereas negative values on a mass per soil weight basis ( $\text{mg kg}^{-1}$ ) or on a storage basis ( $\text{g m}^{-2}$ ) suggest that sediments/soils have no ability to retain additional amounts (Table 3). Therefore, sediments and wetland soils at MacArthur #5, and

Nubbin Slough and sediments at Popash Slough seem P saturated. Pairwise correlation suggests that SPSC was inversely related to PSR ( $r = -0.679$ ;  $p < 0.001$ ;  $n = 49$ ).

#### Relationship between Single and Sequential Phosphorus Sorption Isotherms

To determine the relationship between  $S_{\text{max}}$  values (as determined using a linear version of the Langmuir equation) under aerobic/anaerobic conditions and a single incubation of sediment or soil at saturated P conditions ( $1000 \text{ mg P kg}^{-1}$ ), we used samples from four sites. Those samples were collected within Chandler Slough, Cypress Slough, Fisheating Creek, and Istokpoga Marsh (Figure 1). Wetland soils and stream sediments for these sites had similar P sorption capacities as determined by  $S_{\text{max}}$  or a single incubation of sediment/soil at saturated P conditions ( $1000 \text{ P mg kg}^{-1}$ ). Mean

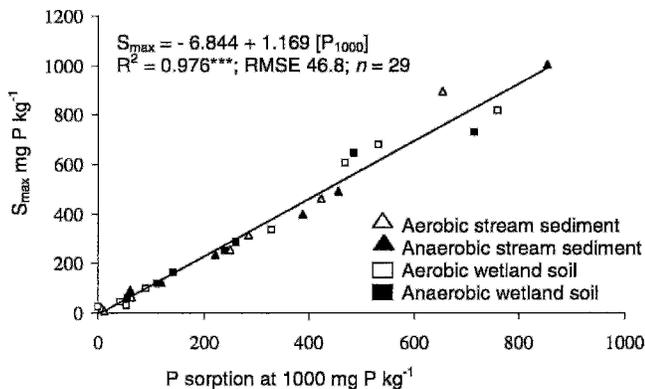


Figure 2. Relationship between P sorption maximum ( $S_{\max}$ ) determined for stream sediments and wetland soils incubated under aerobic and anaerobic conditions with P sorption at 1000 mg P per kg of soil.

$S_{\max}$  values were 318 and 308 mg P kg<sup>-1</sup> for stream sediments and wetland soils, respectively, while P sorbed at saturated P conditions was 274 and 313 mg P kg<sup>-1</sup> for stream sediments and wetland soils, respectively.

Regression analysis suggests that  $S_{\max}$  can be predicted using a single incubation of sediment or soil equilibrated with a 1000 mg P kg<sup>-1</sup> and that this relationship was sufficiently robust to predict  $S_{\max}$  under both aerobic and anaerobic conditions (Figure 2). This analysis does not take into account a site at Istokpoga Marsh, as we regarded this value (569 mg P kg<sup>-1</sup> sorbed when equilibrated at 1000 mg P kg<sup>-1</sup>;  $S_{\max}$  = 61 mg P kg<sup>-1</sup>) as an extreme data outlier. We are unable to suggest what environmental factors may cause this error; rather, we believe this sample was mishandled during sampling, preparation, processing, and/or analyses. Although the relationship between  $S_{\max}$  and P sorbed at saturated P conditions shown in Figure 2 suggests that  $S_{\max}$  values were, on average, about 17% greater than P sorbed at saturated P conditions, there was no significant difference between  $S_{\max}$  and P sorbed at saturated P conditions.

Under anaerobic conditions,  $S_{\max}$  values were about 70% of  $S_{\max}$  values under aerobic conditions ( $R^2$  = 0.62;  $n$  = 14;  $S_{\max}$  anaerobic = 116.2 + 0.70 [ $S_{\max}$  aerobic]; RMSE = 185); however,  $S_{\max}$  under aerobic conditions was not significantly different from  $S_{\max}$  values under anaerobic conditions. Similarly, there was no difference between aerobic and anaerobic incubations of P sorbed at saturated P conditions. Phosphorus sorbed at saturated P conditions under anaerobic conditions was about 66% of the P sorbed under aerobic conditions ( $R^2$  = 0.48;  $n$  = 14;  $P_{[1000]}$  anaerobic = 120.5 + 0.66 [ $P_{[1000]}$  aerobic]; RMSE = 182). As we found good

relationships between  $S_{\max}$  and the single incubation at saturated P conditions for these four sites, we used the single incubation at saturated P conditions as an estimate of P sorption capacity in the other 10 stream and 9 wetland sites sampled in the Basin.

#### Phosphorus Sorption under Ambient and Saturated Conditions

At ambient P conditions (SRP = 0.03 – 1.22 mg L<sup>-1</sup>), sediments of Fisheating Creek, Nubbin Slough, and Yates Marsh and wetland soils of Fish Slough all released P, while the remaining sites all sorbed P (Table 4). Sites that sorbed the greatest amounts of P included stream sediments of Turkey Slough, Palaez, and Archbold Sawgrass and wetland soils from Turkey Slough, Larson Dixie, and Popash Slough.

When samples were incubated at saturated P conditions (1000 mg P kg<sup>-1</sup>), P sorption was variable both between and within sites and across ecosystem type (Table 4). Wetland soils retained greatest amounts, which was nearly twice the amount of P sorbed by stream sediments. Wetland soils, on average retained 238 ± 21 mg P kg<sup>-1</sup>, while stream sediments retained 146 ± 14 mg P kg<sup>-1</sup>. Trends in stream site-specific data suggest that sediments of Archbold Sawgrass sorbed most P, whereas sediments collected in Yates Marsh sorbed least. Wetland soils collected at the MacArthur #5 site retained greatest amounts of P (Table 4), which also had highest concentrations of P in ambient site surface waters.

