

Wetlands and Aquatic Processes

Phosphorus Retention by Wetland Soils used for Treated Wastewater Disposal

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ABSTRACT

Wetlands function as buffers for nutrients loaded from terrestrial ecosystems through drainage and surface discharges. The objectives of our study were to (i) determine the P retention capacity of representative wetland soils being used for disposal of treated wastewater and (ii) relate P retention characteristics to selected physicochemical properties to evaluate likely mechanisms of P removal in the soils. Intact soil cores (0–40 cm) and bulk soil samples (0–15 cm) were collected from a system of natural and constructed wetlands currently being used for disposal of treated wastewater. Floodwater P concentrations of the intact soil cores were monitored over time to determine the rate of P removal. Batch experiments were conducted to determine maximum P retention capacity of the soils. Soil samples were analyzed for inorganic P pool sizes, and selected physicochemical properties. During a 21 d hydraulic retention time, the constructed wetlands (sandy, low organic matter soils) retained 52 to 66% of added P, as compared with 46 to 47% retained by the natural wetlands (high organic matter soils). The P retention maximum, as estimated using the Langmuir model, ranged from 196 to 1821 mg P kg⁻¹ (aerobic incubations) and from 32 to 1415 mg P kg⁻¹ (anaerobic incubations). The P sorption maximum for these soils could be predicted by batch equilibration with a single high P solution. Anaerobic conditions increased P solubility. Organic P pools and the Fe–Al-bound fraction seemed to control P chemistry in these natural and constructed wetlands.

WETLANDS frequently are used to remove N and P from treated wastewater prior to release into receiving ground and surface waters (Kadlec, 1987). Elevated N and P concentrations in wastewater have been associated with pollution of surface waters and N, as NO₃, is associated with pollution of groundwaters. Nitrification and denitrification effectively reduce floodwater N loads in

treated wastewater applied to wetland systems (Gale et al., 1993a, b). Several studies (Boyt et al., 1977; Fetter et al., 1978; Schwartz, 1989) suggest that freshwater wetlands, swamps, marshes, and flooded soil systems can also reduce P levels of nutrient laden waters. Richardson (1985) cautioned, however, that wetland soils can function as either source or sink for P to the overlying floodwater moving through the wetland.

Physical, chemical, and biological processes functioning in overlying water and underlying sediments regulate P dynamics in wetlands. A significant portion of floodwater and porewater P can be removed through uptake by macrophytes and algae (Kloptek, 1975; Toth, 1972; Syers et al., 1973). Kadlec (1989) states, however, that litter and sediments are the key components of a wetland system in the regulation of nutrient cycling.

Patrick and Khalid (1974) found that under anaerobic conditions, soils released P to solutions low in soluble P and sorbed P from solutions containing high concentrations of soluble P. Reactions of P that occur in flooded soils include reduction of FeP, dissolution of occluded P, hydrolysis of Fe- and Al-bound P in acid soils, increased mineralization of organic P in acid soils, greater P diffusion, and increased solubility of Ca-P in calcareous soils (Sanchez, 1976).

The amount of soluble P released into overlying waters of wetlands depends on the capacity of the soil to desorb or adsorb P from solution, mineralization of organic P, and diffusion of P from sediment to overlying waters (Nichols, 1983). These processes help determine whether the P concentration in the interstitial and overlying water is adequate for the nutritional requirements of plants and aquatic organisms, and whether these systems can be used

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Abbreviations: BOD, biochemical oxygen demand; SRP, soluble reactive phosphorus; IR, infrared; AAS, atomic adsorption spectrophotometry; ANOVA, analysis of variance; HRT, hydraulic retention time; EPC, equilibrium phosphorus concentration.

to remove P from the overlying waters. Inorganic P exchange rates depend on the capacity of the sediment to adsorb and desorb P (Reddy, 1983a). Mineralization of organic P depends upon the amount of P containing organic matter and the rate of phosphatase enzyme production (Golterman, 1984). Soil factors affecting P retention include: amount and type of clay, amount of Fe and Al oxides and Ca compounds, and pH (Froelich, 1988; Golterman, 1984; Khalid et al., 1977; Richardson, 1985).

The city of Orlando, FL, currently uses a series of constructed and natural wetlands for the disposal of treated wastewater. The constructed wetlands consist of sandy, low organic matter soils, whereas the natural wetlands consist of high organic matter soils. The treated wastewater alternately flows through constructed and natural wetlands at the site. Our objectives were to determine the rate of soil-mediated P removal and to estimate the potential capacity for P removal by soils indigenous to both the constructed and natural wetlands. These data were compared to soil physicochemical properties to determine the mechanisms most likely responsible for P removal in these soils.

