**Drainage ditches have sufficient adsorption capacity but inadequate residence time for
phosphorus retention in the Everglades**

Steven D. Collins^a

Phone: 1-717-332-3734

Email: stevendouglascollins@gmail.com

Sanjay Shukla^a, corresponding author

Phone: 1-239-658-3425

Email: sshukla@ufl.edu

Niroj K Shrestha^a

Phone: 1-239-658-3458

Email: nirojshrestha@ufl.edu

^aDepartment of Agricultural and Biological Engineering
Southwest Florida Research and Education Center, University of Florida
2685 State Road 29 North, Immokalee, Florida 34142, USA

22 **Abstract**

23 Although considered a sink of nutrients, limited information exists to verify
24 phosphorus (P) and nitrogen (N) retention in drainage networks such as ditches and canals.
25 Nutrient retention within two ditches on a cattle ranch in the greater Everglades region was
26 measured using in-situ mesocosms. Phosphorus and N concentrations of water inside the
27 mesocosms were increased or decreased to evaluate the effect of P and N concentration on
28 P and N flux across the sediment-water interface. Ditch sediments possess high P retention
29 capacity which was related to aluminum and iron contents. Soluble reactive P (SRP)
30 retention over seven days varied between 13 and 55% of the starting water column
31 concentration, though retention was significant after one day ($p = 0.035$). Significant P
32 release, although observed only at one site, does indicate the potential for the ditch to be a
33 source of P to downstream locations. The P uptake and release were greater and more rapid
34 in a ditch with organic sediment and emergent macrophytes compared to a ditch with a
35 mineral substrate. P retention over time was rate-limited by diffusion and sediment pore-
36 water exchange. Nitrogen transformation processes were unsubstantial, possibly because in
37 warm sub-tropical Florida most nitrate is denitrified in the presence of an energy source.
38 Several empirical P models predicted ($r^2 > 0.90$) P retention based on the known water
39 column SRP concentrations and hydraulic residence time. The residence time of the site
40 (0.46 and 0.11 days for the two ditches) is not long enough to significantly reduce P loads
41 passing through the ditches under the current drainage regime. Delaying the drainage by
42 increased water retention as a voluntary Best Management Practices (BMPs) or the
43 Payment for Environmental Services (PES) program can help increase the residence time

to reduce P leaving the ranch. Although these results are derived from a cattle ranch, similar benefits can be expected for drainage ditches in other agricultural systems such as agronomic (e.g. sugarcane) or horticultural (e.g. citrus, vegetable) crops, and the models presented in this paper may be useful for basin-scale water quality management.

Keywords

BMP, Nitrogen, Mesocosm, Desorption, Organic sediment, Surface water

1. Introduction

Construction of an extensive drainage system for agricultural development in the Lake Okeechobee (LO) watershed beginning in 1950 has resulted in large unnatural flows and nutrient loads to the lake, the largest freshwater lake in the southeastern US (Steinman et al., 2002; Kelly and Gore, 2008). Excessive flows and accompanying nutrient loads have resulted in accelerated eutrophication (Engstrom et al., 2006). Inorganic P is the limiting nutrient in the LO (Steinman and Rosen, 2000) and excessive P loading to the lake from the LO watershed is one of the major problems the lake is facing (Tweel and Bohlen, 2008; Pollman and James, 2011). In 2001 the Florida Department of Environmental Protection adopted a Total Maximum Daily Load (TMDL) limiting the incoming P load to 140 T/year (US EPA, 2008). Cow-calf ranches encompass 38.7% of the area of the basin with more than 65% of area under improved and semi-improved pasture, and fertilizer for improved pasture contributes nearly 60% of the annual net P imports (Boggess et al., 1995; Shrestha and Alavalapati, 2004). Several Best Management Practices (BMPs) including cattle, field, and feed manipulation have been used to reduce P loading from the basin. One promising

BMP is to store water on ranchlands by raising the spillage (drain) levels in culverts fitted with riser boards, though this has not been field-verified with regard to P load reduction in the Everglades. Storing water on site has the potential to reduce P loads due to reduction in flow volumes (Bohlen and Villapando, 2011; Goswami and Shukla, 2014) and/or adsorption of P to ditch sediment. The latter effect has not yet been field-verified.