Phosphorus desorbed from sediment and soil samples was generally greater, after samples were equilibrated with ambient site surface waters (Table 4). After samples were incubated at saturated P conditions, sediments and soils desorbed less than 3% of initial P sorbed. Wetland soils desorbed less (0.64 ± 0.1%) than stream sediments (1.14 ± 0.2%) (F ratio = 5.4; df = 47;  $p$  = 0.02;  $n$  = 49).

#### Relationships between Soil/Sediment Physicochemical Properties and Phosphorus Retention

Table 5 shows correlation coefficients of P sorption/desorption at ambient and saturated P conditions with soil physicochemical properties and the different metal extractions (KCl, HCl, and ammonium oxalate). Phosphorus sorption under ambient P conditions was negatively correlated with bulk density and positively correlated with TP and organic matter content. Sediment/soil Ca, Mg, and Fe (as extracted with KCl and HCl) were positively

Table 4. Phosphate sorption and desorption capacity of stream sediments and wetland soils incubated with ambient site water conditions and incubated at saturated P conditions (1000 mg P kg<sup>-1</sup>). Values are parameter means ± one standard deviation (n = 10 sampled streams; n = 9 sampled wetlands).

Site	Depth cm	Ambient water	P sorbed at ambi-		P sorbed at		P desorbed		P desorbed at	
		mg L <sup>-1</sup>	ent conditions		1000 mg kg <sup>-1</sup>		at ambient		1000 mg P kg <sup>-1</sup>	
			mg kg <sup>-1</sup>		mg kg <sup>-1</sup>		mg kg <sup>-1</sup>		mg kg <sup>-1</sup>	
<b>Streams</b>										
Archbold Sawgrass	0–10	0.889	16.9	± 0.34	297	± 13.6	2.06	± 0.05	1.64	± 0.2
Fish Slough	0–10	0.051	0.2	± 0.13	107	± 0.3	0.94	± 0.2	0.81	± 0.3
Fisheating Creek	0–10	0.047	-0.5	± 0.13	84	± 2.8	1.90	± 0.2	1.30	± 0.1
Larson Dixie	0–13	0.749	16.7	± 0.16	150	± 0.8	2.75	± 0.5	0.39	± 0.03
McArthur #5	0–10	0.775	2.9	± 0.45	65	± 0.6	3.40	± 0.4	0.97	± 0.04
McArthur #5	10–20	0.775	2.7	± 0.10	67	± 17.1	3.46	± 0.04	1.92	± 0.4
Nubbin Slough	0–10	0.644	-3.5	± 2.67	124	± 0.9	6.36	± 1.2	1.90	± 0.5
Nubbin Slough	10–20	0.644	-4.8	± 0.28	233	± 7.3	8.49	± 0.4	2.16	± 0.1
Pelaez	0–10	0.507	34.3	± 0.06	212	± 3.7	4.23	± 1.1	0.94	± 0.4
Pelaez	10–20.5	0.507	12.3	± 0.07	317	± 65.1	1.55	± 0.1	2.20	± 0.0
Popash Slough	0–10	0.763	0.1	± 0.06	53	± 9.5	1.71	± 0.1	1.01	± 0.3
Popash Slough	10–20	0.763	9.6	± 0.17	197	± 24.3	0.46	± 0.1	1.30	± 0.1
Turkey Slough	0–10	1.215	35.2	± 0.21	131	± 13.7	2.12	± 0.01	0.57	± 0.01
Turkey Slough	10–20	1.215	13.3	± 0.15	212	± 3.4	5.56	± 0.1	1.84	± 0.1
Yates Marsh	0–10	0.071	-0.1	± 0.15	59	± 0.4	0.48	± 0.01	1.03	± 0.8
<b>Wetlands</b>										
Archbold Sawgrass	0–10	0.889	5.2	± 0.39	207	± 3.0	5.8	± 0.45	1.8	± 0.3
Fish Slough	0–10	0.051	-2.0	± 0.73	379	± 18.4	1.6	± 0.1	1.2	± 0.1
Fisheating Creek	0–10	0.047	0.1	± 0.15	101	± 14.9	0.6	± 0.01	1.3	± 0.3
Larson Dixie	0–10	0.749	13.7	± 0.08	227	± 6.5	0.7	± 0.02	1.0	± 0.1
McArthur #5	0–16	0.775	13.6	± 0.47	405	± 3.6	6.3	± 0.02	1.4	± 0.2
Nubbin Slough	0–12.5	0.644	7.1	± 0.70	293	± 0.6	3.9	± 0.3	1.7	± 0.1
Popash Slough	0–10	0.763	10.8	± 0.15	149	± 5.4	2.0	± 0.1	1.1	± 0.3
Turkey Slough	0–10	1.215	26.3	± 0.64	267	± 0.3	2.5	± 0.3	1.6	± 0.2
Yates Marsh	0–10	0.071	1.5	± 0.01	178	± 6.0	0.6	± 0.01	0.8	± 0.1
Yates Marsh	10–20	0.071	0.84	± 0.01	179.2	± 5.1	0.2	ND	1.4	± 0.04

† ND = Not determined; percent desorbed was not calculated, as phosphorus was desorbed during sorption incubations with ambient water.

correlated to P sorption under ambient P conditions, whereas there was no relationship between P sorption at ambient P conditions and sediment/soil Al content. Phosphorus desorbed after samples were incubated with 0.01 M KCl containing no P, correlated with about 50% of the physicochemical and metal characteristics. Bulk density, organic

matter, along with Ca and Mg, had some effect on P desorption.

