

# Phosphorus Sorption and Potential Phosphorus Storage in Sediments of Lake Istokpoga and the Upper Chain of Lakes, Florida, USA

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Phosphorus (P) can be an important nutrient in regulating primary productivity in lakes. The ability of lake sediments to retain P from external sources depends on the physiochemical characteristics of the sediment. To assess the P dynamics in Lake Istokpoga and the upper chain of lakes that drain into Lake Okeechobee, Florida, USA, sorption properties of batch sediment samples for Lakes Tohopekaliga, Cypress, Hatchineha, Kissimmee, and Istokpoga were characterized under aerobic and anaerobic conditions. Langmuir model parameters fit the experimental data well (in general,  $r^2 > 0.70$ ). There were strong correlations between P sorption and total C, total P, Ca, Mg, Fe, and Al ( $r = 0.83\text{--}0.97$ ). Equilibrium P concentration values ranged between 0.001 and 0.192 mg L<sup>-1</sup> for aerobic conditions. A single-point isotherm (initial concentration, 5 mg L<sup>-1</sup>) was found for a wide range of sediment types, which allows estimation of the maximum potential sorption ( $S_{\text{max}}$ ) as 1.7 times the sorption ( $S_{\text{max}} = 1.7 S_s$ ). Results suggest that although these sediments have high P sorption capacities, the lake sediments may release P into the water column by desorption under aerobic conditions if water-column P concentrations are low enough (<0.036 mg L<sup>-1</sup> for Lake Tohopekaliga and <0.003–0.027 mg L<sup>-1</sup> for the other four lakes). Current watershed management strategies must balance efforts to reduce P inputs into the lakes from point and nonpoint sources against lowering the water-column P concentration to such a low level that the lake sediments become a source of P to downstream Lake Okeechobee.

PHOSPHORUS (P) can be an important nutrient in regulating primary productivity in lakes and is a major contributor to eutrophication in aquatic systems. Knowledge about the role of the internal sediment P load on surface-water P enrichment is limited (Pant and Reddy, 2001; Reddy et al., 2007). The ability of lake sediments to retain P depends on the physiochemical characteristics of the sediments and oxidation–reduction conditions at the sediment–water interface (Istvanovics et al., 1989; Bostic and White, 2007). High loading of inorganic P in lake water can lead to P retention by oxides and hydrous oxides of iron and aluminum or calcium carbonate, and at low P loadings, flooded soils or sediments can release P (Pant et al., 2001; White et al., 2004, 2006). For many lakes, reduction in external nutrient loads does not result in immediate improvement in water quality. Lake sediments can function as a source of or sink for dissolved nutrients to the overlying water column (Fisher et al., 2005). For example, the sediments of Lake Okeechobee, a large (1730 km<sup>2</sup>), shallow (average depth of 2.7 m) lake in the peninsula of south Florida, strongly influence the overlying water quality. These sediments are a large internal source of P (Moore et al., 1998), are a potential source of ammonium (James et al., 1997), and, when resuspended, affect light availability (Philips et al., 1995). The majority of sediments in this lake are organic mucks that cover 44% of the lake bottom (Reddy et al., 2007).

Phosphate sorption by single solid phases usually can be modeled as a two-step process. The first step involves rapid adsorption on the surfaces of solid phases, which occurs immediately after solids come in contact with the P in solution. The second step involves slow diffusion into the solid phase (Froenlich, 1988). Phosphorus sorption isotherm studies reported in the literature usually ignore the two-step model and express P sorption in a one-step model due to a variety of complex mechanisms involved in P adsorption and absorption. For practical applications, it may be sufficient to express the combined effect of P adsorption on and absorption by solid

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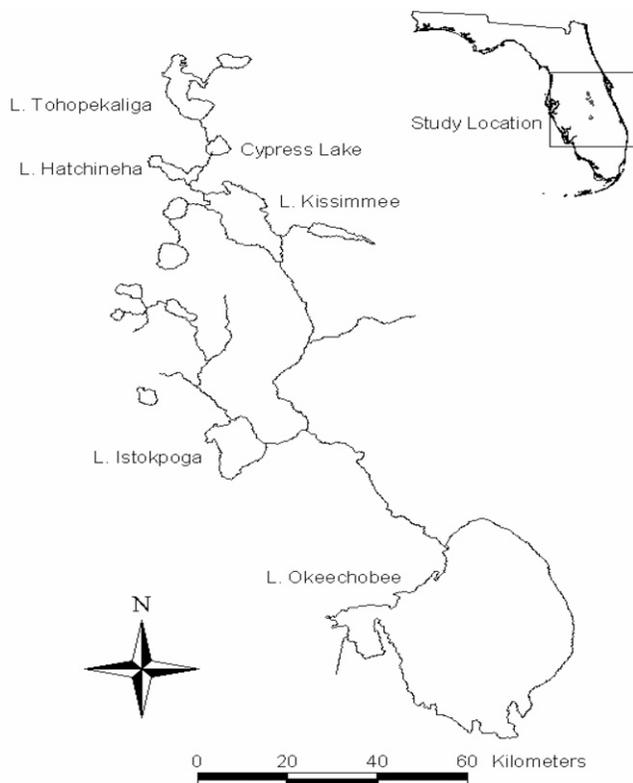
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**Abbreviations:** EPC<sub>0</sub>, equilibrium phosphorus concentration; KUCL, Lake Kissimmee and upper chain of lakes; LOI, loss on ignition; Ox-Al, oxalate-extractable aluminum; Ox-Fe, oxalate-extractable iron; P<sub>areal-capr</sub>, areal P sorption capacity; P<sub>capr</sub>, P sorption capacity; S<sub>max</sub>, sorption maximum; SRP, soluble reactive phosphorus; t<sub>sorb</sub>, time over which the sediments will continue to sorb P entering the lake; TC, total carbon; TP, total phosphorus.



**Fig. 1. Lake Istokpoga and upper chain of lakes, which includes, Lakes Kissimmee, Hatchineha, Cypress, and Tohopekaliga.**

phases. This combined effect is usually referred to as P sorption by the solid phase (McGechan and Lewis, 2002). Mobility of inorganic P in wetland soils and lake sediments is governed, in part, by the P sorption capacity. Phosphorus sorption not only depends on the sediment physio-chemical properties, but also on the diffusion rate of P from overlying water into the sediment (Malecki et al., 2004). These exchange processes at the sediment–water interface can potentially dictate the efficiency of P retention (Grace et al., 2008).

The equilibrium phosphorus concentration ( $EPC_0$ ) can be used to predict the extent to which the internal load will be released after external P load reductions. The  $EPC_0$  is defined as the concentration of P in solution that is in equilibrium with the P in the solid phase. In other words,  $EPC_0$  is the P concentration in the water where there is no net sorption or release of P (Olila and Reddy, 1993). If water-column soluble reactive phosphorus (SRP) concentrations exceed the  $EPC_0$ , P is predicted to be retained by the sediments. At concentrations  $<EPC_0$ , the sediments may serve as a P source. Therefore, the  $EPC_0$  can be a useful tool for water managers to determine target SRP concentrations. Another important sorption parameter is the sorption maximum ( $S_{max}$ ), which is the maximum concentration of P that can be sorbed by the sediment.