MATERIALS AND METHODS

Site Description

The wastewater treatment facility, located in Orlando, FL, uses a five-stage Bardenpho process that provides advanced biological treatment. This process is followed by sand filtration, chlorination, post-aeration, and a supplemental alum feed. This treatment provides enhanced removal of N, P, and BOD (Table 1). Three options are available for reuse of the treated wastewater. These are infiltration basins for groundwater recharge, industrial reuse as cooling water, and an overland flow-wetland augmentation system. The overland flow-wetland augmentation system currently receives $\approx 8.5 \text{ mL d}^{-1}$, one-third of the treated wastewater.

Treated wastewater is discharged into the first constructed wetland (CW1) and flows overland into the first natural wetland (NW2, Fig. 1). After exiting NW2 the treated wastewater is distributed into the second constructed wetland (CW3) by means of a collection channel and redistribution structure. Flow from this wetland (CW3) is overland into the second natural wetland (NW4), from which it leaves the site. A berm surrounds the entire experimental wetland system, hydrologically isolating it from the surrounding landscape. A natural wetland (NWO) receives water inputs only through rainfall and runoff, and serves as a control for the experimental system. The constructed wetlands have mineral soils classified as Smyrna fine sands (sandy, siliceous, hyperthermic Aeric Haplaquods). In contrast, the natural wetlands are high organic matter soils mapped as Sanibel mucks (sandy, siliceous, hyperthermic Histic Humaquepts).

Table 1. Average composition of treated wastewater entering wetland system (1992).

Parameter†	Concentration
	mg L ⁻¹
BOD ₅	<1
TSS	1.4
TN	1.2
TP	0.1
pH	7.4

† BOD, biochemical oxygen demand; TSS, total suspended solids; TN, total nitrogen; and TP, total phosphorus.

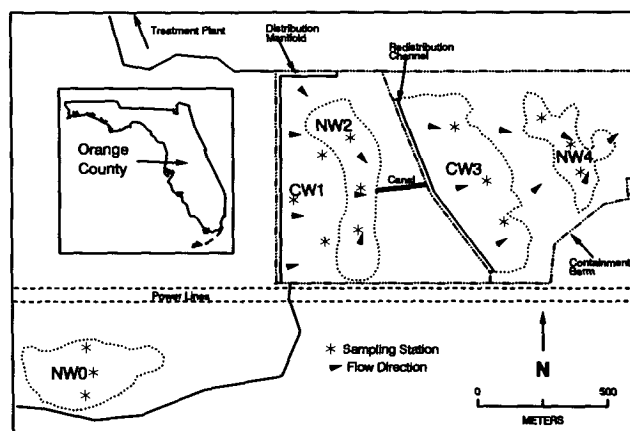


Fig. 1. Map of the Orange County Florida experimental exemption wetland site.

Sample Collection

Surface soil samples (0 to 15 cm) were collected from three locations in each wetland for characterization and use in P sorption studies. Soil samples were kept at 5 °C, in a moist condition, until their use in these experiments. For kinetic studies, three soil cores were collected from the central portion of each wetland. A 60 cm length of 10 cm diameter polyvinyl chloride pipe was driven to a depth of ≈ 40 cm, and then removed intact with a shovel. The bottom end of each core was sealed with a cap and silicone sealant to ensure a water tight seal. The intact cores were transported to an air-conditioned greenhouse for the incubation experiments.

Soil Characterization

Subsamples of the soils were characterized for various soil physical and chemical characteristics, including bulk density and percent moisture. Soil pH was measured in a 1:1 (soil/water) mixture. Water soluble forms of ammonium, NO_3 plus NO_2 , and soluble reactive phosphorus (SRP) were quantified on an autoanalyzer using methods 351.2 (USEPA, 1979), 418-F and 424-G (APHA, 1989), for $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$, and SRP analyses, respectively. Total N and P were determined using a block digestion technique and automated analysis of the digestate. The colorimetric methods 351.2 and 365.4 (USEPA, 1979) were used to quantify N and P, respectively, in these digestates. Soluble organic C was measured with a persulfate oxidation and IR analysis of the CO_2 produced on a TOC apparatus (OI, College Station, TX).

Air-dry soil samples were analyzed for metal cations, known to influence P solubility. Exchangeable Fe and Al were measured in oxalate extracts (Khalid et al., 1977) using atomic adsorption spectrophotometry (AAS). Likewise AAS was used to quantify Ca concentrations in double acid (Mehlich I) soil extracts (Olson and Sommers, 1982).

The forms of P in these soils were determined using chemical fractionation. The P fractionation scheme is a modification of one proposed by van Eck (1982) and has been successfully used to characterize P in upland soils, lake sediments, and wetland soils (Scinto and Reddy, 1990; Reddy and Ivanoff, 1990). The fractionation procedure separates P into: exchangeable P (1 M KCl), Fe- and Al-bound P (0.1 M NaOH), hydrolyzable organic P (digested 0.1 M NaOH extract), Ca-bound P (0.5 M HCl), and organic P (digested residue). All analyses were done in triplicate using a randomized complete-block design. Statistical com-

parisons were made using the ANOVA procedures of PC-SAS (SAS Institute, 1987).