Under saturated P conditions, most physicochemical and metal characteristics were significantly related to P sorption and desorption (Table 5). However, there were no relationships with soil/sediment pH. The strongest relationships under

Table 5. Pairwise correlation coefficients of soil physicochemical properties with P sorption/desorption under ambient and saturated P conditions (n = 49).

Soil parameters	Ambient P conditions				Saturated P conditions			
	P sorbed		P desorbed		P sorbed		P desorbed	
pH	0.101	NS	0.150	NS	-0.205	NS	0.170	NS
Bulk density, g cm <sup>-3</sup>	-0.683	***	0.463	**	-0.657	***	0.712	***
Organic matter, %	0.684	***	-0.442	**	0.698	***	-0.576	***
Total P, mg kg <sup>-1</sup>	0.401	**	-0.311	NS	0.805	***	-0.483	***
TP, g m <sup>-2</sup>	0.052	NS	-0.299	NS	0.777	***	-0.375	**
KCl-Ca, mg kg <sup>-1</sup>	0.555	***	-0.388	*	0.648	***	-0.517	***
KCl-Mg, mg kg <sup>-1</sup>	0.772	***	-0.369	*	0.414	**	-0.471	***
HCl-Ca, mg kg <sup>-1</sup>	0.466	***	-0.329	*	0.636	***	-0.462	***
HCl-Mg, mg kg <sup>-1</sup>	0.795	***	-0.385	*	0.446	**	-0.495	***
HCl-Al, mg kg <sup>-1</sup>	0.190	NS	-0.288	NS	0.838	***	-0.443	***
HCl-Fe, mg kg <sup>-1</sup>	0.712	***	-0.396	NS	0.682	***	-0.562	***
Ox-P, mg kg <sup>-1</sup>	0.216	NS	-0.223	NS	0.716	***	-0.354	**
Ox-Al, mg kg <sup>-1</sup>	0.093	NS	-0.260	NS	0.842	***	-0.408	***
Ox-Fe, mg kg <sup>-1</sup>	0.647	***	-0.357	*	0.680	***	-0.540	***

† = Not significant.

\*, \*\*, \*\*\* is significance at the p = 0.05, 0.01, and 0.001 level.

saturated P conditions were between P sorption, Al, TP, and Fe. At saturated P conditions, Al and Fe extracted with HCl or ammonium oxalate explained about 76% and 74% of the variability in P sorption, respectively (Figure 3).

## DISCUSSION

We found that P sorption under ambient P conditions covaried best with P concentrations in site surface waters, which suggested that, as P concentration in site surface waters increased, P sorption also increased. Several researchers reported that, as P loading increases in a wetland or stream, the amount of P retained also increases because the P concentration in overlying water is greater than

the interstitial soil/sediment porewater P concentration, causing a P concentration gradient from overlying water to underlying substrate (Richardson 1985, Reddy et al. 1998, Pant and Reddy 2003). At the ecosystem-scale, other site-specific factors influence whether streams and wetlands retain or release P. These factors, among others, include channel shape, water velocity, discharge volume/water levels, stream reach, travel time of water from P inputs, P loading rate, water residence time/hydraulic loading rate, vegetation, flow paths, and sedimentation/resuspension (Richardson et al. 1997, Nairn and Mitsch 2000, Braskerud 2002, Hanrahan et al. 2003, Bowes et al. 2005, Jarvie et al. 2005).

Typically, wetland soils are reported to have large amounts of organic matter (Mitsch and Gosselink 1993, Axt and Walbridge 1999, Bridgman et al. 2001); however, little information is reported on the organic matter content of wetland surface waters. High concentrations of dissolved organic acids in wetland site waters can inhibit decomposition (Qualls and Richardson 2000), contributing to accumulating organic matter within wetlands, which is considered important for long-term P storage (Axt and Walbridge 1999, Reddy et al. 1999, Bruland and Richardson, 2004).

Greater P storage in wetlands was much more variable relative to P storage in streams (Table 3). This within-wetland variability may be attributed to various biogeochemical and physical processes occurring at wetland sites, which are not occurring (or at least not occurring at the same intensity), in adjacent stream systems. These processes can in-

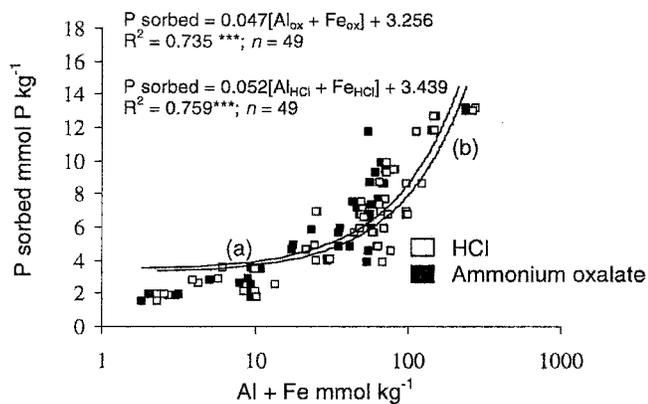


Figure 3. Graph of P sorbed at saturated P conditions (1000 mg P kg<sup>-1</sup>) with Al and Fe extracted with 1 M HCl (a) and 0.2 M ammonium oxalate (b).

clude high sedimentation rates, which have been reported for riverine wetlands (Johnston, 1991); hydrologic disturbances such as surface and subsurface inputs and overbank flooding (Bruland and Richardson 2004); sorption and precipitation of P, which is governed by sediment/soil Fe and Al oxide content for acidic wetland soils (Richardson 1985, Reddy *et al.* 1999); and within-system organic matter accumulation and accretion (Reddy *et al.* 1999).