To describe the release of P from sediments, it is important to determine (i) the P buffering capacity of these sediments and (ii) the factors regulating the P buffering capacity of these sediments. For watershed management purposes, it is useful to develop relationships between lake-sediment sorption parameters

and sediment physio-chemical properties. In the case of the Lake Okeechobee watershed, which includes the five lakes studied in this work, water managers have begun reducing the external P loads into these water bodies. It might be considered wasted effort to reduce the concentrations of P at the sediment–water interface to  $<EPC_0$  because the sediment will then become a source of P to the water column. The sediment would not be an infinite source of P to the water column, but it would represent an important restriction to P management, which should be maintained at very low concentrations in these lakes. Therefore, the specific objectives of this study were (ii) to determine the soil P sorption capacity of sediments from these five connected lakes, known locally as Lake Istokpoga and the Kissimmee Upper Chain of Lakes; (ii) to establish the relationship between P sorption capacity and related physiochemical properties of the sediments; (iii) to determine whether the sediments are sources or sinks of P; and (iv) to demonstrate how sediment sorption parameters can be used to estimate time to sediment P saturation.

## Materials and Methods

### Site Description

Lake Istokpoga and the Kissimmee Upper Chain of lakes (KUCL) include the subtropical lakes Tohopekaliga (98.4 km<sup>2</sup>), Cypress (22 km<sup>2</sup>), Hatchineha (71.6 km<sup>2</sup>), Kissimmee (179 km<sup>2</sup>), and Istokpoga (112 km<sup>2</sup>) (Fig. 1). These are shallow, eutrophic lakes that provide a major source of surface water inflow to Lake Okeechobee (Williams, 2001; Walker and Havens, 2002). The research goal was, in part, to determine the potential of sediments in these lakes to release P downstream to Lake Okeechobee, which is currently the focus of a large-scale concerted effort to decrease water-column P concentrations to historical levels of  $\sim 0.05$  mg L<sup>-1</sup>. The mean depths are 2.6, 1.9, 2.1, 3.4, and 2.7 m for Lakes Tohopekaliga, Cypress, Hatchineha, Kissimmee, and Istokpoga, respectively (Havens et al., 2000; Walker and Havens, 2002). In 2004, the spatially averaged water column SRP concentrations were reported to be 0.005, 0.009, 0.011, 0.002, and 0.003 mg L<sup>-1</sup>, respectively (Martin, 2004), already well below the target of 0.05 mg L<sup>-1</sup>. The surface-water pH ranges from 6 to 8, and Secchi depth ranges from 0.6 to 1.2 m for all lakes (Havens et al., 2000; Walker and Havens, 2002).

Lake Istokpoga and the KUCL have seen many changes since the 1890s due to modifications for navigation and flood control. In the 1960s, the Central and Southern Florida Flood Control Project was established to control flooding. A series of canals and water-control structures was created to control lake water levels. The South Florida Water Management District controls water levels in each lake to prevent extremes of high and low water levels,

The bottom sediments within the lakes are characterized as sand, clay, and muck. The vegetation generally consists of *Nuphar luteum* (spatterdock), *Scirpus lacustris* (bulrush), *Typha sp.* (cattail), and *Potamogeton confervoides* (pondweed). Herbicides are used to control exotic vegetation, primarily *Hydrilla verticillata*.

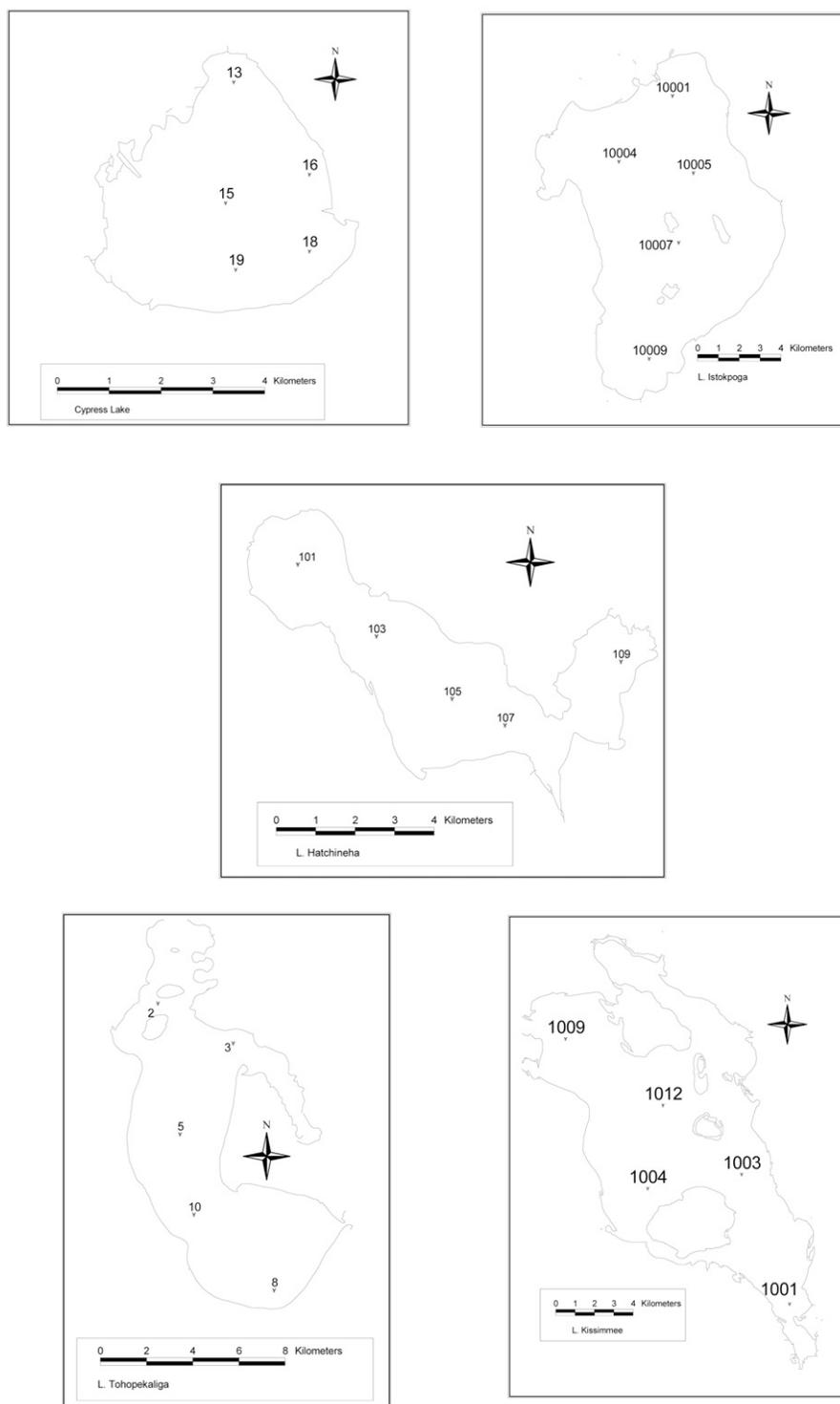


Fig. 2. Sampling sites at Lakes Istokpoga, Kissimmee, Hatchineha, Cypress, and Tohopekalgia.

### Sampling and Analyses

Five stations per lake were selected to include organic and mineral sediments (Fig. 2). Sediment cores, consisting of the top 10 cm of sediments, were taken with Plexiglas (7 cm ID) tubes by a scuba diver. Sediments were extruded, homogenized, purged with N<sub>2</sub>, and stored at 4°C until subsamples were taken for physiochemical analyses and sorption experiments.

