Phosphorus Sorption in Organic Soils in South Florida

Lalitha Janardhanan Samira H. Daroub*

Everglades Research and Education Center and Soil and Water Science Dep. Univ. of Florida Belle Glade, FL 33430 The Everglades Agricultural Area (EAA), downstream of Lake Okeechobee in South Florida, was initially drained in the early 20th century for agriculture and flood protection. Drainage water from the EAA, enriched with P, has impacted the downstream Everglades ecosystem. The organic soils in the EAA have become shallower as a result of continuing oxidation. Mixing of the organic soils with the underlying limestone bedrock may have resulted in increased CaCO₃. Our objectives were to determine the P sorption capacity of selected Histosols in the EAA with various soil depths and its relationships with selected physicochemical properties of the soils. Sorption experiments were performed on field-moist soils representing three series. These soils are taxonomically similar and differ in O horizon depth to bedrock. Both Langmuir and Freundlich sorption models fit the data well. Langmuir P sorption maxima (S_{max}) on a mass basis ranged from 733 to 6767 mg kg⁻¹ and are comparable to mineral soils on a volume basis. In general, P sorption variables were not different among the soils investigated except for the Freundlich sorption coefficient $K_{\rm P}$ which was lowest in the Pahokee soil, indicating lower P sorption capacity. Langmuir S_{max} was positively correlated with pH and oxalate-extractable Fe and Al, but not with CaCO₃ content. The S_{max} was inversely correlated with organic matter and water-extractable Fe and Al oxides, but we found no evidence that shallower soils had higher sorption capacities due to increased CaCO₃ as hypothesized.

Abbreviations: EAA, Everglades Agricultural Area; OM, organic matter; Fe_{ox}, oxalate-extractable Fe; Al_{ox}, oxalate-extractable Al; Pw, water-extractable phosphorus.

On 28 Sept. 1850, an area of drained peat soil south of Lake Okeechobee was designated for agricultural purposes (Bottcher and Izuno, 1994) and is now known as the EAA. The EAA consists of an artificially drained area of approximately 280,000 ha of organic soils and encompasses 27% of the historic Everglades, where sugarcane (*Saccharum officinarum* L.) is the major crop (Bottcher and Izuno, 1994; Lodge, 2004; Richardson, 2008). The beginning of the drainage era in 1906 inaugurated Florida's agricultural industry. The industry intensified after the federal government launched a massive drainage campaign in 1950. South of the EAA are areas of peat soils that are less suitable for agriculture and are designated as water conservation areas (WCAs) (Lodge, 2004; Richardson, 2008). These areas are maintained in an undeveloped state, but a system of dikes and canals allows the water levels to be manipulated to achieve management objectives that include flood control, water supply, and wildlife habitat.

The EAA, with 146,000 ha under production, provides approximately 40% of the nation's winter vegetables and 23% of the nation's sugar (Glaz et al., 2008) and is also the largest single source of P to the Everglades (Flaig and Reddy, 1995). Runoff water containing P from the EAA, as well as other developed areas, has enriched the Everglades, which was historically adapted to very low nutrient levels. Excessive nutrient loading, particularly P, has altered the ecological structure and function of approximately 2430 ha in WCA 1 (Izuno et al., 1991; South Florida Water Management District, 2008). Phosphorus control is a high priority of most national and regional water quality programs because excess P in the water is a contributing factor to eutrophication and the degradation of water quality. An average of 429 Mg of P enters the Everglades

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^{*}Corresponding author (sdaroub@ufl.edu).

 $[\]ensuremath{\mathbb C}$ Soil Science Society of America, 5585 Guilford Rd., Madison WI 53711 USA

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WCAs each year, with approximately 40% derived from rainfall and the remainder contributed by agricultural runoff (Richardson and Vaithiyanathan, 1995). In the EAA, reported P losses to drainage waters have ranged from 1.25 to 9.55 kg ha⁻¹ yr⁻¹ (Izuno et al., 1991). The state of Florida has adopted several measures to restore the Everglades and reduce P loads from agricultural and urban areas (South Florida Water Management District, 2008). The implementation of best management practices (BMPs) in agricultural watersheds (Daroub et al., 2009) and the construction of storm water treatment areas (STAs) are designed to remove nutrients primarily from agricultural runoff originating within the EAA (Flaig and Reddy, 1995; South Florida Water Management District, 2008). Since 1994, STAs and BMPs together have removed nearly 2700 Mg of P that otherwise would have entered the Everglades, with the P unit area load in EAA drainage water averaging 0.49 kg ha⁻¹ in Water Year 2008 (South Florida Water Management District, 2008).