The purpose of using a range of P indices is to get an integrated measure of how much P is presently sorbed under ambient conditions (single incubation at ambient P conditions); whether the sediment or soil is P saturated (PSR); the capacity of sediment or soil to retain additional amounts of P, without causing an environmental risk (SPSC); and the maximum amount of P a soil or sediment can retain (PSI, single incubation at saturated P conditions, and sequential P isotherm). In general, all indices calculated suggested that wetlands were less P saturated than stream sediments, and wetland soils had a greater ability to retain additional amounts of P (Table 3).

Bach and Williams (1971) initially suggested that a single point P sorption index, in comparison to traditional sequential P sorption isotherms, was an adequate measure of soil P sorption, with amount of P sorbed being a function of sorption sites. Sallade and Sims (1997) calculated a PSI for surface sediments (0–5 cm) dominated by organic material and subsurface sediments (5–15 cm) dominated by mineral components, of agricultural drainage ditches in Delaware, USA. They found that PSI values ranged between 50 and 5819 L P kg<sup>-1</sup>, with surface sediments having much higher PSI values, implying that surface sediments were sorbing more P than their subsurface sediments. Nguyen and Sukias (2002) observed somewhat similar PSI values (931–2328 L P kg) for drainage ditch sediments receiving runoff from agricultural catchments in New Zealand. The values we calculated for wetland soils and stream sediments for Okeechobee Basin were much lower (32–330 L P kg; Table 3) than the reported studies, indicating that these wetland soils and adjacent stream sediments have much fewer (more than ten times less) sorption sites. Similar to Axt and Walbridge (1999), we found that PSI was a function of landscape position, as wetlands had greater PSI values than stream sediments.

Typically, DPS or the similar index PSR is used for agricultural soils, where there is a need to assess P loss from soil to water (Nair *et al.* 2004). In their study, Nair and Harris (2004) suggested that a PSR value greater than about 0.15 can have a negative

impact on water quality. This is a best estimate of a threshold value (0.1–0.15) where values above it gave a rapid increase in water soluble P. Also, Sallade and Sims (1997) reported that a PSR of about 0.2 for drainage sediments (Inland Bays, Delaware) was critical, with values greater than this posing a threat to water quality. Wetland soil and stream sediment PSR values we report were within bounds observed by Nair *et al.* (2004); however they investigated impacted terrestrial agricultural soils. In general, our study showed that wetlands had a lower PSR than stream sediments, with PSR being inversely correlated with SPSC. If the ranges we observed in soils and sediments are comparable to agricultural soils within the basin, PSR values of wetland soils and stream sediments indicate that about 40% of stream sediments sampled and 22% of wetland soils sampled have the potential to negatively impact water quality (Table 3). D'Angelo (2005) reported that the best predictor of P exchange rate (whether a soil retains or releases P to overlying water) for early and late successional bottomland wetland soils was an index similar to PSR, which was determined as the percent molar concentration of Mehlich III P/(Al + Fe). This indicator of P retention/release rate accounted for about 64% of the variability in net P exchange rate between wetland soil and overlying water as determined in a laboratory soil water column study.

Estimating SPSC is particularly suitable for soils/sediments that have both low phosphorus content and a low ability to sorb P (Nair and Harris 2004). In general, wetland soils had greater SPSC than adjacent stream sediments, suggesting that wetland soils had a greater ability to retain additional P loading. In some situations, neither wetland soils nor stream sediments had any capacity to retain additional amounts of P (Table 3), implying that soils and sediments sampled had the potential to release P. However, in general, about 70% of wetland soils and 50% of stream sediments sampled could retain additional amounts of P. When the SPSC is expressed in storage per area basis (g m<sup>-2</sup>; Table 3) the indicator may be of particular use in estimating the potential for additional P storage in soils and sediments. With knowledge of P loading into these systems, an estimate of P retention longevity could be determined for sampled soils and sediments. This may be of particular use within a TMDL process, where load retention could be associated with particular landscape units such as wetlands and streams.

The tedious and monetarily costly nature of undertaking sequential P sorption isotherms to determine P sorption parameters has been recog-