As a proxy for organic matter, mass loss on ignition (LOI) was measured by difference after combustion in a muffle furnace at 550°C for 4 h (White and Reddy, 1999). Moisture content was determined after drying a known amount of moist sediment at 70°C to constant weight. Dry weight bulk density was measured using the Core Method 13-2 as described by Blake and Hartge (1986). Total C and N were determined on dried, ground

(passed through a 0.25-mm sieve) subsamples and analyzed on a C-N-S analyzer (White and Reddy, 2000). Total P was determined on 0.5 g of dried ground subsamples by ignition in a muffle furnace at 550°C for 4 h. The ash was treated with 20 mL of 6 mol L<sup>-1</sup> HCl and placed on a hot plate at approximately 120°C (Andersen, 1976). Samples were filtered through Whatman #41 (Clifton, NJ) filter paper, and total phosphorus (TP) concentrations were determined using an automated molybdate blue colorimetric technique (Method 365.4; USEPA, 1993).

Oxalate-extractable Al (Ox-Al) and oxalate-extractable Fe (Ox-Fe) were determined as described by Sheldrick (1984). Twenty milliliters of 0.2 mol L<sup>-1</sup> oxalate buffer were added to 0.5 g of dry sediment and shaken in the dark for 4 h. The suspensions were centrifuged at 5211 g for 10 min, and the supernatant liquid was filtered through a 0.45- $\mu$ m membrane filter. The filtrates were analyzed for Al and Fe by inductively coupled Ar plasma spectrometry.

Hydrochloric acid-extractable Ca (HCl-Ca) and HCl-extractable Mg (HCl-Mg) were determined by placing 0.5 g of dried, ground sediment in a centrifuge tube and adding 25 mL of a 1 mol L<sup>-1</sup> HCl (Malecki-Brown et al., 2007). The tubes were agitated on a mechanical shaker for 3 h and centrifuged at 5211 g for 10 min. The supernatant was filtered through a 0.45- $\mu$ m membrane filter and analyzed for Ca and Mg by inductively coupled Ar plasma spectrometry as described by Reddy et al. (1998b).

### Sorption–Desorption Characterization

Aerobic sorption–desorption experiments were done in triplicate by placing 5 g of field-moist sediment in 50-mL centrifuge tubes and adding 10 mL of 0.01 mol L<sup>-1</sup> NaCl solution containing the following concentrations of P: 0.00, 0.03, 0.06, 0.12, 0.25, 0.50, 1.00, 3.00, and 5.00 mg P L<sup>-1</sup>. The purpose of the NaCl addition was to approximate the ionic strength of soil pore water. It is suggested that for a Ca-dominated system, CaCl<sub>2</sub> would be a better choice. Tubes were placed on an end-to-end mechanical shaker for a 24-h equilibration period at 25°C. Samples were centrifuged at 5211 g for 10 min, and the supernatant liquid was decanted and filtered through a 0.45- $\mu$ m membrane filter. Phosphorus not recovered in the solution was assumed to be sorbed by the sediment (S', in mg kg<sup>-1</sup>). After the P sorption experiment, 10 mL of 0.01 mol L<sup>-1</sup> NaCl were added to each tube, and the samples were equilibrated for 24 h in a mechanical shaker. The samples were centrifuged at 5211 g for 10 min, and the supernatant liquid was decanted and filtered through a 0.45- $\mu$ m membrane filter. All extracts were frozen (–20°C) until analyzed for SRP (USEPA, 1993). The increase of SRP in the solution was assumed to be the P desorbed (P<sub>des</sub>) from the sediment. The tubes were weighed after the first filtration to correct for any moisture increase or decrease between the sorption and the desorption experiments. Samples were centrifuged until there was no visual sediment loss from the tubes during filtering. The P retained (P<sub>r</sub>) in the sediment was calculated as P<sub>r</sub> = S' – P<sub>des</sub>.

Anaerobic sorption–desorption experiments were conducted by placing 5-g samples of field-moist sediment into 50-mL centrifuge tubes fitted with airtight caps and rubber septa. The samples were purged with 99.99% pure N<sub>2</sub> to create an O<sub>2</sub>-free environment

and incubated in the dark at 25°C for 4 wk to ensure anaerobic conditions. The samples were placed in a water bath to maintain constant temperature. After this initial incubation, 10 mL of SRP solutions, previously purged with N<sub>2</sub>, were added to the samples. The solutions were prepared in 0.01 mol L<sup>-1</sup> NaCl solution at concentrations of 0.00, 0.03, 0.06, 0.12, 0.25, 0.50, 1.00, 3.00, and 5.00 mg P L<sup>-1</sup>, allowed to equilibrate for 24 h in an end-to-end shaker, and centrifuged at 5211 g for 10 min. The supernatant liquid was removed with a syringe and filtered anaerobically (under N<sub>2</sub> atmosphere) through a 0.45- $\mu$ m membrane filter. Phosphorus not recovered in the solution was assumed to be retained by the sediment (S'). Ten milliliters of P-free 0.01 mol L<sup>-1</sup> NaCl were added to each sample, purged with N<sub>2</sub>, and equilibrated for 24 h in an end-to-end shaker. The samples were centrifuged at 5211 g for 10 min, and the supernatant liquid was filtered anaerobically through a 0.45- $\mu$ m membrane filter. All samples were stored frozen at –20°C until analyzed for SRP using automated colorimetric techniques (USEPA, 1993). The increase of SRP in the solution was assumed to be the P desorbed from the sediment. The tubes were weighed after the first filtration to correct for any moisture loss/gain between the sorption and the desorption experiments.

All calculations were referenced back to an oven-dry sediment basis. Statistical analysis was performed using Microsoft Excel (Microsoft, Redmond, WA). Phosphorus sorption parameters were tested for correlation with sediments' physiochemical properties using Pearson product moment correlation coefficients. Total C was used in the correlations in lieu of LOI because they were well correlated.

The total amount of P sorbed by sediments (S) was calculated (mg kg<sup>-1</sup>) as the sum of measured P sorbed (S') plus the initial P sorbed in the sediment (S<sub>0</sub>) (Olila and Reddy, 1993):

$$S = S' + S_0 \quad [1]$$

The value of S<sub>0</sub> (mg L<sup>-1</sup>) was estimated from the isotherms using a least-squares fit of S' measured at low equilibrium concentrations (C) (i.e., the linear part of the isotherm):

$$S' = K' C - S_0 \quad [2]$$

where K' is the linear sorption coefficient (L kg<sup>-1</sup>), generally referred to as buffer capacity (Olila and Reddy, 1993).

The EPC<sub>0</sub> is defined as the concentration of P in solution where adsorption equals desorption (S' = 0). Therefore, EPC<sub>0</sub> = S<sub>0</sub>/K' (Pant and Reddy, 2001). Langmuir isotherm parameters were calculated by using a least-squares fit of C/S vs. C (Rao and Davidson, 1979; Mansell and Selim, 1981):

$$C/S = 1/(kS_{\max}) + C/S_{\max} \quad [3]$$

where k is the Langmuir sorption coefficient, and S<sub>max</sub> is the maximum sorption capacity of the sediment.