When inorganic P is added to the soil, the soluble form immediately reacts with the soil and forms other compounds that become less soluble with time (Gale et al., 1994; Brady and Weil, 1999); however, a large proportion of the P removed from solution is sorbed onto soil surfaces (Gale et al., 1994). The term Psorption refers to an instantaneous physical reaction of P with the soil (Havlin et al., 1999). Depending on the soil mineralogy, the oxidation-reduction changes can significantly alter P solubility and sorption mechanisms (Reddy et al., 1998). Phosphorus sorption is closely related to the characteristics of the soil, such as its surface area (Olsen and Watanabe, 1957), CaCO₃ content (Richardson and Vaithiyanathan, 1995), and pH (Khalid et al., 1977; Reddy et al., 1998). The P sorption characteristics of northern Everglades peat soils were reported to probably be regulated by CaCO₃ (Richardson and Vaithiyanathan, 1995). Phosphorus sorption was also related to the hydrous Fe and Al oxyhydroxide content of the soil (Khalid et al., 1977; Reddy et al., 1998; Villapando and Graetz, 2001). Oxalate-extractable Fe and Al have been shown to be reliable predictors of the P sorption capacity of peat soils in the Everglades (Reddy et al., 1998; Giesler et al., 2005). Ammonium oxalate extracts active (poorly crystalline) Fe and Al (McKeague and Day, 1966; Loeppert and Inskeep, 1996) with adsorption capacity much higher than the crystalline forms due to their larger surface area per unit volume (Khalid et al., 1977; Darke and Walbridge, 2000). Several researchers have also reported a positive relationship between P sorption and OM content (Richardson and Vaithiyanathan, 1995; Villapando and Graetz, 2001). The role of OM content in increasing the ability of soils to sorb P has been attributed to the soil OM's association with Fe, Al, and Ca cations (Villapando and Graetz, 2001). The P sorption capacity of in-stream wetland sediments was found to be strongly correlated with organic C content, with regression analysis showing organic-complexed Al accounting for a high percentage of the variation in P sorption (Novak and Watts, 2006).

Soils in the EAA are classified as Histosols, suborder Saprists (Rice et al., 2002). The organic soils, formed from the decay and accumulation of saw-grass (*Cladium jamaicense* Crantz) and other lush vegetation, range from discontinuous shallow patches

to accumulations of peat and muck 2.4 to 3 m thick near Lake Okeechobee and less deep farther away from the lake (Davis et al. (1994).). Typically, these soils have an OM content ranging from 710 to 910 g kg⁻¹ (Porter and Sanchez, 1992) and overlie calcareous limestone deposits ranging in depth from about 0.3 to 1 m. Peat soils in general have extremely acidic pH while most Everglades soils have a circumneutral pH (Zhou and Li, 2001; Rice et al., 2002). The P cycle in Histosols is quite complex (Porter and Sanchez, 1992) due to high soil OM, organic forms of P, and Fe transformations as a result of a periodic wet and dry cycle. In addition, the EAA Histosols have underlying limestone bedrock and a higher pH compared with other Histosols (Snyder, 2005).

Due to drainage and subsequent cropping in the EAA, OM decomposition has been exceeding production, resulting in soil subsidence and lowering of the surface elevations in these Histosols (Snyder, 2005). Historically, the oxidation of OM under drained conditions has accounted for soil subsidence at a rate of 2.54 cm yr⁻¹ (Snyder, 2005). Maintaining a high water table along with implementation of other BMPs have resulted in reducing the present-day subsidence rate to 1.45 cm yr^{-1} (Reddy et al., 1993; Shih et al., 1998; Snyder, 2005). Subsidence may have caused the soils to have a higher mineral content and be composed of less easily degraded OM than earlier (Snyder, 2005). The incorporation of bedrock CaCO₃ into the soil by tillage as these soils become shallower due to subsidence and irrigation with high-Ca water from Lake Okeechobee may have increased the pH values considerably, as has been reported in the southern Everglades (Zhou and Li, 2001). Most of the organic soils in the EAA are very closely associated taxonomically and vary only based on the depth of the O horizon to the limestone bedrock (Rice et al., 2002). Reclassification of soils in some areas has been done as they become shallower (Shih et al., 1998).

We hypothesized that the changes in soil properties as soils become shallower, such as increased pH and $CaCO_3$, may have increased the ability of the EAA's soils to sorb P. Given that soil P sorption is directly related to P eutrophication in the downstream ecosystems (Flaig and Reddy, 1995), it becomes necessary to study the physicochemical properties that affect the P sorption capacity of the organic soils in the EAA. The objectives of this study were to: (i) determine the P sorption capacity of selected Histosols in the EAA in relation to O horizon depth to bedrock; (ii) determine how the P sorption capacity varies in the surface (0–20-cm) and below-surface (20–40-cm) layers; and (iii) evaluate the relationship between the P sorption capacity and selected soil physicochemical properties to determine if the sorption capacity of these soils has increased with the increase in mineral content.

MATERIALS AND METHODS

Three soil series from the EAA were selected for the study, Dania, Lauderhill, and Pahokee, with OM content ranging from 600 to 900 g kg⁻¹ according to the 1978 soil survey of Palm Beach County (Soil Conservation Service, 1978; Soil Survey Staff, 1999; Rice et al., 2002). When found under natural environmental conditions, the water table of these soil series is at or above the surface for much of the year; in other ar-

eas, humans control the water table. The three soil series are closely associated and the difference is related to their depth to the limestone bedrock, and they have been classified accordingly. The Dania soil series (euic, hyperthermic, shallow Lithic Haplosaprists) consists of shallow, very poorly drained, rapidly permeable organic soils in freshwater marshes or swamps on the fringes of areas of deeper organic soils. They rest on limestone bedrock with a soil depth (O horizon) <51 cm. The Lauderhill series (euic, hyperthermic Lithic Haplosaprists) consists of nearly level and very poorly drained, rapidly permeable soils formed in organic deposits of freshwater marshes and have a 51- to 91-cm-thick O horizon over the limestone bedrock. The Pahokee series (euic, hyperthermic Lithic Haplosaprists) consists of very poorly drained, rapidly permeable soils formed in organic deposits of freshwater marshes and are 91 to 130 cm thick over the limestone bedrock (Soil Conservation Service, 1978; Soil Survey Staff, 1999).