nized for many years (Bache and Williams 1971). In addition, procedures used by researchers can vary widely; however, efforts were made in the past to standardize sorption methods (Nair et al. 1984, Graetz and Nair, 2000). Bach and Williams (1971) initially suggested that using a single incubation of soil with a solution containing a high P concentration was sufficient to determine P sorption. Subsequently, many studies use a single incubation to describe P sorption capacities of terrestrial soils (Bache and Williams 1971, Simard et al. 1994, Bolland and Allen, 2003), and this index was later used for wetland soils (Reddy et al. 1998, Axt and Walbridge 1999, Bridgham et al. 2001, Bruland and Richardson 2004, Bruland and Richardson 2005, D'Angelo, 2005). Most of these wetland studies use this single incubation with slight modification. These single incubations of wetland soils with solutions are generally undertaken under aerobic conditions. No wetland study to our knowledge directly compared P sorption as determined by a single incubation with  $S_{\max}$  across ecosystem type (wetlands and streams) and under different redox conditions to determine a P sorption indices predictive robustness. However, Reddy et al. (1998) did find similar relationships to ours between  $S_{\max}$  and P sorption at saturated P conditions for stream sediments and wetland soils at two dairy sites in the Okeechobee Basin. In their study, they found that  $S_{\max}$  values were about 15% greater than what was estimated using a single incubation at saturated P conditions, whereas we found that  $S_{\max}$  values were about 20% greater. Phosphorus sorption, estimated either with  $S_{\max}$  or with a single incubation at saturated P conditions in our study, was typically less under anaerobic conditions versus aerobic conditions, about 68%. Other researchers (Gale et al. 1994, Reddy et al. 1998) reported similar differences between P sorption under aerobic and anaerobic conditions for constructed and natural wetland soils, respectively. Patrick and Khalid (1974) initially observed that even though anaerobic soils release P to solutions low in P, they are often capable of sorbing more P than aerobic soils from solutions high in P. They reported that, under anaerobic conditions, ferrous forms have more surface area exposed to solution P than ferric forms. The reduction of P sorption under anaerobic conditions in our study may be attributable to ferric phosphate reduction to ferrous forms, whereas Al components are not affected by redox changes (Mitsch and Goseelink 1993, Reddy et al. 1998, D'Angelo, 2005).

When ambient site waters of wetland soils and stream sediments were less than about  $50 \mu\text{g P L}^{-1}$ , soils and sediments generally released P. Patrick and

Khalid (1974) originally suggested that, at low P concentrations in solution, wetland soils and stream sediments tend to release P. Sites with higher SRP concentrations in ambient site waters, and therefore higher P sorption, tended to have greater amounts of Ca and Mg, (as extracted by HCl and KCl) and greater amounts Al and Fe (as extracted by HCl and ammonium oxalate). These sites also had lower soil bulk densities and higher TP values than sites, that had lower concentrations of P in ambient site surface waters.

Under saturated P conditions (single incubation at  $1000 \text{ mg P kg}^{-1}$ ), wetland soils having lower pH, bulk densities, and higher TP values sorbed greatest amounts of P. Most of the P sorbed by soils and sediments did not desorb when they were extracted with  $0.01 \text{ M KCl}$  containing no P. This may indicate that the majority of P sorbed diffused into solid phase and as little desorption occurred, a hysteresis effect is observed (Bohn et al. 1985).

Phosphorus sorption during single incubations at saturated P conditions could be predicted by both Al and Fe (Figure 3). Similar to our Figure 3, Reddy et al. (1998) reported ammonium oxalate extractions of Al and Fe accounted for 78% of the variability in  $S_{\max}$  values of soils and sediments impacted by dairy effluent. In addition, Nair and Graetz (2002) found that  $S_{\max}$  values of soils from active dairies, abandoned dairies, native areas, and beef cattle pastures within Okeechobee Basin could also be predicted about 68% of the time by ammonium oxalate extractable Al and Fe. In several other studies, P sorption capacity covaried well with Al ( $r = 0.73$ ) and Fe ( $r = 0.76$ ) for riverine soils in Minnesota and Wisconsin (Bridgham et al. 2001); in forested wetlands of Virginia, where P sorption was predicted 80% of the time by Al (Axt and Walbridge 1999); in acid to near neutral wetland soils of riparian wetlands in North Carolina (Bruland and Richardson 2004); and mitigated and late successional bottomland hardwood forests in Kentucky (D'Angelo 2005). Ammonium oxalate extracts for poorly ordered, amorphous, active forms of Fe and Al oxides, which can include water-soluble, exchangeable, and a fraction of organically bound Fe and Al (Bertsch and Bloom 1996, Loeppert and Inskeep, 1996). In general, we found wetland soils to contain greater ammonium oxalate extractable Fe (mean =  $1398 \text{ mg kg}^{-1}$ ) and Al ( $1301 \text{ mg P kg}^{-1}$ ) relative to Fe ( $845 \text{ mg kg}^{-1}$ ) and Al ( $508 \text{ mg kg}^{-1}$ ) content of stream sediments.

We found that by adding organic matter content to either HCl extracted or ammonium oxalate extracted Al and Fe in a stepwise regression accounted for less than a 2% better prediction of P