## Results and Discussion

### Sediment Characterization

Overall, the sediments represented a range from low organic matter content (estimated by LOI) to organic muds with high

LOI values (Table 1). Sampling was not spatially balanced because we were seeking to include the range of sediment types in each lake with only five sampling stations per lake. A more detailed mapping of the bottom sediments in each lake would be required to precisely determine the contribution of each sediment type to the internal sediment load of P on an area-weighted basis.

Bulk density of the surface sediments gives an indication as to how susceptible the material may be to resuspension events caused by wind-driven waves, an important driver of nutrient release in shallow lakes. The wide range of measured dry-weight basis bulk densities (0.04–1.17 Mg m<sup>-3</sup>) suggests that some of the sediments studied are susceptible to resuspension (organic sediments with low bulk density), which could lead to large pulse releases of P from sediments into the surface waters (Table 1). The sandier stations with higher bulk densities are not likely susceptible to resuspension except under the most extreme weather events. In general, as the organic matter in the sediment increased, the TP content increased and the bulk density decreased. Therefore, organic-rich sediments are more likely to be resuspended and can potentially release more P than the sandy sediments (Reddy et al., 2005).

The TP concentration of sediments can give an indication of recent P loading to aquatic systems (Reddy et al., 2007). The average TP concentrations in sediments for lakes Cypress, Hatchineha, Istokpoga, Kissimmee, and Tohopekaliga were 955, 797, 449, 919, and 188 mg kg<sup>-1</sup>, respectively (Table 1). These data suggest that lakes Tohopekaliga and Istokpoga have been affected less by P input from the surrounding watershed. On the other hand, the higher P concentrations in the sediments in Lake Cypress, Hatchineha, and Kissimmee suggest a greater historical external load of P to these lakes. However, due to the variability in TP due to sediment type, there were no statistically significant differences among the collected sediment samples for TP.

Correlations of sediment characteristics give an indication of the distribution of TP in relation to other physical and chemical characteristics. Total C was significantly correlated with TP ( $r = 0.95$ ). The organic sediments contained higher HCl-extractable Ca, HCl-extractable Mg, and oxalate-extractable Fe and Al than the sands (Table 1). These metals can increase the capacity of the sediment to bind or retain P. Calcium, Mg, Fe, and Al were significantly correlated with sediment TP ( $r = 0.90, 0.87, 0.90,$  and  $0.95$ , respectively). Although P bound to Fe oxides can be released under anaerobic conditions, the well mixed, shallow nature of these lakes suggests that anaerobic water column conditions may rarely persist for any great length of time.

## Sorption Characterization

The sorption isotherms obtained for aerobic and anaerobic conditions show the typical Langmuir-shaped curve (Fig. 3; site K1009 as an example). Both  $S_0$  and  $EPC_0$  were calculated by linear regression using the linear part of the isotherms (Fig. 3). High values of regression coefficients were obtained, with the exception of the aerobic isotherm of stations T2 and anaerobic isotherm of H109 (Tables 2 and 3). As expected, the values of these parameters were highly variable due to the diversity in the sediment types.

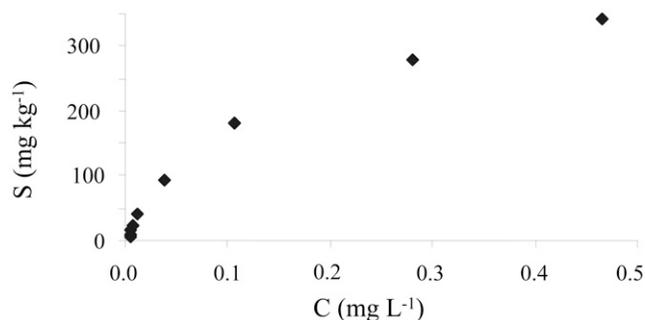
The C/S ratio was plotted vs. C to calculate  $S_{max}$  and k according to the Langmuir model (Eq. [3]). In every case, an almost

**Table 1. Select physicochemical characteristics of sediments from Lake Istokpoga and the upper chain of lakes.**

Station	Bulk density	TC†	TP	HCl-Ca	HCl-Mg	Ox-Fe	Ox-Al
	Mg m <sup>-3</sup>						
Lake Cypress							
C13	0.31	31.3	216	1010	170.7	854.9	670.8
C15	0.08	139.9	1036	6686	1360	8502	3086
C16	0.05	203.8	1702	8221	1649	12,384	4349
C18	0.05	201.6	1670	7125	1694	10,904	4669
C19	0.56	21.0	153	711.5	120.2	852.6	566.1
Lake Hatchineha							
H101	0.08	187.7	1121	11,585	1684	4057	3990
H103	0.17	72.8	494	4214	679.6	1306	1506
H105	0.67	13.0	40	562.8	21.7	252.4	285.2
H107	0.06	180.5	1126	9619	1636	3077	3381
H109	0.06	127.5	1206	12,367	2756	4065	2483
Lake Istokpoga							
I10001	1.17	5.1	54	1299	38.6	116.5	197.8
I10004	0.13	139.1	768	6257	1153	3657	3076
I10005	0.93	15.0	55	843.9	87.8	163.0	227.9
I10007	0.13	115.3	589	4419	856.0	807.8	1901
I10009	0.08	179.3	778	7400	1295	1687	2854
Lake Kissimmee							
K1001	0.20	51.8	225	1631	206.3	1700	434.1
K1003	0.04	272.5	1641	8816	1225	14602	2973
K1004	0.57	7.6	60	274.3	7.3	29.7	15.1
K1009	0.06	192.0	1335	8181	1481	10,312	3177
K1012	0.05	244.8	1333	7303	1252	13,847	2883
Lake Tohopekaliga							
T1	0.98	6.97	86	9770	2369	199.8	170.2
T2	0.25	57.9	422	3088	563.4	1211	1278
T3	0.50	41.7	273	1701	240.3	629.3	953.0
T5	0.94	5.4	61	629.8	BDL‡	122.3	140.1
T8	0.45	22.1	224	1048	108.2	1177	478.2
T10	1.06	5.4	61	289.9	BDL	71.1	140.0

† HCl-C, HCl-extractable calcium; HCl-Mg, HCl-extractable magnesium; Ox-Al, oxalate-extractable aluminum; Ox-Fe, oxalate-extractable iron; TC, total carbon; TP, total phosphorus.

‡ BDL, below detection limit.