The sampling was done at nine locations (three locations per soil series), with two samples from each location at two depths (0-20 and 20-40 cm) for a total of 36 samples (Table 1). The depth to bedrock was measured at the time of sampling. Individual soil samples were homogenized and stored at 5°C at field moisture content until they were used for the P sorption experiments. For the P sorption studies, 3 g of fieldmoist soil was equilibrated with 30 mL of solution (Porter and Sanchez, 1992 and Pant and Reddy, 2001) containing 0, 10, 30, 50, 100, 250, or 500 mg L⁻¹ of P as KH₂PO₄ (Richardson and Vaithiyanathan, 1995; Reddy et al., 1998). An ionic medium of 0.01 mol L^{-1} KCl was used in this study (Giesler et al., 2005). Quality assurance or control was strictly followed, with duplicates analyzed every 10 samples. The soil samples with P solutions were shaken for 24 h at ambient temperature (20–24°C) on an orbital shaker, centrifuged for 15 min at $1770 \times g$, and immediately filtered through a 0.45-µm membrane filter (Zhou and Li, 2001; Giesler et al., 2005; Litaor et al., 2005). The P concentration of the filtrates was analyzed by the ascorbic acid method (Murphy and Riley, 1962) using a Flow IV segmented-flow analyzer (OI Analytical, College Station, TX). All data were corrected for moisture content and are presented on an oven-dry basis. Linear Langmuir equation and linear Freundlich equation isotherm models were used to determine the P sorption maximum and other P retention parameters.

The data were evaluated using a transformed version of the Langmuir model (Pant and Reddy, 2001; Essington, 2003):

$$\frac{C}{S} = \frac{1}{K_{\rm L}S_{\rm max}} + \frac{C}{S_{\rm max}}$$
[1]

where *C* is the solution P concentration measured after 24-h equilibration (mg L⁻¹), *S* is the amount of P sorbed on the solid phase (mg kg⁻¹), S_{max} is the P sorption maximum (mg kg⁻¹), and K_{L} is a sorption constant related to the P bonding energy (L mg⁻¹). The Langmuir isotherm was constructed by plotting *C* vs. *C/S* such that the slope was equal to $1/S_{\text{max}}$ and the intercept was equal to $1/(K_{\text{L}}S_{\text{max}})$ (Pant and Reddy, 2001). Least-squares linear regression analysis was used to compute the Langmuir constants. One advantage of using the Langmuir model is the determination of a sorption maximum (Olsen and Watanbe, 1957). The sorption constant K_{L} , a measure of the intensity of the sorption isotherm, is equal to the reciprocal of the equilibrium P concentration at one-half saturation (Essington, 2003; Olsen and Watanbe, 1957). The data were also evaluated using the linear Freundlich equation (Donald, 2003; Essington, 2003):

$$\log S = \log K_{\rm F} + N \log C$$
 [2]

where $K_{\rm F}$ is the Freundlich sorption coefficient (L kg⁻¹) and N is a correction factor. Plotting logS against logC yields a straight line with slope N and intercept log $K_{\rm F}$ Both $K_{\rm F}$ and N are empirical constants and are not normally interpreted as having physical meaning (Essington, 2003); however, $K_{\rm F}$ is numerically equal to S when C = 1. The term $K_{\rm F}$ implies that the energy of sorption on a homogenous surface is independent of the surface coverage (Donald, 2003), while N is a measure of the heterogeneity of the sorption sites on the soil (Zhou and Li, 2001). As N approaches unity, surface site homogeneity increases, indicating that there is a narrow distribution of adsorption site types (Essington, 2003). One of the disadvantages of the Freundlich equation is that it does not predict a sorption maximum (Donald, 2003).

The soil pH was measured using 10 g of field-moist soil mixed with 20 mL of distilled, deionized water for 10 min and the suspension was allowed to stand undisturbed for 30 min before determination by means of a pH electrode in combination with a pH meter (Thermo Orion Model 720A, Thermo Fisher Scientific, Waltham, MA) (Thomas, 1996). The ash content and soil OM were determined by the loss-on-ignition method (Soil Survey Laboratory Staff, 1996; Porter and Sanchez, 1992). The ash content was determined by the loss of mass between a soil sample dried to a constant mass at 105°C in an oven and another sample held at 400°C to a constant mass in a muffle furnace. The OM content was calculated as the difference between the oven-dry soil sample mass and the ash content. Total C includes inorganic C from carbonates and organic materials in the soil (Brady and Weil, 1999). Loss-on-ignition is a good estimate of the OM content in these organic soils because the CaCO₃ content was found to be <5 g kg⁻¹ (0.5%).