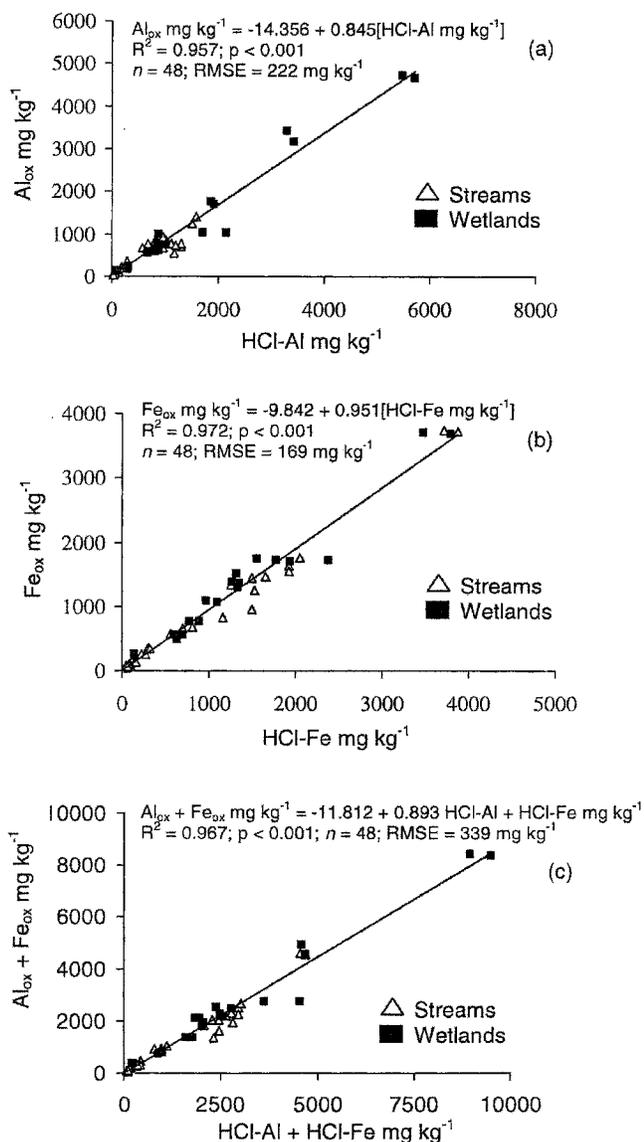


Figure 4. Relationships between 0.2 M ammonium oxalate and 1 M HCl extracts for (a) aluminum (Al), (b) iron (Fe) and (c) Al + Fe content of stream sediments and wetland soils of Okeechobee Basin.

sorbed (P sorbed at saturated P conditions). When P sorbed was regressed independently with organic matter, organic matter accounted for about 42% of the variability in P sorption ( $\text{P sorbed} = 7.25[\text{organic matter}] + 97.32$ ; (F ratio = 40.8; df = 47;  $n = 49$ ;  $p < 0.001$ )), suggesting colinearity of organic matter with Fe and Al content. Therefore, Fe and Al may be complexed with organic matter, with organic matter having an indirect effect on P sorption (Syers *et al.* 1973). Few studies report the specific influence of organically bound Al and Fe on P sorption; however, many studies suggested that there are positive relationships between soil/sediment organic matter often measured as organic carbon or total

carbon and P sorption (Gale *et al.* 1994, Reddy *et al.* 1998, Nguyen and Sukias 2002). D'Angelo (2005) suggested that the Fe and Al bound to organic material was, in part, responsible for late successional wetland soils having higher P sorption capacities than early successional soils.

We determined negligible differences between P sorption prediction power of Al and Fe extracted with 0.2 M ammonium oxalate and 1 M HCl (Figure 4) with both methods extracting similar amounts of Al and Fe. Hydrochloric acid extractions accounted for about 15% more Al and about 5% more Fe than ammonium oxalate extractions did. Ammonium oxalate is somewhat difficult to prepare (Nair *et al.* 2004), as the reagent requires pH adjusting; it is awkward to use in the laboratory, soil solutions need incubating in the dark, and ammonium oxalate decomposes under light conditions. Also, high concentrations of oxalate can result in clogging of analytical instruments; therefore, samples often require diluting (Loeppert and Inskeep 1996). In comparison, the 1 M HCl solution, which extracts for metals bound to soil/sediment inorganic P fractions (Reddy *et al.* 1998a) can be easily prepared, soil extracts can be incubated in the light, extraction time is three hours, in comparison to four hours for ammonium oxalate extractions, and metal concentrations in extracted solutions can be analyzed with little analytical instrument difficulty. Thus, we propose the use of a 1 M HCl extract.

## CONCLUSIONS

Our findings suggest that the P concentrations of *in-situ* wetland or stream water were important in determining whether wetland soils or stream sediments retained or released P. When site waters had soluble reactive P concentrations less than about  $50 \mu\text{g L}^{-1}$ , soils and sediments were more likely to release P. This concentration gradient from overlying water to underlying soil is important in determining P retention under ambient P conditions. The indices we used implied that wetland soils retained more P and had a greater capacity to retain additional amounts of P than stream sediments. We used the PSR to determine that wetland soils had less likelihood of negatively impacting water quality than stream sediments. Most of the variability in P sorption (about 75%) was accounted for by Al and Fe content with HCl extracting similar amounts to an ammonium oxalate extraction. Also, changes in redox conditions had some impact on P sorption capacity (< 35% difference between aerobic and anaerobic incubations).

The use of these biogeochemical indices to quantify P dynamics of different landscape units can inform watershed management and policies aimed at reducing P impacts. Providing information on P retention and release by wetland soils and stream sediments using indices can help water quality managers make decisions prior to watershed-scale water quality management within the Okeechobee Basin. Finally, the methodologies we used (with some local calibration) could be useful for other watersheds that are nutrient-impacted.

#### ACKNOWLEDGMENTS

This research was funded by the South Florida Water Management District. We thank the Wetland Biogeochemistry Laboratory staff and students for help with laboratory and field analyses.