**Fig. 3. Sorption isotherm, under aerobic conditions, for sediments at station K1009 of Lake Kissimmee. C, equilibrium concentrations; S, total amount of P sorbed by sediments.**

vertical line appeared in the isotherm at low equilibrium concentrations (C) (Fig. 4). This behavior has been observed previously in studies of P sorption by soils and sediments (Ryden et al., 1972a, 1972b; Syers et al., 1973; McCallister and Logan, 1978). An explanation for this behavior is that the equilibrium solu-

**Table 2. Phosphorus sorption characteristics of sediments from Lake Istokpoga and the upper chain of lakes under aerobic conditions.**

Station	S' = K'C + S <sub>0</sub> †				Langmuir			f
	K'	S <sub>0</sub>	EPC <sub>0</sub>	r <sup>2</sup>	S <sub>max</sub>	k	r <sup>2</sup>	Pr/S
	L kg <sup>-1</sup>	mg kg <sup>-1</sup>	mg L <sup>-1</sup>		mg kg <sup>-1</sup>	L mg <sup>-1</sup>		kg kg <sup>-1</sup>
C13	603	3.8	0.006	0.94	40.9	17.1	0.98	0.944
C15	3812	43.1	0.011	0.77	469	9.42	0.87	0.988
C16	9951	36.8	0.004	0.64	557	25.4	0.53	0.996
C18	10,925	67.8	0.006	0.63	96.6	547	0.43	0.996
C19	1545	13.0	0.008	0.97	51.1	48.4	0.98	0.988
H101	7496	17.1	0.002	0.88	170	74.6	1.00	0.990
H103	896	4.3	0.005	0.94	126	7.77	0.98	0.964
H105	125	0.2	0.001	0.86	18.2	27.0	0.99	0.911
H107	545	8.4	0.015	0.50	199	14.8	0.91	0.979
H109	6315	12.4	0.002	0.96	394	19.6	0.99	0.989
I10001	30	1.7	0.055	0.93	18.2	2.31	1.00	0.864
I10004	2190	35.7	0.016	1.00	378	6.78	0.89	0.991
I10005	98	3.3	0.034	0.79	21.2	6.30	0.98	0.876
I10007	ND	ND	ND	ND	ND	ND	ND	ND
I10009	1850	2.2	0.001	0.79	201	21.2	0.64	0.990
K1001	3036	2.1	0.001	0.59	79.0	36.6	0.83	0.985
K1003	68,581	37.1	0.001	0.98	331	356	1.00	0.995
K1004	4862	0.9	0.000	0.59	23.9	331	0.97	0.998
K1009	2572	14.3	0.006	0.96	446	7.10	0.99	0.968
K1012	7273	41.8	0.006	0.93	537	17.2	0.99	0.986
T1	26	1.7	0.063	0.79	23.9	1.26	0.99	0.838
T2	767	1.0	0.001	0.07	85.5	15.9	0.96	0.976
T3	336	1.6	0.005	0.91	39.2	11.7	0.98	0.957
T5	34	0.5	0.016	0.43	27.5	1.64	0.84	0.905
T8	361	0.9	0.019	0.95	29.9	97.4	1.00	0.984
T10	5	0.6	0.110	0.77	8.26	1.08	0.97	0.714

† EPC<sub>0</sub>, equilibrium P concentration; f, fraction of P retained; k, Langmuir sorption coefficient; K', linear sorption coefficient; ND, not determined; Pr, P retained; S, P sorbed; r, coefficient of determination of the fit to the sorption model; S', uncorrected P sorption; S<sub>0</sub>, initial P sorbed; S<sub>max</sub>, sorption maximum.

tion included some P-containing colloidal particles that passed a 0.45-µm filter but that did not take part in the sorption process. Such colloids would cause a large overestimation of SRP (Koopmans et al., 2005). Therefore, C values remain approximately constant at low additions of P, resulting in high values of C/S (Syers et al., 1973; McCallister and Logan, 1978). Consequently, the data points to the right of the almost-vertical line (those that correspond to the higher P additions) were used in a linear correlation to obtain S<sub>max</sub> and k from the slope and the intercept of Eq. [3] (Fig. 4). The selected data fit the Langmuir model well, which suggests that the data were adequately represented by the single-phase form of the sorption equation. Slightly better model fits were observed for aerobic conditions than for anaerobic conditions (Tables 2 and 3).

There was a range of S<sub>max</sub> values among the stations of each lake (Fig. 5). Lake Tohopekaliga had the lowest S<sub>max</sub> values, with a mean of 35.7 mg kg<sup>-1</sup> under aerobic conditions and a mean of 63.9 mg kg<sup>-1</sup> under anaerobic conditions. Other researchers have reported greater S<sub>max</sub> values in soils and sediments subjected to aerobic incubation than when incubated anaerobically (Gale et al., 1994; Reddy et al., 1998a; Pant and Reddy, 2001). However, the S<sub>max</sub> values obtained under aerobic conditions in this study were not statistically different from the ones obtained under anaerobic conditions.

**Table 3. Phosphorus sorption characteristics of sediments from Lake Istokpoga and the upper chain of lakes under anaerobic conditions.**

Station	S' = K'C - S0†				Langmuir			f
	K'	S <sub>0</sub>	EPC <sub>0</sub>	r <sup>2</sup>	S <sub>max</sub>	k	r <sup>2</sup>	Pr/S
	L kg <sup>-1</sup>	mg kg <sup>-1</sup>	mg L <sup>-1</sup>		mg kg <sup>-1</sup>	L mg <sup>-1</sup>		kg kg <sup>-1</sup>
C13	35	0.5	0.016	0.68	403	0.06	0.002	0.785
C15	1041	2.8	0.003	0.75	152	18.0	0.91	0.978
C16	1756	9.1	0.005	0.81	550	5.10	0.72	0.990
C18	1266	2.2	0.002	0.98	662	2.18	1.00	0.978
C19	184	1.1	0.006	0.80	25.4	35.0	0.88	0.988
H101	947	8.8	0.009	0.93	149	12.0	1.00	0.954
H103	175	1.1	0.006	0.85	220	1.10	0.21	0.951
H105	44	5.2	0.118	0.79	24.8	2.57	1.00	0.846
H107	241	0.7	0.003	0.98	482	0.67	0.09	0.909
H109	328	5.9	0.018	0.31	226	1.65	0.49	0.843
I10001	14	1.4	0.098	0.97	68.8	0.24	0.06	0.911
I10004	714	7.1	0.010	0.94	166	4.87	0.85	0.973
I10005	24	0.4	0.016	0.97	27.8	1.26	0.99	0.851
I10007	77	2.1	0.027	0.76	250	0.43	0.07	0.854
I10009	201	0.9	0.005	0.88	101	4.51	0.91	0.903
K1001	251	1.5	0.006	0.83	54.9	5.02	0.97	0.936
K1003	2333	29.8	0.013	0.94	372	6.80	0.99	0.978
K1004	120	0.15	0.001	0.64	35.1	4.65	0.85	0.959
K1009	2021	5.7	0.003	0.77	206	15.7	0.98	0.971
K1012	7313	48.5	0.007	0.59	260	32.4	0.99	0.976
T1	10	2.1	0.203	0.89	33.6	0.39	0.75	0.839
T2	101	1.0	0.010	0.98	228	0.51	0.09	0.957
T3	117	1.9	0.016	0.89	33.4	6.73	0.95	0.970
T5	6	0.4	0.063	0.97	19.8	0.44	0.98	0.828
T8	33	1.2	0.038	0.65	35.2	2.07	0.66	0.878
T10	5	1.0	0.192	0.92	34.0	0.19	0.11	0.958

† EPC<sub>0</sub>, equilibrium P concentration; f, fraction of P retained; k, Langmuir sorption coefficient; K', linear sorption coefficient; Pr, P retained; S, P sorbed; r, coefficient of determination of the fit to the sorption model; S', uncorrected P sorption; S, P sorbed; S<sub>0</sub>, initial P sorbed; S<sub>max</sub>, sorption maximum.