Total P was determined by H2SO4 digestion of the ashed soil (Murphy and Riley, 1962; Anderson, 1976; Sanchez 1990), followed by photometric analysis. Four milliliters of soil was mixed with 50 mL of water for water-extractable P (Pw) or with 0.5 mol L⁻¹ acetic acid for acetic acid extractable P (Pa) (Sanchez, 1990). The soil solution was allowed to stand overnight, shaken on an end-over-end shaker for 1 h, and filtered through Whatman no. 2 filter paper; Pa and Pw were determined by the ascorbic acid method (Murphy and Riley, 1962). Total CaCO₃ was determined by a titrimetric procedure based on dissolution of the carbonate present in air-dried soil in a digestion chamber (Loeppert and Suarez, 1996). Oxalate-extractable Fe (Fe_{ox}) and Al (Al_{ox}) were extracted with ammonium oxalate at pH 3.0 in darkness (Bertsch and Bloom, 1996; Loeppert and Inskeep 1996; McKeague and Day, 1966) and the extracts were analyzed using an inductively coupled plasma spectrophotometer. Extractable Ca and Mg were determined using 0.5 mol L⁻¹ acetic acid, as the extracting solution (Sanchez, 1990) and analyzed using an atomic absorption spectrophotometer (Varian Inc., Palo Alto, CA).

Statistical differences in sorption parameters were tested using the PROC MIXED procedure in SAS for the effect of series, layer depth, and series × layer depth interaction (SAS Institute, 2002). Soil series and layer depth were considered fixed effects, while location and samples within location were considered random effects (Little et al., 1996). Means among soil series

Series	Sample depth	Location	Depth to bedrock	Cropping history	рН	Ash content	OM†	TP‡	Pa§	Pw¶	Fe _{ox} #	Al _{ox} #	Ca	Mg	CaCO ₃
	cm		cm							– mg kg	g ⁻¹				
Dania		1	46	sugarcane	7.3	190	810	1672	83.0	6.6	8826	1534	9122	2156	1279
		I	49	sugarcane	6.9	180	820	1537	138.0	17.3	7409	1271	7821	1576	182
	0-20	2	45	sugarcane	7.1	170	830	829	68.0	7.7	5747	2047	8298	1284	916
		2	48	sugarcane	7.3	180	820	812	117.0	8.4	5528	2150	14043	2168	364
		3	46	sugarcane	7.8	220	780	1286	120.0	4.3	12020	2366	11256	2461	10740
		5	43	sugarcane	7.3	200	800	1492	138.0	7.5	10652	2179	10250	2115	907
		1	46	sugarcane	7.2	360	640	842	83.0	8.1	5688	2017	7900	1572	1828
		I	49	sugarcane	7.4	350	650	614	61.0	2.5	3519	3596	6869	1469	730
	20-40	2	45	sugarcane	7.7	640	360	287	25.0	1.0	3048	2899	31592	981	2821
		2	48	sugarcane	7.4	300	700	693	166.0	2.3	3695	3459	10475	1384	2002
		2	46	sugarcane	8.0	200	800	1162	81.0	4.0	8251	2161	16198	3537	6540
		5	43	sugarcane	7.8	220	780	1112	67.0	3.3	8429	2910	16146	2819	4021
Lauderhill		1	78	sugarcane	7.5	230	770	1680	152.0	8.5	13837	2200	9293	1702	978
		I	59	sugarcane	7.6	370	630	3419	163.0	8.8	12233	2040	10571	1965	3113
	0–20	2	61	corn	8.0	250	750	1449	91.0	3.0	10978	1987	9774	2099	3677
		2	90	sugarcane	7.4	210	790	1713	117.0	4.6	11038	1877	12050	2664	2376
		2	77	sugarcane	6.9	220	780	1765	84.0	1.5	16012	2056	7937	1609	3350
		5	73	corn	6.8	220	780	1569	65.0	1.4	13139	2078	9541	1302	3473
		1	78	sugarcane	7.3	190	810	650	90.0	4.1	5168	1056	7681	1129	2948
		I	59	sugarcane	7.3	200	800	848	173.0	6.0	7970	1861	9914	1510	2954
	20-40	2	61	corn	7.6	210	790	1155	74.0	2.9	10714	1814	10769	2289	2215
		2	90	sugarcane	7.3	200	800	1098	96.0	3.5	11355	2022	12112	2532	2211
		2	77	sugarcane	7.0	210	790	1212	84.0	2.7	12421	2174	8676	1022	3244
		5	73	corn	6.8	220	780	1449	80.0	3.7	13829	2259	7518	1003	2446
Pahokee		1	112	sugarcane	6.7	160	840	1490	145.0	22.0	5913	1187	11330	1900	910
		I	97	sugarcane	6.2	160	840	1755	112.0	10.6	3652	808	10022	1376	< dl
	0–20	2	92	corn	7.1	190	810	1775	143.0	9.8	5462	1126	8770	1230	3277
		2	93	sugarcane	6.9	200	800	2013	187.0	30.2	5518	1150	9327	1355	539
		2	96	sugarcane	6.6	170	830	1291	108.0	12.8	3600	769	8804	1190	< dl
		5	117	corn	6.4	160	840	1233	91.0	12.0	3806	782	8191	1086	546
		1	112	sugarcane	6.1	140	860	273	28.0	13.8	2404	954	6590	901	< dl
		I	97	sugarcane	6.8	150	850	246	24.0	11.0	1793	754	7061	1039	7615
	20-40	2	92	corn	7.2	170	830	849	55.0	5.7	3339	680	8084	1045	907
		2	93	sugarcane	7.1	170	830	800	63.0	10.0	3897	735	7074	1112	727
		2	96	sugarcane	6.9	150	850	1032	49.0	13.4	1898	409	9920	1342	1635
		3	117	corn	6.7	130	870	444	40.0	16.1	1973	362	11625	1762	7167
Avg.	0-20		46		7.3	190	810	1271	110.7	8.6	8364	1925	10132	1960	2398
Dania	20-40		46		7.6	345	655	785	80.5	3.5	5438	2840	14863	1960	2990
Avg.	0–20		73		7.4	250	750	1933	112.0	4.6	12873	2040	9861	1890	2827
Lauderhill	20-40		73		7.2	205	795	1069	99.5	3.8	10243	1864	9445	1580	2669
Avg.	0–20		101		6.7	173	827	1593	131.0	16.2	4659	970	9407	1356	1318
Pahokee	20-40		101		6.8	152	848	607	43.2	11.7	2552	649	8392	1200	3610
+ Organic															