Kinetic Studies

Two experiments were conducted under controlled greenhouse conditions to assess the ability of wetland soils to remove P from treated wastewater. This was accomplished by flooding soil columns collected from each wetland with treated wastewater of a known composition and monitoring the changes in the SRP concentration of the floodwater. The first experiment utilized a batch feed system where treated wastewater of known composition was added to each soil core at the same rate. The second experiment involved the use of a sequential feed system where the treated wastewater was initially added to cores collected from the CWI site. Wastewater remained for a predetermined 5 d HRT (hydraulic retention time), and was then transferred to the next wetland soil in the sequence (NW2). This process was continued through the same sequence of soils present at the experimental wetland site.

Periodically dissolved O₂, pH, and electrical conductivity of the column floodwater were measured. A 10 mL water sample was removed, filtered through 0.45- μ m membrane filters, and analyzed for SRP (soluble reactive P) using previously described techniques. The incubation experiments were conducted and analyzed using a split-plot design where main effects were due to wetland type and subplots included time. A complete description of the incubation experiments can be found in Gale et al. (1993a).

Adsorption Isotherms

Batch incubation experiments were conducted to measure the capacity of wetland soils to remove added P from solution. Either 2 g of field moist mineral soil or 5 g of field moist organic soil was placed into 50 mL centrifuge tubes. To these soils 20 mL of an amending solution was added containing a known amount of P. The concentration of P, as KH₂PO₄, was either 0, 0.01, 0.1, 1, 10, 50, or 100 mg L⁻¹ in a 0.01 M KCl matrix. The tubes were then sealed, placed on a mechanical shaker, and shaken in the dark for 24 h. Samples were then removed, allowed to settle for 1 h, and filtered through 0.45- μ m membrane filters. Filtrates were acidified with one drop of concentrated sulfuric acid and stored at 5 °C until analysis.

In another experiment, soil samples were placed into centrifuge tubes as described above. To each sample, 10 mL of deionized water was added and the samples were sealed, evacuated, and purged with N₂ gas containing 5% CO₂ (v/v). Samples were then placed in the dark at 25 °C, for 8 wk to encourage development of anaerobic conditions. At the end of 8 wk, 10 mL of a P spiking solution was injected into the centrifuge tubes through a septum that had been inserted into a hole drilled in the cap. The spiking solutions contained either 0, 0.02, 0.2, 2, 20, 100, or 200 mg P L⁻¹ in a 0.02 M KCl matrix. This resulted in final P concentrations the same as those used in aerobic isotherms. After addition of the spike, samples were evacuated and purged with the N₂-CO₂ mixture used initially. Samples were then treated in an analogous manner to those in aerobic incubations, except that filtration was done under anoxic conditions.

All of the isotherms were conducted in duplicate. Filtrates from these experiments were analyzed for SRP using an automated ascorbic acid technique (APHA, 1989). The difference between P detected in filtrates and that of a control (spiking solution only) was assumed removed by the soil.

The amount of phosphate retained or released by the soils was calculated as described by Reddy (1990):

$$(C_o \times V - C_t \times V) / M = S^i \quad [1]$$

where

C_o = concentration of P added, mg L⁻¹

V = volume of liquid, L

C_t = concentration of P in solution after 24-hour equilibration period, mg L⁻¹

M = mass of dry soil, kg

S^i = P sorbed by solid phase, mg kg⁻¹

Equation [1] does not reflect the amount of native P initially present in the adsorbed phase; however, this amount can be estimated using a least squares fit of S^i data measured at low equilibrium concentrations, C . At low concentrations, the relationship between S^i and C was linear and was described by the following equation:

$$S^i = (K' \times C) - S_o \quad [2]$$

where

S_o = y-axis intercept, representing the initial soil or sediment P present in the adsorbed phase, mg kg⁻¹

C = phosphorus in solution, mg L⁻¹

K' = linear adsorption coefficient (estimated without considering native adsorbed P, S_o), L kg⁻¹

The sum of ($S^i + S_o$) represents the actual amount of P adsorbed at the respective equilibrium P concentration. After correcting the accumulated data for the native adsorbed P, the following adsorption models were used to describe P sorption in the wetland soils.

The Langmuir model was initially used to describe adsorption of gases onto surfaces (Langmuir, 1918). It has since been found to be useful in describing adsorption of ions in solution onto soil particles (Sposito, 1989). For this study the following equation was used.