The mean EPC<sub>0</sub> values were similar under aerobic and anaerobic conditions for sediments from lakes Cypress, Istokpoga, and Kissimmee. Lake Hatchineha and Lake Tohopekaliga sediments showed higher mean EPC<sub>0</sub> values under anaerobic conditions (Fig. 6). The average EPC<sub>0</sub> values obtained under anaerobic conditions suggest that, in order for the release of P from the sediment to occur, the concentrations of P in the water column need to be <0.087 mg L<sup>-1</sup> for Lake Tohopekaliga, <0.007 mg L<sup>-1</sup> for Lake Cypress, <0.031 mg L<sup>-1</sup> for Lakes Hatchineha and Istokpoga, and <0.006 mg L<sup>-1</sup> for Lake Kissimmee (Fig. 6). Similarly, under aerobic conditions, concentrations of P in the water column need to be <0.036 mg L<sup>-1</sup> for Lake Tohopekaliga, <0.007 mg L<sup>-1</sup> for Lake Cypress, <0.005 mg L<sup>-1</sup> for Lake Hatchineha, <0.003 mg L<sup>-1</sup> for Lake Kissimmee, and <0.027 mg L<sup>-1</sup> for Lake Istokpoga in order for the sediments to release P into the water column (Fig. 6).

If we compare the EPC<sub>0</sub> values to the SRP concentrations recorded by Martin (2004) for these lakes, we can conclude that the sediments from Lakes Istokpoga (SRP = 0.003 mg L<sup>-1</sup>) and Tohopekaliga (SRP = 0.005 mg L<sup>-1</sup>) could act as sources of P and that sediments of Lakes Cypress (SRP = 0.009 mg L<sup>-1</sup>) and Kissimmee (SRP = 0.002 mg L<sup>-1</sup>) could be sinks of P (Fig. 6). For Lake Kissimmee, however, taking into account the uncertainties in these calculations and the fact that the P in the water column (0.002 mg L<sup>-1</sup>) is close to the EPC<sub>0</sub> for aerobic con-

ditions (0.003 mg L<sup>-1</sup>), it is suspected that, under the prevailing aerobic conditions, the lake water is neither gaining P from the sediments nor losing P to them. Lake Hatchineha (SRP = 0.011 mg L<sup>-1</sup>) may act as a source of P under anaerobic conditions but may be a sink under aerobic conditions (Fig. 6).

The conclusions mentioned above should be taken only as a guide of the trend of the sediments' capacity for P sorption or release. The limited data about SRP concentrations in these lakes and the uncertainties associated in the calculation of EPC<sub>0</sub> do not allow us to be very conclusive. Further monitoring of SRP in the water column of the lakes and spatial characterization of the sediments in the lakes is necessary to achieve more accurate conclusions.

The obtained EPC<sub>0</sub> values and the SRP concentrations suggest that current watershed management that involves reduction of P inputs from point and nonpoint sources in the watersheds of Lakes Cypress and Hatchineha will likely be effective in reducing water-column TP because these lake sediments do not act as an internal source of P until very low concentrations of P in the lake water is reached. For Lakes Tohopekaliga, Kissimmee, and Istokpoga, efforts to further reduce the water-column P concentration below the EPC<sub>0</sub> could lead to a release of the P stored in the sediment and would yield less water quality benefit relative to more intensive watershed nutrient management.

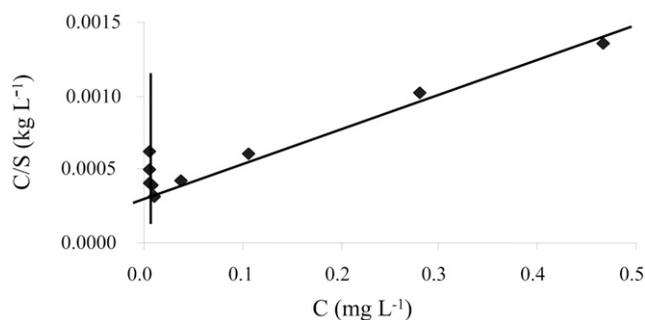
Phosphorus retained (P<sub>r</sub>) was divided by P sorbed (S) for each station to yield the fraction of P retained in the sediment after desorption (f). The retained P fraction (f) was large for all lakes at all stations under aerobic and anaerobic conditions (Tables 2 and 3). The mean values were >0.89 kg kg<sup>-1</sup>. This result suggests that once P is sorbed, only a small amount of the total is readily released back into the water column.

When the sediment was equilibrated with a 5 mg L<sup>-1</sup> P solution (S<sub>5</sub>), S<sub>max</sub> and f, P sorption was correlated with TC, TP, HCl-Ca, HCl-Mg, Ox-Fe, and Ox-Al (Table 4). The S<sub>5</sub> values were strongly correlated with TC and TP for aerobic and anaerobic conditions, suggesting that organic matter plays a significant role in P sorption in these lake sediments. In addition, the fraction of P retained (f) was significantly and positively correlated with TC, TP, Ox-Fe, and Ox-Al under aerobic and anaerobic conditions. The strong relationships between S<sub>5</sub> and Ox-(Fe+Al) under aerobic and anaerobic conditions (Fig. 7) suggest that P sorption in these sedi-

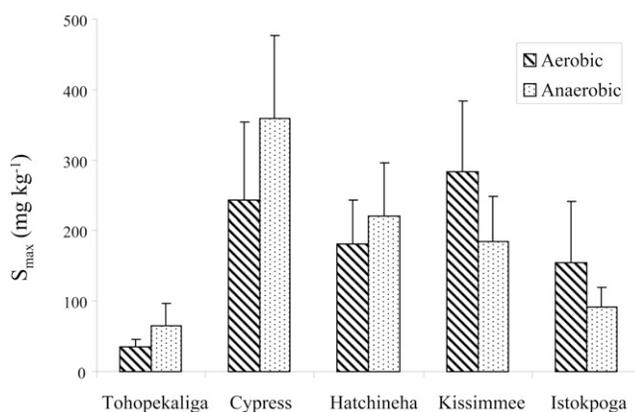
**Table 4. Correlation coefficients between P sorption parameters (5 mg L<sup>-1</sup> P solution [S<sub>5</sub>], sorption maximum [S<sub>max</sub>], and fraction of P retained (f)) and selected properties of the sediments from Lake Istokpoga and the upper chain of lakes under aerobic and anaerobic conditions (n = 26; r > 0.396 significant to α = 0.05; r > 0.505 significant to α = 0.01).**

	S <sub>5</sub> †		S <sub>max</sub>		f	
	Aerobic	Anaerobic	Aerobic	Anaerobic	Aerobic	Anaerobic
TC	0.96	0.96	0.80	0.68	0.55	0.46
TP	0.97	0.95	0.81	0.77	0.54	0.46
HCl-Ca	0.86	0.84	0.75	0.59	0.50	0.27
HCl-Mg	0.83	0.77	0.73	0.61	0.55	0.23
Ox-Fe	0.94	0.94	0.81	0.64	0.43	0.53
Ox-Al	0.89	0.84	0.75	0.74	0.56	0.47
Ox-(Al+Fe)	0.97	0.96	0.83	0.72	0.51	0.54
HCl-(Ca+Mg)	0.86	0.84	0.75	0.61	0.51	0.32

† HCl-Ca, HCl-extractable Ca; HCl-Mg, HCl-extractable Mg; HCl-(Ca+Mg), HCl extractable Ca plus Mg calculated by adding mol kg<sup>-1</sup>; LOI, loss on ignition; Ox-Al, oxalate-extractable Al; Ox-Fe, oxalate-extractable Fe; Ox-(Al+Fe), oxalate-extractable Al plus Fe calculated by adding mol kg<sup>-1</sup>; TC, total carbon; TP, total phosphorus.