Table 1. Sampling details and selected chemical analyses of Dania, Lauderhill, and Pahokee soil series from three locations each and at two layer depths.

+ Organic matter.

‡ Total P.

§ Acetic acid extractable P.

¶ Water-extractable P.

Fe or Al extracted by ammonium oxalate.

and layer depth were separated using the least square means (LSMEANS) statistical procedure. Empirical relationships between the P sorption parameters and soil properties were established using untransformed data with Pearson correlation analysis (SAS Institute, 2002). Statistical differences were determined at the 0.05 probability level unless otherwise indicated.

RESULTS AND DISCUSSION Soil Properties

The Histosols under consideration in the EAA have high soil OM content, averaging 733, 773, and 838 g kg⁻¹ at 0 to 40 cm in the Dania, Lauderhill, and Pahokee series, respectively. Even

Table 2. Phosphorus sorption variables as estimated by the Langmuir equation for three soil series at two soil layer depths.

	Dani	a			Laude	rhill		Pahokee					
Location+	S _{max} ‡	<i>K</i> L§	<i>r</i> ²	Location†	S _{max}	KL	<i>r</i> ²	Location+	S _{max}	KL	r ²		
	mg kg ⁻¹	L mg ⁻¹			mg kg ⁻¹	L mg ⁻¹			mg kg ⁻¹	L mg ⁻¹			
1U	1715	0.009	0.98	1U	2696	0.014	0.98	1U	1919	0.004	0.74		
1U	2911	0.004	0.78	1U	6767	0.008	0.92	1U	2438	0.005	0.88		
2U	733	0.069	0.96	2U	3923	0.019	0.92	2U	2532	0.007	0.91		
2U	2532	0.010	0.92	2U	3393	0.011	0.94	2U	2300	0.004	0.90		
3U	3738	0.013	0.97	3U	3601	0.016	0.94	3U	2570	0.005	0.85		
3U	3964	0.007	0.95	3U	4155	0.014	0.92	3U	828	0.034	0.95		
1L	1363	0.015	0.93	1L	1783	0.043	0.99	1L	5808	0.002	0.72		
1L	3716	0.012	0.88	1L	2831	0.017	0.96	1L	4697	0.003	0.75		
2L	2133	0.020	0.98	2L	4739	0.021	0.92	2L	1717	0.006	0.83		
2L	2746	0.021	0.99	2L	5781	0.007	0.85	2L	2060	0.005	0.80		
3L	2922	0.023	0.99	3L	4024	0.012	0.95	3L	1241	0.010	0.99		
3L	4640	0.007	0.87	3L	2948	0.011	0.91	3L	1331	0.009	0.94		
Avg.													
U	2599	0.019			4089	0.014			2098	0.010			
L	2920	0.016			3684	0.019			2809	0.006			
0–40 cm	2760	0.018			3887	0.016			2453	0.008			

+ U = 0−20 cm, L = 20−40 cm.

 $= S_{max'}$ P sorption maximum.

§ $K_{L'}$ sorption constant related to P bonding energy.

with such high OM content, these soils have a circumneutral pH averaging 7.5, 7.3, and 6.8 at 0 to 40 cm in Dania, Lauderhill, and Pahokee series, respectively (Table 1). The Fe_{ox} content averaged 7.355 g kg⁻¹ and ranged from 1.793 g kg⁻¹ in Pahokee at 20 to 40 cm to 16.012 g kg⁻¹ in Lauderhill at 0 to 20 cm (Table 1). The Al_{ox} content averaged 1.715 g kg⁻¹, with the highest content of 3.596 g kg⁻¹ measured in the Dania series at 20 to 40 cm and the least content of 0.362 g kg⁻¹ measured in the Pahokee series at 20 to 40 cm (Table 1). Total CaCO₃ content averaged 2.694, 2.748, and 2.464 g kg⁻¹ at 0 to 40 cm in the Dania, Lauderhill, and Pahokee soils, respectively. Calcium carbonate values were surprisingly low considering that limestone bedrock underlies the O horizon and that these soils are continuously undergoing oxidation and subsidence. The total CaCO3 content varied considerably among the locations investigated, however, ranging from a low of 0.182 to a high of 10.740 g kg^{-1} , both in the Dania series, with a few samples from the Pahokee series showing undetectable levels (Table 1). Differences in CaCO₃ content are probably related to variation in soil depth, tillage depth, irrigation water, and the degree of mixing with the limestone bedrock. In summary, these organic soils from the EAA generally have an average soil OM content of 780 g kg⁻¹, ash content of 220 g kg⁻¹, near-neutral pH, CaCO₃ content averaging 3 g kg⁻¹, and extractable Fe and Al content averaging 7 and 2 g kg⁻¹ soil, respectively.