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

where

S = total amount of P in adsorbed phase ($S^i + S_o$), mg kg⁻¹

S_{max} = P sorption maximum, mg kg⁻¹

k = constant related to the bonding energy, L mg P⁻¹

C = solution P concentration measured after 24 h equilibration period, mg L⁻¹

The sorption maximum (S_{max}) is a measure of the capacity of the system to remove P, while the binding energy (k) is considered a measure of its binding intensity.

If it is assumed that all of the binding sites for adsorption are the same a special case of the Langmuir equation, the Freundlich model, is obtained:

$$S = K_f \times C^N \quad [4]$$

where

S = total amount of P in adsorbed phase ($S^i + S_o$), mg kg⁻¹

K_f = Freundlich adsorption constant, L kg⁻¹

N = empirical constant ($N < 1$)

C = solution P concentration measured after 24 h equilibration period, mg L⁻¹

Equation [4] assumes an exponential decrease of the bonding energy with coverage of sorption sites. The linear forms of Eq. [3] and [4] were used to determine Langmuir and Freundlich coefficients for the P adsorption data. The GLM functions of PC-SAS (SAS Institute, 1987) were used to determine the values of the coefficients for the adsorption data. A means comparison test was used to evaluate differences between wetland soils.

Table 2. Selected physicochemical characteristics of the wetland soils (upper 15 cm) found at the experimental site.

Wetland	Water content	Bulk density	Total C	Total N	Total P	pH	Soluble organic C	Oxalate extract		Mehlich I Ca
								Al	Fe	
	%	kg m ⁻³	g kg ⁻¹		mg kg ⁻¹		mg kg ⁻¹			
CW1†	18.5	1400	27	0.9	49	5.8	54	98	59	52
CW3	24.5	1400	21	0.7	32	6.1	75	58	44	20
NW2	89.6	100	445	19.9	536	6.2	126	2970	333	2170
NW4	85.9	100	437	16.4	670	5.1	147	5460	792	923
NWO	88.8	100	484	21.0	837	4.6	152	3720	1330	1780

† CW, constructed wetland and NW, natural wetland: numbers 1 to 4 are impacted by treated wastewater.

RESULTS

The constructed wetland soils (CW1 and CW3) are mineral soils with low nutrient and water contents and high bulk densities (Table 2). In contrast, the natural wetland soils (NW2, NW4, and NWO) are organic soils with higher concentrations of nutrients (expressed on a weight basis) and lower bulk densities. Mineral and organic soils had similar soil pHs. The soil pH of the natural wetland closest to the treated wastewater inflow (NW2, pH = 6.2) was more similar to that of the constructed wetlands (CW1, pH = 5.8 and CW3, pH = 6.1) than those of the other natural wetlands (NW4, pH = 5.1 and NWO, pH = 4.6). The treated wastewater has a pH of 7.4 (Table 1) and is loaded into the wetland system at a rate of 13.2 mL d⁻¹. This high loading into the wetland system is probably increasing the pH of the natural wetlands.

The constructed wetland soils had total P concentrations 10 to 20 times less than those of the natural wetland soils, when compared on a weight basis (data not shown). However, when expressed on an areal basis the difference between constructed and natural wetlands was greatly reduced (Fig. 2). The wetland receiving the initial influx of wastewater, CW1, has greater concentrations of P in exchangeable and organic fractions than the other mineral soil (CW3). This is most likely due to the influx of wastewater resulting in increased vegetative biomass. In contrast, soil collected from the natural wetlands (NW2 and NW4) receiving the flow of treated wastewater had less P in the organic pools than the soil collected from the natural wetland not impacted by the treated wastewater (NWO). This suggests that organic P pools within these wetlands are being mineralized.

Kinetic Study

Soil column incubations were conducted to measure the rate of P removal from overlying floodwater (treated wastewater). During incubations, floodwater dissolved O₂ concentrations fluctuated between 3 and 6 mg O₂ L⁻¹, thus ensuring that the floodwater remained oxidized throughout the study. The pH of overlying floodwater was influenced by the type of underlying soil column. The mineral soils (CW1 and CW3) maintained floodwater pH values slightly above 7; however, in the organic soils (NW2, NW4, and NWO) the pH of the accompanying floodwater ranged from 5 to 6.5, with the unimpacted wetland soil (NWO) supporting floodwaters with the lowest pH (4.8). The electrical conductivity associated with the floodwaters of the

various soils also depended upon soil type. The organic soils maintained waters of lower conductivity (0.27 ± 0.03 dS m⁻¹), and the conductivity fluctuated less, than those associated with mineral soils (0.44 ± 0.07 dS m⁻¹).