**Fig. 4. Linearized Langmuir sorption isotherm, under aerobic conditions, for station K1009 of Lake Kissimmee, demonstrating the vertical linearity seen at very low phosphorus concentrations. C, equilibrium concentrations; S, total amount of P sorbed by sediments.**



**Fig. 5. Average sorption maxima (S<sub>max</sub>) for sediments of Lake Istokpoga and upper chain of lakes under aerobic and anaerobic conditions. The error bars represent standard error.**

ments was associated not only with organic matter but also with amorphous and poorly crystalline forms of Fe and Al (McCallister and Logan, 1978). Calcium also appears to contribute to P sorption (Table 1). Correlations were done using mmol kg<sup>-1</sup> as units to represent the molar ratio between S<sub>5</sub> and Ox-(Fe+Al). The low slope values for these correlations (0.020 for aerobic and 0.017 for anaerobic; Fig. 7) suggest that the Fe and Al oxides in these lake sediments are less sorptive than those of other studies, where the molar ratio is close to 0.5 (Pant and Reddy, 2001).

A strong relationship was found between S<sub>max</sub>, estimated from the Langmuir model under aerobic conditions, and P

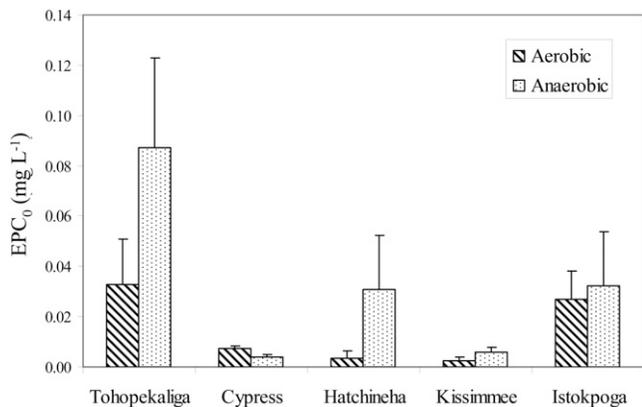


Fig. 6. Average equilibrium phosphorus concentration ( $EPC_0$ ) for Lake Istokpoga and upper chain of lakes under aerobic and anaerobic conditions. The error bars represent standard error. The horizontal line shows the water column soluble reactive phosphorus concentration for each lake.

sorbed by sediments when equilibrated with  $5 \text{ mg P L}^{-1}$  solution (the highest experimental point in the sorption isotherm;  $S_5$ ) under aerobic conditions (Fig. 8). The slope of the graph indicates that the Langmuir  $S_{\text{max}}$  values could be estimated as about 1.7 times  $S_5$ . Despite of the uncertainty associated with this model, this finding could be useful in predicting  $S_{\text{max}}$  for similar sediments ( $S_{\text{max}} \approx 1.7 S_5$ ) using the less laborious single-point isotherm method. Other researchers have reported the use of single-point estimate of P sorption capacity for a variety of mineral soils and conditions (Bache and Williams, 1971; Harris et al., 1996; Reddy et al., 1998a).

Although our sampling design does not allow us to make definitive calculations about the whole-lake capacity of each lake to retain P, we can use mean values of sediment characteristics to make first-approximation predictions. Areal P capacities were estimated for the top 10 cm of sediment using the mean dry-weight bulk densities and average  $S_{\text{max}}$  values obtained under anaerobic and aerobic conditions Eq. [6] (Table 5):

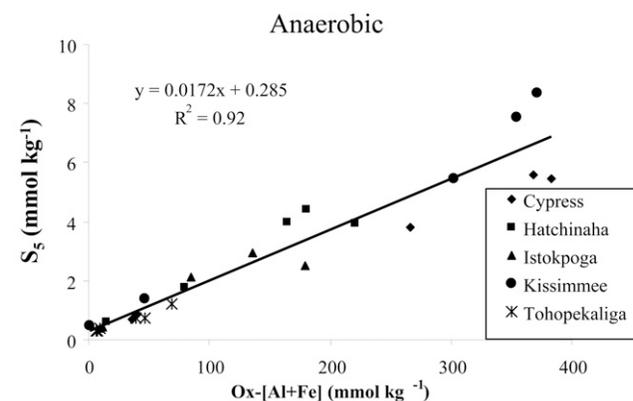
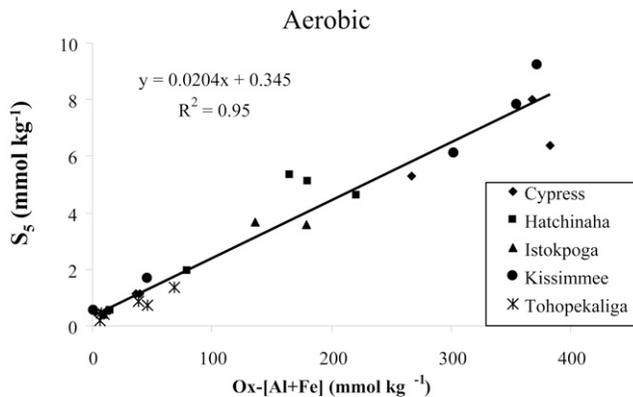


Fig. 7. Correlation between the amount of P sorbed when equilibrated with  $5 \text{ mg P L}^{-1}$  solution and oxalate-extractable Fe and Al for sediments of Lake Istokpoga and upper chain of lakes under aerobic and anaerobic conditions.  $S_5$ ,  $5 \text{ mg P L}^{-1}$  solution.

$$P_{\text{areal-cap}} = (S_{\text{max}})(0.1 \text{ m})(\text{BD}) \quad [5]$$

where  $P_{\text{areal-cap}}$  is the areal P capacity in  $\text{g m}^{-2}$ ,  $S_{\text{max}}$  is the average  $S_{\text{max}}$  in  $\text{g kg}^{-1}$ ,  $0.1 \text{ m}$  is the top 10 cm of sediment, and  $\text{BD}$  is the average bulk density in  $\text{kg m}^{-3}$ . The top 10 cm were selected

Table 5. Average sorption maximum ( $S_{\text{max}}$ ), average bulk density (BD), maximum aerial P sorption capacity ( $P_{\text{areal-cap}}$ ), Lake Area (A), P load ( $P_{\text{load}}$ ), P capacity ( $P_{\text{cap}}$ ), and estimated time until sediments are saturated with respect to P ( $t_{\text{sorb}}$ ) as a function of the reduction of the current external P load to each lake determined from the sorption isotherm study.