#### LITERATURE CITED

- APHA, American Public Health Association. 1989. Standard Methods for the Examination of Water and Wastewater. 16<sup>th</sup> Edition. American Public Health Association, Washington DC, USA.
- Andersen, J. M. 1974. An ignition method for determination of total phosphorus in lake sediments. *Water Resources* 10: 329–331.
- Anderson, D. L., O. H. Tuovinen, A. Faber, and I. Ostrokowski. 1995. Use of soil amendments to reduce soluble phosphorus in dairy soils. *Ecological Engineering* 5:229–246.
- Axt, J. R. and M. R. Walbridge. 1999. Phosphate removal capacity of palustrine forested wetlands and adjacent uplands in Virginia. *Soil Science Society of America Journal* 63:1019–1031.
- Bach, B. W. and E. G. Williams. 1971. A phosphate sorption index for soils. *Journal of Soil Science* 22:289–301.
- Bertsch, P. M. and P. R. Bloom. 1996. Aluminum. p. 517–551. *In* Methods of Soil Analysis, Part 3. Soil Science Society of America Inc. and American Society of Agronomy Inc., Madison, WI, USA.
- Boggett, C. F., E. G. Flaig, and R. C. Fluck. 1995. Phosphorus budget-basin relationships for Lake Okeechobee tributary basins. *Ecological Engineering* 5:143–162.
- Bohn, H. L., B. L. McNeal, and G. A. O'Connor. 1985. Soil Chemistry. John Wiley and Sons Inc., New York, USA.
- Bolland, M. D. A. and D. G. Allen. 2003. Phosphorus sorption by sandy soils from Western Australia; effect of previously sorbed P on P buffer capacity and single-point P sorption indices. *Australian Journal of Soil Resources* 41:1369–1388.
- Bowes, M. J., W. A. House, R. A. Hodgkinson, and D. V. Leach. 2005. Phosphorus-discharge hysteresis during storm events along a river catchment: the River Swale, UK. *Water Resources* 39:751–762.
- Braskerud, B. C. 2002. Factors affecting phosphorus retention in small constructed wetlands treating agricultural non-point source pollution. *Ecological Engineering* 19:41–61.
- Bridgman, S. C., C. Johnston, J. P. Schubauer-Berigan, and P. Wesihampel. 2001. Phosphorus sorption dynamics in soils and coupling with surface and pore water in riverine wetlands. *Soil Science Society of America Journal* 65:577–588.
- Bruland, G. L. and C. J. Richardson. 2004. Hydrologic gradients and topsoil additions affect soil properties of Virginia created wetlands. *Soil Science Society of America Journal* 68: 2069–2077.
- Bruland, G. L. and C. J. Richardson. 2005. A spatially explicit investigation of phosphorus sorption and related properties in two riparian wetlands. *Journal of Environmental Quality* 33:785–794.
- D'Angelo, E. 2005. Phosphorus sorption capacity and exchange by soils from mitigated and late successional bottomland forest wetlands. *Wetlands* 25:297–305.
- Environmental Protection Agency (EPA). 2002. The twenty needs report: how research can improve the TMDL program. Environmental Protection Agency, Washington DC, USA.
- Flaig, E. G. and K. R. Reddy. 1995. Fate of phosphorus in the Lake Okeechobee basin, Florida, USA: overview and recommendations. *Ecological Engineering* 5:127–143.
- FDEP, Florida Department of Environmental Protection. 2001. Total maximum daily load for total phosphorus Lake Okeechobee, Florida. Florida Department of Environmental Protection, Tallahassee, FL, USA.
- Gale, P. M., K. R. Reddy, and D. A. Graetz. 1994. Wetlands and aquatic processes: phosphorus retention by wetland soils used for treated wastewater disposal. *Journal of Environmental Quality* 23:370–377.
- Graetz, D. A. and V. D. Nair. 2000. Phosphorus sorption isotherm determination. p. 35–38. *In* G. M. Pierzynski (ed.) Methods of Phosphorus Analysis for Soils, Sediments, Residuals and Water. North Carolina State University, Raleigh, NC, USA.
- Hanrahan, G., M. Gledhill, W. A. House, and P. J. Worsfold. 2003. Evaluation of phosphorus concentrations in relation to annual and seasonal physico-chemical water quality parameters in a UK chalk stream. *Water Resources* 37:3579–3589.
- Havens, K. E., R. T. James, T. L. East, and V. H. Smith. 2003. N:P ratios, light limitation, and cyanobacterial dominance in a subtropical lake impacted by non-point source nutrient pollution. *Environmental Pollution* 122:379–390.
- Hiscock, J. G., C. S. Thourot, and J. Zang. 2003. Phosphorus budget-land use relationships for the northern Lake Okeechobee watershed, Florida. *Ecological Engineering* 21:63–74.
- Hooda, P. S., A. R. Rendell, A. C. Edwards, P. J. A. Withers, M. N. Aitken, and V. W. Truesdale. 2000. Relating soil phosphorus indices to potential phosphorus release to water. *Journal of Environmental Quality* 29:1166–1171.
- Jarvie, H. P., M. D. Jürgens, R. J. Williams, C. Neal, J. J. L. Davies, C. Barrett, and J. White. 2005. Role of river bed sediments as sources and sinks of phosphorus across two major eutrophic UK river basins: the Hampshire Avon and Herefordshire Wye. *Journal of Hydrology* 304:51–74.
- Johnston, C. A. 1991. Sediment and nutrient retention by freshwater wetlands: effects on surface water quality. *Critical Reviews in Environmental Control* 21:491–565.
- Khalid, R. A., W. H. Patrick, Jr., and R. D. DeLaune. 1977. Phosphorus sorption characteristics of flooded soils. *Soil Science Society of America Journal* 41:305–310.
- La Peyre, M. K., M. Reams, and I. A. Mendelsohn. 2001. Linking actions to outcomes in wetland management overview of U.S. state wetland management. *Wetlands* 21:66–74.
- Loeppert, R. H. and W. P. Inskeep. 1996. Iron. p. 639–664. *In* Methods of Soil Analysis, Part 3. Soil Science Society of America Inc. and American Society of Agronomy Inc., Madison, WI, USA.
- McKeague, J. A. and J. H. Day. 1966. Dithionite and oxalate extractable Fe and Al as aids in differentiating various classes of soils. *Canadian Journal of Soil Science* 46:13–22.
- Mitsch, W. J., C. L. Dorage, and J. R. Wiemhoff. 1979. Ecosystem dynamics and a phosphorus budget of an alluvial cypress swamp in Southern Illinois. *Ecology* 60:116–1124.
- Mitsch, W. J. and J. G. Gosselink. 1993. Wetlands. 2<sup>nd</sup> Edition. Jon Wiley and Sons, Inc., New York, NY, USA.
- Nair, V. D. and D. A. Graetz. 2002. Phosphorus saturation in Spodosols impacted by manure. *Journal of Environmental Quality* 31:1279–1285.