Phosphate Sorption Isotherms

The sorption isotherms obtained for all locations showed the typical L-shaped curve (not shown). The C/S ratio was plotted vs. C to calculate S_{max} and K_L according to the Langmuir model (Eq.[1]), and logS was plotted vs. logC to calculate K_F and N according to the Freundlich model (Eq.[2]). Both the Langmuir and Freundlich models described the P sorption data adequately (Tables 2 and 3). The Langmuir sorption model provided a highly significant fit to the data, with r^2 values of 0.72 or greater (Fig. 1; Table 2). Average $S_{\rm max}$ values at 0 to 40 cm were 2760, 3887, and 2453 mg kg⁻¹ in the Dania, Lauderhill, and Pahokee series, respectively (Table 2). The average values of the Langmuir constant, $K_{\rm L}$, were 0.018, 0.016, and 0.008 L mg⁻¹ for the Dania, Lauderhill, and Pahokee series, respectively (Table 2). The Langmuir constant $K_{\rm L}$ is a measure of the intensity of the adsorption isotherm or bonding energy.

The Freundlich sorption model also provided highly significant fit to the data, with r^2 values >0.85 (Fig. 2; Table 3). Although the Freundlich parameters have no physical meaning, K_F is numerically equal to *S* when C = 1 (Essington, 2003) and is a measure of the P sorption capacity of the soil (Zhou and Li, 2001). The term *N* has been shown to be a measure of the heterogeneity of adsorption sites and relates to the bonding energy (Zhou and Li, 2001). As *N* approaches unity, surface site homogeneity increases, indicating that there is a narrow distribution of adsorption site types (Essington, 2003). Average values of K_F were 117.5, 159.7, and 36.5 L kg⁻¹ at 0 to 40 cm for the Dania, Lauderhill, and Pahokee locations, respectively (Table 3). Average values of *N* were 0.53, 0.53, and 0.63 at 0 to 40 cm for the Dania, Lauderhill, and Pahokee locations, respectively.

For the locations investigated in this study, there was no effect of soil series on the Langmuir $S_{\rm max}$, indicating similar P sorption capacities in these soils (Table 4). Although $K_{\rm L}$ was two times lower in Pahokee than in the Dania and Lauderhill series, there was no significant effect of soil series on $K_{\rm L}$, indicating similar P sorption intensity in the locations investigated. In addition, there were no differences between the two layer depths (0–20 and 20–40 cm) and no interaction between the two factors of soil series and layer depth on the Langmuir $S_{\rm max}$ or $K_{\rm L}$ (Table 4).

Table 3. Phosphorus sorption variables as estimated by the Freundlich equation for three soil series at two soil layer depths.

	Dan	ia			Lauderhill				Paho		
Location†	K _F ‡	N§	<i>r</i> ²	Location+	K _F	N	<i>r</i> ²	Location+	K _F	N	r ²
	L kg ⁻¹				L kg ⁻¹				L kg ⁻¹		
1U	52.9	0.55	0.99	1U	94.7	0.57	0.98	1U	29.6	0.59	0.95
1U	25.4	0.71	0.97	1U	115.6	0.67	0.99	1U	26.8	0.70	0.96
2U	89.5	0.46	0.90	2U	216.7	0.49	0.97	2U	63.1	0.57	0.99
2U	98.0	0.52	0.91	2U	111.1	0.56	0.98	2U	23.0	0.70	0.99
3U	135.5	0.55	1.00	3U	185.0	0.49	0.97	3U	34.5	0.65	0.99
3U	58.2	0.69	0.98	3U	174.0	0.52	0.99	3U	51.3	0.51	0.83
1L	58.0	0.54	0.91	1L	173.8	0.42	0.89	1L	15.2	0.86	0.98
1L	190.1	0.47	0.86	1L	165.4	0.47	0.95	1L	31.5	0.72	0.99
2L	187.1	0.40	0.99	2L	309.5	0.46	0.95	2L	40.7	0.56	0.99
2L	215.6	0.42	0.98	2L	123.1	0.6	0.99	2L	46.9	0.56	0.98
3L	185.2	0.48	0.88	3L	136.4	0.56	0.99	3L	39.9	0.56	0.97
3L	114.3	0.57	0.99	3L	110.6	0.52	0.98	3L	35.1	0.59	0.93
Avg.											
U	76.6 A¶	0.58			149.5	0.55			38.1	0.62	
L	158.4 B	0.48			169.8	0.51			34.9	0.64	
0–40 cm	117.5 b#	0.53			159.7 b	0.53			36.5 a	0.63	

+ U = 0-20 cm, L = 20-40 cm.

 $= K_{F'}$ sorption coefficient.

§ N, correction factor.

 \P When the effect of layer depth was significant, uppercase letters were used to separate means according to the PROC MIXED test at P < 0.05.

When the effect of soil series was significant, lowercase letters were used to separate means according to the PROC MIXED test at P < 0.05.