When the soil columns were flooded with treated wastewater of a known P concentration, the floodwater P concentration decreased until an equilibrium was established (Fig. 3). The equilibrium P concentration (EPC) has been defined by Taylor and Kunishi (1971) as the concentration of P where no net change in adsorption and desorption occurs. The EPC was reached within 7 d in the CW1, NW2, and CW3 columns that received P loadings of 0.11 g P m⁻² or more. These three wetland soils attained similar EPC values of 0.38, 0.30, and 0.34 mg P L⁻¹ for the CW1, NW2, and CW3 samples, respectively, that were not significantly different. In contrast, the soil columns collected from the NW4 wetland were slower to reach equilibrium (14 d) and had higher EPC values (0.64 mg P L⁻¹).

When treated wastewater was sequentially loaded into the columns to mimic the flow pattern found at the experimental site, similar results were obtained (Fig. 4). Floodwater P concentration was reduced with time throughout the CW1, NW2, and CW3 soil columns. However, when floodwater was transferred to the NW4 soil column, P was released to the overlying floodwater. This is not too surprising as the SRP concentration of the floodwater added

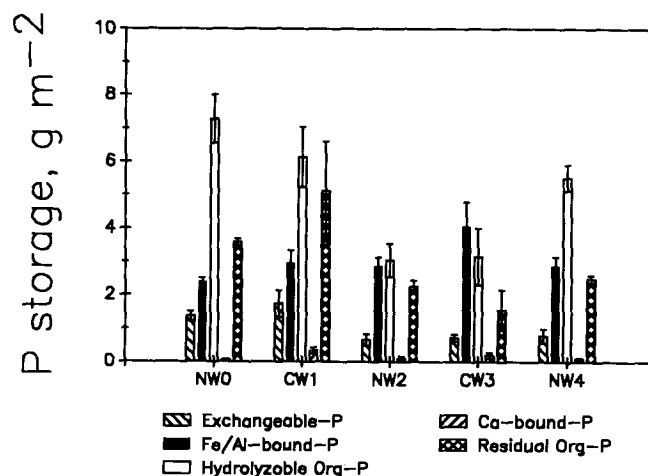


Fig. 2. Selected P pools determined by chemical fractionation for the constructed and natural wetland soils being used for the disposal of treated wastewater.

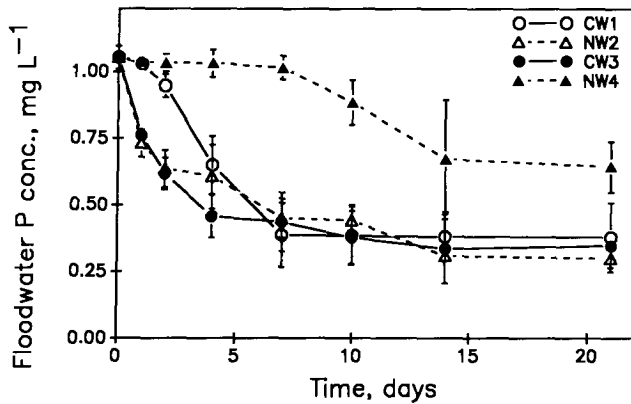


Fig. 3. Changes in floodwater P concentrations when soil columns were flooded with a single application of P spiked treated wastewater.

to this wetland is well below the EPC value as measured in the batch feed incubations.

Adsorption Isotherms

The calculated P sorption parameters were less for constructed wetland soils than natural wetland soils (Table 3). This is reflective of lower soil concentrations of P, C, Fe, Al, and Ca (Table 2). In general, the constructed wetland soils had similar sorption parameters, whereas greater variability was observed among natural wetland soils. When determined under anaerobic conditions, sorption parameter values decreased significantly. This is indicative of the important role of oxidation-reduction reactions in these soils.

DISCUSSION

First-order rate constants for P removal were calculated for each of the wetland soils (Table 4). The highest rate constant and percentage of removal was observed for the NW2 wetland soil. Lowest values were obtained in the NW4 soil columns. Sompongse (1982) found P removal rate constants, for Florida soils receiving agricultural drainage waters, to range from 0.05 to 0.08 d⁻¹. For the soils in the

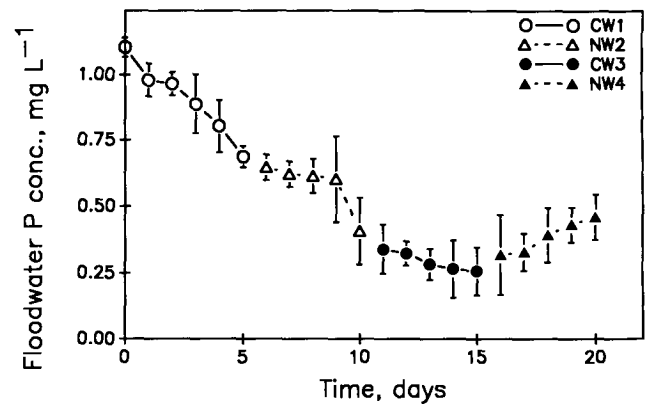


Fig. 4. Changes in floodwater P concentrations when the spiked wastewater was added to the CW1 soil cores initially, held for 5 d, and then transferred to the NW2 soil cores. This process was repeated throughout the core to mimic the flow of treated wastewater at the field site.