- Nair, V. D. and W. G. Harris. 2004. A capacity factor as an alternative to soil test phosphorus in phosphorus risk assessment. *New Zealand Journal of Agricultural Research* 47:491–497.
- Nair, V. D., K. M. Portier, D. A. Graetz, and M. L. Walker. 2004. An environmental threshold for degree of phosphorus saturation in sandy soils. *Journal of Environmental Quality* 33:107–113.
- Nairn, R. W. and W. J. Mitsch. 2000. Phosphorus removal in created wetlands ponds receiving river water. *Ecological Engineering* 14:107–126.
- Nguyen, L. and J. Sukias. Phosphorus fractions and retention in drainage ditch sediments receiving surface runoff and sub-surface drainage from agricultural catchments in the North Island, New Zealand. *Agriculture Ecosystems and the Environment*, 92:46–49.
- Pant, H. K. and K. R. Reddy. 2003. Potential internal loading of phosphorus in a wetland constructed in agricultural land. *Water Research* 37:965–972.
- Patrick, Jr., W. H. and R. A. Khalid. 1974. Phosphate release and sorption by soils and sediments: effect of aerobic and anaerobic conditions. *Science* 186:53–55.
- Qualls, R. G. and C. J. Richardson. 2000. Phosphorus enrichment affects litter decomposition, immobilization, and soil microbial phosphorus in wetland mesocosms. *Soil Science Society of America Journal* 64:799–808.
- Reddy, K. R., O. A. Diaz, L. Scinto, and M. Agami. 1995. Phosphorus dynamics in selected wetlands and streams of the lake Okeechobee Basin. *Ecological Engineering* 5:183–207.
- Reddy, K. R., E. G. Flaig, and D. A. Graetz. 1996. Phosphorus storage capacity of uplands, wetlands and streams of the Lake Okeechobee Watershed, Florida. *Agriculture, Ecosystems and the Environment* 59:203–216.
- Reddy, K. R., Y. Wang, W. F. DeBusk, M. M. Fisher, and S. Newman. 1998a. Forms of soil phosphorus in selected hydrologic units of the Florida Everglades. *Soil Science Society of America Journal* 62:1134–1147.
- Reddy, K. R., G. A. O'Connor, and P. M. Gale. 1998. Phosphorus sorption capacities of wetland soils and stream sediments impacted by dairy effluent. *Journal of Environmental Quality* 27:438–447.
- Reddy, K. R., R. H. Kadlec, E. Flaig, and P. M. Gale. 1999. Phosphorus retention in streams and wetlands: a review. *Critical Review in Environmental Science and Technology* 29:83–146.
- Richardson, C. J. 1985. Mechanisms controlling phosphorus retention capacity in freshwater wetlands. *Science* 228:1424–1427.
- Richardson, C. J. and P. E. Marshall. 1986. Processes controlling movement, storage, and export of phosphorus in a fen peatland. *Ecological Monographs* 56:279–302.
- Richardson, C. J., A. Qian, C. B. Craft, and R. G. Qualls. 1997. Predictive models for phosphorus retention in wetlands. *Wetlands Ecology and Management* 4:159–175.
- Sallade, Y. E. and J. T. Sims. 1997. Phosphorus transformations in sediments of Delaware's Agricultural Drainage ways: I. Phosphorus forms and sorption. *Journal of Environmental Quality* 26:1571–1579.
- Simard, R. R., D. Curtis, G. Gangbazo, and A. Pesant. 1994. Phosphorus sorption and desorption indices for soils. *Communications in Soil Science and Plant Analysis* 25:1483–1494.
- Sims, J. T. 2000. A phosphorus sorption index. *In* Pierzynski, G. M. (ed.) *Methods of Phosphorus Analysis for Soils, Sediments, Residuals and Water*. North Carolina State University, Raleigh, NC, USA.
- Sims, J. T., R. O. Maguire, A. B. Leytem, K. L. Gartley, and M. C. Paulter. 2002. Evaluation of Mehlich 3 as an agricultural soil phosphorus test for the Mid-Atlantic United States of America. *Soil Science Society of America Journal* 66:2016–2032.
- SFWMD, South Florida Water Management District. 1993. *Surface Water Improvement and Management (SWIM) Plan Update for Lake Okeechobee, Volume 1, Planning Document*. South Florida Water Management District, West Palm Beach, FL, USA.
- Syers, J. K., R. F. Harris, and D. E. Armstrong. 1973. Phosphate chemistry in lake sediments. *Journal of Environmental Quality* 2:1–14.
- USEPA, U.S. Environmental Protection Agency. 1993. *Methods for chemical analysis of water and wastes*. U.S. Environmental Protection Agency, Environmental Monitoring Support Laboratory, Cincinnati, OH, USA.
- Van der Zee, S. E. A. T. M. and W. H. Van Riemsdijk. 1988. Model for long term phosphate reaction kinetics in soil. *Journal of Environmental Quality* 17:35–41.
- Wetzel, R. G. 2001. *Limnology: Lake and River Ecosystems*. 3<sup>rd</sup> edition. Academic Press, San Diego, CA, USA.

Manuscript received 12 December 2005; revision received 31 July 2006; accepted 25 August 2006.