Considering the Freundlich sorption parameters, there were effects of soil series, layer depth, and series × layer depth interaction on $K_{\rm F}$ (Table 4). The Freundlich $K_{\rm F}$ was significantly lower in the Pahokee soil (36.5 L kg⁻¹ at 0–40 cm) compared with soils from the two other series, with no differences between Dania and Lauderhill (Table 3). The series × layer depth interaction showed significant differences in the Dania soils between the two layer depths. This may be an indication of an effect of some soil properties on P sorption. There was no effect of series, layer depth, or in-

teraction between layer depth and series on *N*, indicating that the soils were similar in terms of homogeneity of P adsorption sites.

Relationship between Langmuir Phosphorus Sorption Maximum and Soil Properties

The soil series in the EAA are classified based on the depth of the O horizon to the limestone bedrock. The Langmuir $S_{\rm max}$ showed no correlations with depth to bedrock but was found to correlate positively with Fe_{ox} (r = 0.64, P < 0.01), Al_{ox} (r = 0.48,



Fig. 1. Linear Langmuir sorption isotherms of Dania, Lauderhill, and Pahokee series soils sampled from three locations each at two depths. Each isotherm is an average of two samples from each location.



Fig. 2. Linear Freundlich sorption isotherms of Dania, Lauderhill, and Pahokee series soils sampled from three locations each at two depths. Each isotherm is an average of two samples from each location.

P < 0.05), and pH (r = 0.51, P < 0.05) and negatively with OM (r = -0.86, P < 0.01) (Fig. 3) and Pw (r = -0.34, P < 0.05) at the 0- to 20-cm depth (Table 5). Sorption maxima showed no significant correlation with CaCO₃ content or extractable Ca in the soils under consideration (Table 5). Porter and Sanchez (1992) calculated a P sorption index for EAA soils that was well correlated with pH, total Ca, and free carbonates. Extractable Fe and Al were significant factors if they were a component of linear models that included pH or free carbonates (Porter and Sanchez, 1992). A study by Darke and Walbridge (2000) on mineral soils concluded amorphous Al to be more strongly correlated with inorganic P sorption than extractable amorphous Fe. Villapando and Graetz (2001) also found Al to be a dominant factor in P retention by the Bh horizon of Florida Spodosols. Strong correlations were found between P sorption and total C, total P, Ca, Mg, Fe, and Al in sediments from Lake Istokpoga and the upper chain of lakes in Florida (Belmont et al., 2009). In the current study, Langmuir S_{\max} showed a weaker but still significant correlation to ${\rm Al}_{\rm ox}$ than to ${\rm Fe}_{\rm ox}$ (Fig. 3). Oxalate-extractable Al is much lower than Fe in EAA Histosols (Porter and Sanchez, 1992), which may explain the weaker correlation.

Soils with a high ash content (lower OM) had a higher pH, Al_{ox} , Fe_{ox} , and S_{max} (Table 5). The relationship between soil ash content and S_{max} indicated an increase in P sorption with an increase in soil mineral matter content; conversely, P sorption decreased with increasing soil OM (Fig. 3). There are two types of interactions, direct and indirect, that explain the relationship

between P sorption and soil OM (Hue, 1991). Kang et al. (2009) used path analysis to examine the direct and indirect effects of soil properties on $S_{\rm max}$ using soils with a wide range of OM content. The $S_{\rm max}$ was highly influenced by the indirect effect of Fe_{ox} and Al_{ox} through the OM content (Kang et al., 2009). Indirect interactions between soil OM and Fe and Al oxides occur as a result of different organic acids produced, like acetic and malic acids (Hue, 1991). These indirect interactions inhibit crystallization and thereby increase the P sorption capacity and lead to a positive correlation between OM and P sorption (Borggaard et al., 1990; Darke and Walbridge, 2000). Hue (1991) reported that the influence of OM on P sorption varied with the type of organic acid. For example, they observed that less P was sorbed in the presence of malic acid than in the presence of acetic acid (Hue, 1991).

Direct interactions occur where OM and P compete for sorption sites, leading to decreased P sorption (Borggaard et al., 1990; Darke and Walbridge, 2000). According to one-point P sorption results, dissolved OM in the form of humic acid, oxalate, and decomposed clover (*Trifolium incarnatum* L.) and corn (*Zea mays* L.) residues significantly inhibited P sorption to goethite at concentrations of 50 and 200 mg total soluble C (Hunt et al., 2007). Competition between P and organic anions is likely to be high in this matrix, with >75% OM (Giesler et al., 2005) and could be the reason for the significant negative correlation between S_{max} and OM in the current study (r = -0.86) (Fig. 3). This study showed an inverse relationship between OM and pH (Fig. 3) and a positive relationship between ash content and

Table 4. Results of PROC MIXED test in SAS for the Langmuir P sorption maximum S_{max} and sorption constant $K_{L'}$ and the Freundlich sorption coefficient K_F and correction factor N for the three soil series investigated at two layer depths (0–20 and 20–40 cm).

		S _{max}		KL		k	, F	Ν		
Effect	df	F value	P > F	F value	P > F	F value	<i>P</i> > <i>F</i>	F value	P > F	
Series	2	2.11	0.20	1.47	0.30	15.27	0.0002	2.96	0.13	
Layer depth	1	0.30	0.61	0.02	0.89	7.54	0.015	2.65	0.12	
Series × layer depth	2	0.64	0.54	0.49	0.62	4.45	0.03	1.94	0.17	



Fig. 3. Scatter diagram showing the relationships among the soil properties of soil organic matter (SOM), pH, Fe and Al content, and the Langmuir P sorption maximum (S_{max}) from all three soils.

pH (Table 5). The increase in pH was attributed by Porter and Sanchez (1992) to OM loss due to subsidence and a possible increase in $CaCO_3$ content. In our study, pH correlated with ash, Fe_{ox} , Al_{ox} , $CaCO_3$, and extractable Mg contents (Table 5).