present study, all of the rate constants fell within this range, with the exception of the NW4 soil. The rate constant for P removal in the NW4 soil was 0.035 d⁻¹, not far out of this range. The rate constants can be used to calculate half-lives (time required for a 50% reduction in floodwater P). For these wetland soils, half-life values of 11, 10, 10, and 20 d were calculated for the CW1, NW2, CW3, and NW4 wetland soils, respectively. Under current operating conditions, 10 d is the approximate HRT of the floodwater in the natural wetlands (NW2 and NW4). The constructed wetlands (CW1 and CW3) have HRTs in the range of 2 to 5 d, depending upon treated wastewater loading. Thus, P removal may be kinetically limited in these wetland soils.

These experiments represent soil P removal only. Removal in the field is expected to be greater as plant uptake would also occur. Plant efficiency for removing N and P is greatest at low level additions (Reddy et al., 1987). Because the soils studied are inefficient P removers at low level additions, this fact alone would result in better removal rates in the field. Of the P fractions shown in Fig. 2 only the KCl-P would be immediately available for plant growth,

Table 3. Phosphate sorption parameters determined under aerobic and anaerobic conditions.

Wetland	Linear model			Langmuir model			Freundlich model			pH
	Sorption coefficient K'	Initial P sorbed S_0	r^2	Sorption maximum S_{max}	Sorption energy k	r^2	Sorption constant K_f	Bonding energy N	r^2	
	L kg ⁻¹	mg kg ⁻¹		mg kg ⁻¹	L kg ⁻¹		L kg ⁻¹			
Aerobic										
CW1†	3.0	6.49	0.94	281	0.014	0.90	2.9	0.96	0.97	6.47
CW3	2.9	1.14	0.99	196	0.014	0.94	2.5	0.90	0.99	6.10
NW2	91.9	21.64	0.99	1429	0.058	0.98	65.0	0.75	0.99	6.23
NW4	143.1	17.55	0.99	1821	0.144	0.95	90.2	0.77	0.99	5.12
NW0	58.2	26.55	0.97	1757	0.031	0.95	48.8	0.82	0.99	4.56
Anaerobic										
CW1	1.8	13.38	0.91	32	0.641	0.98	6.1	0.62	0.98	5.83
CW3	1.3	3.81	0.88	113	0.402	0.96	4.0	0.91	0.98	5.28
NW2	11.0	26.38	0.95	1415	0.070	0.97	23.5	0.83	0.93	5.44
NW4	23.6	37.65	0.94	1044	0.128	0.91	100.4	0.69	0.97	4.24
NW0	9.3	9.26	0.93	620	0.136	0.91	10.9	0.97	0.93	4.15
LSD(0.05)	8.2	16.19		514	0.037		36.9	0.10		0.67

† CW, constructed wetland and NW, natural wetland; numbers 1 to 4 are impacted by treated wastewater.

Table 4. First-order rate constants for P removal and % floodwater P retained by soil during column incubation studies (21 d HRT).

Wetland	Rate constant d ⁻¹	r ²	Percent retained %
CW1†	0.062	0.77	52
CW3	0.069	0.85	66
NW2	0.072	0.84	77
NW4	0.035	0.70	46

† CW, constructed wetland; NW, natural wetland; numbers 1 to 4 are impacted by treated wastewater.

Table 5. Correlation coefficient for P sorption parameters and associated physicochemical properties of the wetland soils (n = 15).

	Sorption maximum (S _{max})	Sorption energy k	Sorption coefficient K'	Sorption constant K _f
Aerobic incubations				
pH	NS	NS	NS	NS
P in 0.01 M KCl	NS	NS	NS	NS
Oxalate Fe	0.767**	NS	NS	NS
Oxalate Al	0.851**	0.541*	0.743**	0.820**
Oxalate Fe + Al	0.872**	NS	0.645*	0.738**
Mehlich Ca	0.845**	NS	NS	NS
TOC†	0.836**	NS	NS	NS
WSOC†	0.877**	NS	NS	NS
Anaerobic incubations				
pH	NS	NS	NS	NS
P in 0.01 M KCl	NS	NS	NS	NS
Oxalate Fe	NS	NS	NS	NS
Oxalate Al	0.665**	NS	0.808**	NS
Oxalate Fe + Al	0.628*	NS	0.745**	NS
Mehlich Ca	0.745**	NS	NS	NS
TOC	0.709**	0.559*	NS	NS
WSOC	0.536*	NS	NS	NS

*, ** Significant at the 0.05 and 0.01 probability level; NS, not significant at the 0.05 level.