Lake	Avg. $S_{\text{max}}$ $\text{mg kg}^{-1}$	Avg. bulk density $\text{Mg m}^{-3}$	P areal capacity† $\text{g m}^{-2}$	Lake area ha	P load $\text{Mg yr}^{-1}$	P capacity‡ Mg	Time until P saturation§			
							Current load	25% reduction	50% reduction	75% reduction
							Aerobic conditions			
Tohopekaliga	35.7	0.70	2.49	9840	44	245	5	7	11	22
Cypress	243	0.21	5.14	2200	11	113	10	13	20	39
Hatchineha	182	0.21	3.79	7160	35	272	8	10	15	30
Kissimmee	284	0.18	5.12	17,900	57	917	16	21	31	63
Istokpoga	155	0.48	7.42	11,200	42	831	19	25	38	76
							Anaerobic conditions			
Tohopekaliga	63.9	0.70	4.45	9840	44	438	10	13	19	39
Cypress	359	0.21	7.58	2200	11	167	14	19	29	58
Hatchineha	220	0.21	4.60	7160	35	330	9	12	18	37
Kissimmee	186	0.18	3.36	17,900	57	601	10	14	20	41
Istokpoga	123	0.48	5.88	11,200	42	659	15	20	30	61

†  $P_{\text{areal-cap}} = (S_{\text{max}})(0.1 \text{ m})(\text{BD})$ .

‡  $P_{\text{cap}} = (P_{\text{areal-cap}})(A)$ .

§  $t_{\text{sorb}} = P_{\text{cap}} / [P_{\text{load}} + (P_{\text{deposition}})(A)]$ ,  $P_{\text{deposition}} = 0.01 \text{ g m}^{-2} \text{ yr}^{-1}$ .

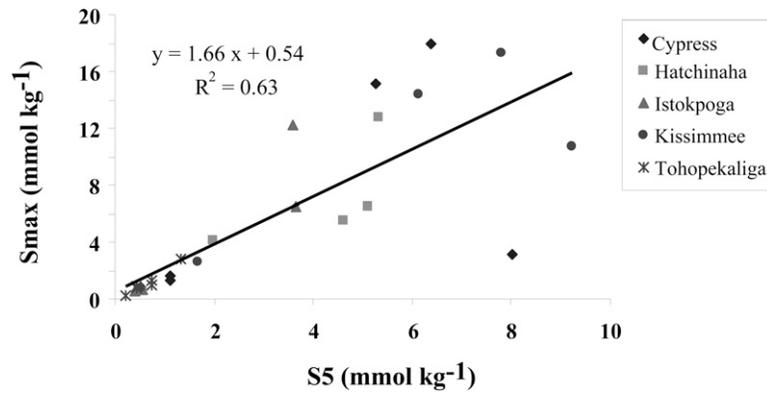


Fig. 8. Relationship between P sorption maximum ( $S_{max}$ ) and the amount of P sorbed when equilibrated with 5 mg P L<sup>-1</sup> solution ( $S_5$ ) under aerobic conditions.

because this is the region of the sediment where the greatest pore water gradients are found, and therefore this region controls the P flux rate (Malecki et al., 2004, Fisher et al., 2005).

Lake Tohopekaliga sediments present the lowest areal P capacity under aerobic conditions, whereas Lake Kissimmee sediments present the lowest under anaerobic conditions. Lake Cypress has the highest areal P capacities under anaerobic conditions, followed by Lake Istokpoga, and Lake Istokpoga showed the highest areal P capacity under aerobic conditions, followed by Lake Cypress. Lake Hatchineha showed intermediate areal P capacities (Table 5).

Phosphorus sorption capacities ( $P_{cap}$ ) for each lake were calculated for the top 10 cm of sediment using the lake area (A) and the areal P capacity ( $P_{areal-cap}$ ), defined as the potential P sorption capacity of sediments on an area basis, calculated with Eq. [6] (Table 5):

$$P_{cap} = (P_{areal-cap})(A) \quad [6]$$

These  $P_{cap}$  values were used to estimate the time until maximum P sorption capacity is reached for the sediments. This approximation is important for nutrient and watershed management purposes (Eq. [7]).

$$t_{sorb} = P_{cap} / [P_{load} + (P_{deposition})(A)] \quad [7]$$

where  $t_{sorb}$  is the period that the sediments would sorb P entering the lake (years),  $P_{load}$  is the actual P load reported by the South Florida Water Management District (SFWMD) (SFWMD, personal communication) ( $kg\ yr^{-1}$ ), A is the area of the lake ( $m^2$ ), and  $P_{deposition}$  is the atmospheric P deposition recorded for Lake Istokpoga:  $0.01\ g\ m^{-2}\ yr^{-1}$  (SFWMD, personal communication). The atmospheric deposition value was used for all lakes because data for individual values were not available and because the atmospheric deposition value is a reasonable approximation due to the close proximity of these five lakes. There are significant uncertainties in these calculations; however, the results are provided to demonstrate the concept and show the relative differences among the lakes. These calculations assume that the lakes will absorb P during all the time calculated. This may not be true for Lakes Istokpoga and Tohopekaliga;  $EPC_0$  values show that their sediments may already be sources of P at low concentrations of P in the water column.

The time until maximum P sorption capacity is reached for the sediments could potentially extend to a decade before reaching saturation, with the exception of Lakes Tohopekaliga and Hatchineha, which, under aerobic conditions, are predicted to be saturated with P after approximately 5 and 8 yr, respectively (Table 5). Lake Istokpoga shows the longest time until saturation ( $\sim 19$  yr) with respect to P. These calculations are based on the sampling of only five points within the lake designed to capture each sediment type and are therefore provided only as a demonstration of this concept. A detailed characterization of the distribution of the lake sediments is required to more accurately represent the time to P saturation based on the overall contribution of each sediment type in the lakes.

Water resource agencies in south Florida are working to reduce the external P loads to Lake Istokpoga and upper chain of lakes to protect these lakes and to reduce the outflow loads to downstream Lake Okeechobee. Current and future efforts to reduce loading of P from the surrounding watershed will increase the time until maximum sorption capacity is reached for the sediments ( $t_{sorb}$ ). These calculations suggest that if current external loads of P are curtailed by 25, 50, or 75% in each of the lakes, the sediments could theoretically act as sinks for P for a significantly longer period of time before complete saturation (Table 5). A benefit of continually reducing P loads to the lakes will be to decrease the rate of enrichment of P in the sediments, but P in the water must be  $>EPC_0$  to allow enrichment to occur.

Results from this study indicate that sediments in Lake Istokpoga and in the Upper Chain of Lakes will continue to act as a sink for P. On average, the sediments were approximately 50 and 62% saturated with P with respect to the  $S_{max}$  predicted for aerobic and anaerobic conditions, respectively. However, the  $S_{max}$  values were determined in the laboratory under constantly shaking conditions, while it is likely that not all sorption sites would be occupied in the lakes due to burial and occlusion. Therefore, the field  $S_{max}$  could be substantially smaller with a shorter time to saturation than the scenarios presented in Table 5. Still, the rank order of values for  $t_{sorb}$  provides us with useful information. Lake managers using this technique could more accurately target lakes for additional load reductions or P removal by dredging (Reddy et al., 2007).

## Conclusions

This research demonstrates a method to predict the relative sorption capacity of lake sediments and provides a calculation of potential saturation of sediments with respect to P. To assess the P retention capability of any lake, however, a detailed sediment map must be constructed to properly weight the contribution of the various sediment types. As the water-column concentrations of P decrease due to concerted management efforts to decrease the external P load for these lakes, the sediments of Lakes Cypress, Kissimmee, and Hatchineha are not likely to act as considerable sources of P. However, the sediments of Lakes Istokpoga and Tohopekaliga already act as sources of P. Further efforts to reduce water-column concentrations to low levels are likely to result in a slow release of P from the sediments for some time, not substantially improving surface water quality.

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