The $S_{\rm max}$ values found in the current study, ranging from 733 to 6767 mg kg⁻¹, are similar to or lower than those reported by Porter and Sanchez (1992). Values of $S_{\rm max}$ reported by Porter and Sanchez (1992) ranged from 790 mg kg⁻¹ in Terra

Table 5. Pearson correlation coefficients ($P < 0.05$) between selected so	oil properties of the three soil series at the 0- to 20-cm soil dep	oth
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		Depth to	Ash									
Parameter	S _{max} +	bedrock	content	OM‡	рН	Fe _{ox} §	Al _{ox} §	CaCO ₃	Pa¶	Pw#	Ca	Mg
S _{max}	1.00											
Depth to bedrock	-0.31	1.00										
Ash content	0.86**	-0.31	1.00									
ОМ	-0.86**	0.31	-1.00	1.00								
рН	0.51*	-0.64**	0.64**	-0.64**	1.00							
Fe _{ox}	0.64**	-0.38	0.65**	-0.65**	0.59**	1.00						
Al _{ox}	0.48*	-0.70**	0.52**	-0.52**	0.77**	0.78**	1.00					
CaCO ₃	0.42	-0.29	0.39	-0.39	0.57*	0.52*	0.51*	1.00				
Pa	0.26	0.16	0.28	-0.28	0.14	-0.09	-0.14	-0.10	1.00			
Pw	-0.34*	0.41	-0.27	0.27	-0.40	-0.59	-0.60	-0.45	0.66**	1.00		
Ca	0.25	-0.13	0.10	-0.10	0.34	0.02	0.36	0.17	0.21	-0.08	1.00	
Mg	0.39	-0.45	0.33	-0.33	0.71**	0.45	0.59**	0.42	0.11	-0.32	0.69**	1.00

* Significant at the 0.05 level.

** Significant at the 0.01 level.

+ Langmuir P sorption maximum.

+ Organic matter.

\$ Fe and Al extracted by ammonium oxalate.

¶ Acetic acid extractable P.

Water-extractable P.

Ceia to 104,000 mg kg⁻¹ in the Pahokee series using air-dried soil samples, while the current study used field-moist samples. In preliminary investigation, we found that air-dried samples underestimated the P sorption compared with the field-moist samples (data not shown). These organic soils from the EAA have a higher capacity to sorb P than mineral soils when compared on a mass basis. Mineral soils like an Ultisol from Delaware had $S_{\rm max}$ values ranging from 95 to 588 mg kg⁻¹ (Sallade and Sims, 1997), while a few Bt horizons of an Ultisol from sandy coastal regions of Florida ranged from 470 to 1500 mg kg⁻¹ (Zhou et al., 1997). Well-drained calcareous Mollisols from Canada with a maximum of 0.4 to 2.1% soil OM had $S_{\rm max}$ values <50 mg kg⁻¹ (Whalen and Chang, 2002). Acidic Appalachian soils, with 0.2 to 17% soil OM, had a P sorption maximum ranging from 970 to 2500 mg kg⁻¹ (Anghinoni et al., 1996). But when the P sorption of the EAA organic soils is compared with mineral soils based on a volume rather than on a mass basis, the sorption seems to be comparable or higher for the mineral soils. For example, a soil sample from the Lauderhill series with a bulk density of 0.58 g cm⁻³ and 630 g kg⁻¹ soil OM has a sorption of 6767 mg kg⁻¹ of soil, equivalent to 3925 g m⁻³. Similarly, the acid Appalachian Ultisol with a bulk density of 0.87 g cm^{-3} , soil OM of 104 g kg^{-1}, and $S_{\rm max}$ of 2325 mg kg^{-1} (Anghinoni et al., 1996) had an S_{max} of 2023 g m⁻³ on a volume basis.

CONCLUSIONS

From a few selected organic soils in the EAA, the Langmuir $S_{\rm max}$ was not increased by a shallower depth of the soil profile (O horizon) or increased CaCO₃ content. On the other hand, the Freundlich $K_{\rm F}$ was lowest in the Pahokee soils, the deepest among the series and locations investigated, which indicated a lower sorption capacity in deeper soils. The Langmuir S_{\max} was significantly correlated with mineral content and negatively correlated with OM. Oxalate-extractable Fe and Al appear to play a role in affecting the P sorption of these soils. The $S_{\rm max}$ values were found to correlate with Fe_{ox}, Al_{ox}, and pH but not with CaCO₃ content. Consequently, we conclude that the P sorption capacity is not affected by the CaCO3 content of the soil as hypothesized, but by an increased amount of noncrystalline and poorly crystalline oxides of Fe and Al. Further subsidence, resulting in increased mineral matter content, may increase the P retention capacity. It is not known, however, how easily P desorption from these organic soils may occur with frequent wetting and drying cycles and occasional flooding of these soils. Wide evaluation of the P sorption capacity and desorption potential of the organic soils in the EAA may be warranted. The use of oxalate-extractable Fe and Al as an indicator for P sorption in these organic soils would be less labor intensive than the use of P sorption isotherms.

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