† TOC, total organic carbon; WSOC, water soluble organic carbon.

however, mineralization of a portion of the organic P pool, which would convert unavailable organic P into available KCl-P, is highly likely in both organic and mineral soils (Reddy, 1983b).

The natural wetland soils (NW2 and NW4) receiving wastewater inputs had lower concentrations of total P than the unimpacted natural wetland (NW0, Table 2). This is also reflected in reduced exchangeable and organic forms of P (Fig. 2). This could be attributed to plant uptake and the flushing effect of the highly dilute treated water. In addition, the Fe- and Al-bound P fraction increased at these stations, a likely result of conversion of insoluble ferric P compounds to more soluble ferrous compounds (under anaerobic conditions), which may become bound with P. Hydrolyzable and residual organic P pools were smaller in the natural wetlands receiving treated wastewater. Lower levels in these P fractions could have resulted from mineralization of P from these pools and subsequent plant uptake. Changes in soil P fractions in constructed wetland soils (CW1 and CW3) resulted primarily from effects of frequent flooding and dilution, rather than from increased P loading (which was minimal, Table 1). Natural wetlands (NW2, NW4, and NW0) had experienced seasonal flooding previous to treated water application; therefore, changes in the distribution of P fractions during the first 4 yr prob-

ably were not the result of increasingly reducing conditions, but of increasing pH and dilution.

The physicochemical data from the soils was compared with the P sorption parameters to determine if any significant relationships existed (Table 5). The sorption maximum (S_{max}) was significantly correlated (P = 0.01) with metal and C concentrations under both aerobic and anaerobic conditions. These results are not surprising as several researchers (Froelich, 1988; Golterman, 1984; Khalid et al., 1977; Richardson, 1985) have shown P retention to be a function of the amount of Fe and Al oxides, Ca compounds, and C in wetland soils. However, correlations of the Langmuir sorption energy (k) with these parameters depended upon the oxidation-reduction status of the samples. Similarly, the K_f value correlations with metals and C was redox dependent. In contrast, the linear adsorption coefficient (K') was significantly correlated with Al and Fe plus Al concentrations under either oxidized or reduced conditions. The dependence of sorption parameters on the oxidation-reduction status of the soils was previously observed by Olila and Reddy (1993) in sediments collected from Florida lakes.

Also strongly correlated with metal and C concentrations was the amount of P sorbed at high addition rates (1000 mg P kg⁻¹). This relationship was observed for both the aerobic and anaerobic isotherms. Correlations were similar to those observed for sorption maximum, so a relationship between the sorption maximum value and the P sorbed at 1000 mg P kg⁻¹ was indicated. The slope of this relationship was 1.26 and had a coefficient of determination of 0.888. This significant relationship suggests that sorption maximum can be predicted using a single high concentration as an equilibrating solution.

Correlation relationships were also evaluated for sorption maxima (S_{max}) and energy (k) and several P pools separated by chemical fractionation (Table 6). Aerobic P adsorption energy (k) was correlated with the various P fractions, except the hydrolyzable organic P pool; however, this parameter (k) was not significantly related to any of the P fractions (except hydrolyzable organic P) when the batch incubations were conducted under anaerobic conditions. In contrast, the S_{max} values were correlated to the P fractionation data only under anaerobic conditions. When aerobic isotherms were used to calculate sorption energy (k), linear sorption coefficient (K'), and Freundlich con-

Table 6. Correlation coefficients for P sorption parameters and associated P fractions of the wetland soils (n = 15).

	Sorption maximum (S _{max})	Sorption energy k	Sorption coefficient K'	Sorption constant K _f
Aerobic incubations				
Exchangeable P	NS	-0.581*	NS	NS
Fe-Al-bound P	NS	0.556*	0.835**	0.919**
Hydrolyzable organic-P	NS	NS	NS	0.560*
Ca-bound P	NS	0.692**	0.907**	0.917**
Anaerobic incubations				
Exchangeable P	-0.755**	NS	NS	NS
Fe-Al-bound P	0.777**	NS	0.699**	NS
Hydrolyzable organic-P	-0.984**	0.898**	NS	NS
Ca-bound P	0.651*	NS	0.766**	NS

*, ** Significant at the 0.05 and 0.01 probability level; NS, not significant at the 0.05 level.

stant (K_f), all of these parameters were significantly correlated with the various chemical fractions of P. Under anaerobic conditions, this relationship failed, with the exception of (K'), which remained significantly correlated with the metal fractions.

Several mechanisms for P sorption by these soils are likely. Sompongse (1982) found that Al-organic matter- PO_4 complexes dominated P chemistry in selected Florida soils. Iron may also play a significant role in P sorption under anoxic conditions (Khalid et al., 1977). They found that reduction of $\text{Fe}(\text{OH})_3$ to $\text{Fe}(\text{OH})_2$ increases P sorption sites. Organic components of the soil can play significant roles in P sorption. Krom and Berner (1980) showed organic matter coatings on sediment particles are responsible for P adsorption. Organic acids (intermediate products of anaerobic decomposition processes) promoted the formation and stability of Al- PO_4 complexes (Huang and Violante, 1986). The P fractionation data (Fig. 2) indicate the majority of P is associated with Fe- and Al-bound and hydrolyzable organic P pools. Thus, it is highly likely that reactions discussed above account for the majority of P reactions occurring within this system.

When alum (AlSO_4) is used to precipitate P in wastewater treatment systems, it is added at a molar ratio that insures 70 to 90% P removal. Thomson and Vignona (1984) suggested that the P/Al ratios should be in the range of 0.4 to 0.7. Similar ratios were recommended for Fe. In Table 7, the potential moles of P adsorbed were compared with extractable concentrations of Al, Fe, and Ca. For these wetland soils, the P/[Al + Fe] ratios were low enough in the organic soils (NW2, NW4, and NW0) to encourage adsorption-precipitation. In contrast, the P/[Al + Fe] ratios determined for the mineral soils (CW1 and CW3) were well above the 0.7 upper limit suggested by Thomson and Vignona (1984). The molar ratios of P/Ca in these soils were greater and had greater variability than those for Fe and Al. This is not surprising in that Ca-bound P was shown to be a minor constituent of the total P pool for both mineral (CW1 and CW3) and organic (NW1, NW2 and NW0) soils.

The differences between organic and mineral soils when compared on a weight basis, become less significant than when compared on a volume basis. When the value of the linear adsorption coefficient (K') was converted to a volume basis, the differences between organic and mineral soils decreased by an order of magnitude (Table 8). The values for S_{max} (expressed on a volume basis) were unaffected by soil type (mineral vs. organic); however, the volume basis S_{max} value suggests that the first constructed

Table 7. Relationship between P sorption maximum and oxalate extractable Al and Fe and Mehlich I extractable Ca.

Wetland	moles P/ moles [Al + Fe]	moles P/ moles Ca
CW1†	1.93	7.03
CW3	2.15	12.66
NW2	0.40	0.85
NW4	0.27	2.55
NW0	0.35	1.28

† CW, constructed wetland; NW, natural wetland; numbers 1 to 4 are impacted by treated wastewater.

Table 8. Phosphate adsorption parameters for the constructed and natural wetland soils expressed on a weight and volume basis.

Wetland	Linear (K')		Langmuir (S_{max})	
	Weight basis	Volume basis	Weight basis	Volume basis
	L kg ⁻¹	L L ⁻¹ (s)	mg kg ⁻¹	mg L ⁻¹ (s)
CW1†	3.0	4.3	281	409
CW3	2.9	3.4	196	234
NW2	91.9	7.0	1429	109
NW4	143.1	16.9	1821	215
NW0	58.2	7.3	1757	221

† CW, constructed wetland; NW, natural wetland; numbers 1 to 4 are impacted by treated wastewater.

wetland (CW1) may have enhanced P adsorption due to continual wastewater additions.

CONCLUSIONS

The wetlands described are functioning favorably when compared with other treatment wetland systems. Kadlec and Newman (1992) evaluated P loading data from treatment wetlands located throughout North America. They found the following significant relationship ($R^2 = 0.73$) between P mass loading output and input data.

$$\text{PLO} = 0.37 \times \text{PLI}^{1.08} \quad [5]$$

where

$$\begin{aligned} \text{PLO} &= \text{P load output, g m}^{-2} \text{ yr}^{-1} \\ \text{PLI} &= \text{P load input, g m}^{-2} \text{ yr}^{-1} \end{aligned}$$

Using P data available for the CW1 and NW2 wetlands (Camp, Dresser, and McKee, 1992) the Kadlec and Newman model predicts 64% removal, while measured retention during this time was slightly higher (66%).

The P retention capacity of the wetland soils was determined by converting the value of S_{max} (easily measured with a single batch equilibration at a high P concentration) to an areal basis. Assuming that P retention was limited to the upper 5 cm of the soil, the capacity of the CW1 wetland for P retention was 205 kg P ha⁻¹. The average annual loading of P into the wetlands was 8 kg ha⁻¹ (Camp, Dresser, and McKee, 1992). At this annual input rate the CW1 wetland soil could continue to remove P from treated wastewater for 25 yr. Limitations to P retention within these wetlands will include the degree of anaerobic conditions that develop in the soil profile and the amount of time the treated wastewater is in contact with the soil.

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