Almost all agricultural lands in south Florida including cow-calf ranches have a long network of drainage ditches. These ditches can provide considerable storage for pasture runoff (Bohlen et al., 2009). Although storing water in wetlands and uplands including ditches may reduce net N and P discharge from the cow-calf operations (Goswami and Shukla, 2014), sufficient data are not yet available to determine the extent of N and P reductions for this practice. Various wetland components play a role in the retention of P. While uptake by plants, periphyton, and microbes can provide an initial rapid removal of P, sediments represent a major long-term P sink in wetlands and especially drainage ditches (Sakadevan and Bavor, 1998; Simon, 2003). Ditches often have wetland vegetation and soils. The effect of drainage ditches, however, to retain or release P is not well understood. Drainage ditches may function as a sink, source, or regulator of the dissolved P concentrations (Smith et al., 2005), and their role can only be determined through understanding of the nutrient dynamics between the ditch sediment and water. Quantifying the retention/release potential of these ubiquitous systems is important for future land and water management including in the LO watershed for meeting the TMDL.

The P retention in the ditch depends on the P retention potential of its sediment. A common practice of determining the P retention potential of sediment is to mix sediment

87 samples with nutrient solutions and measure the P concentration change in the solution
88 (Lai and Lam, 2008). However, the degree of contact between sediment particles and
89 solution in such studies is likely to be much greater than under field conditions. Other
90 researchers have brought intact sediment cores to the laboratory, changing floodwater P
91 concentrations while keeping other variables constant (Nguyen and Sukias, 2002; Tanner
92 et al., 2005), but these experiments usually underestimate actual retention occurring under
93 field conditions (Reddy et al., 1995). Laboratory measurement techniques can neither
94 mimic the field hydrologic and redox fluctuations nor the effects of bioturbation caused by
95 benthic macrofauna (Fisher and Reddy, 2001). Additionally, removing sediment cores
96 from the channels for laboratory studies may disturb the sediments and alter the P retention
97 capacity because of the modified zone of contact between surface water and the sediment.

98 Stream-scale experiments involving coupled nutrient and conservative tracer
99 additions (Triska et al., 1989; Stream Solute Workshop, 1990; Schulz et al., 2003;
100 O'Connor et al., 2010) have the advantage of quantifying the whole aquatic systems,
101 incorporating sediment sorption, advection, diffusion, groundwater influences, and biotic
102 effects. However, stream-scale experiments are unreplicable (Hurlbert, 1984; Zedler, 2003)
103 and cannot simultaneously characterize the water and nutrient dynamics over a range of
104 nutrient concentrations (Triska et al., 1989; Alvarez-Cobelas et al., 2010). Most
105 importantly, nutrient retention estimates will be unreliable if exchange timescales are too
106 long (Wagner and Harvey, 1997) as is the case for south Florida drainage ditches where
107 flow is ephemeral.

To better understand N and P retention capacities, analyses should be conducted in-situ. Measuring nutrient fluxes in the field has several advantages over the laboratory intact sediment column approach. Variables such as water, air, and sediment temperature, photoperiod, dissolved oxygen, pH, dissolved chemical constituents in the water column, benthic organisms, and plant and microbial communities will be representative of the actual field conditions in the in-situ approach. Additionally, by conducting the analysis in-situ, the system will undergo less disturbances than if the sediment were transported to the laboratory (Tolhurst et al., 2000). The current study extends the sediment-core approach by leaving the sediment in place under natural conditions and is conducted over a larger area. Experimental error caused by the differences in advective transport for the mesocosm studies are likely to be small, because flow in the LO drainage ditches is extremely slow (Heatwole et al., 1987; Van den Berg et al., 2005) because of flat topography. Studies that have used mesocosms in south Florida have been limited to developing the relationship between water chemistry and periphyton compositions (McCormick and O'Dell, 1996) and determining the extent of P removal from the effluent of the treatment wetland (DeBusk et al., 2004). Kroger et al. (2008) reported a nearly 44% reduction in the maximum inorganic P load from ditches in a field study in the Mississippi watershed, but the flows in their study were not measured. They estimated the flow from Manning's equation, introducing high uncertainty in the estimates and raising question about the reliability of the results.

Modeling tools to estimate nutrient retention/release are needed for programs that encourage water storage through voluntary BMP programs or through a Payment for Environmental Services (PES) program. Different models have been used for simulating P

adsorption/desorption from an overlying water column to sediment (Whalen and Cheng, 2002; McGechan and Lewis, 2002; Barlow et al., 2004; Zhou et al., 2005; Zhuan-xi et al., 2009; Liu et al., 2013). These models can be used for predicting net P flux and kinetic P flux. While net P flux models estimate total adsorption, kinetic P flux models can predict adsorption with time. Watershed models such as WAM (Bottcher et al., 2012) and MIKE-SHE (Staes et al., 2009) have been used for evaluating flows from wetland under different water management/wetland restoration alternatives, however, they are limited in their ability to predict phosphorus adsorption/desorption, especially in the wetland ditches. Although MIKE SHE, a hydrological model, coupled with ECOLab, an ecological modeling tool that can simulate chemical transport, uses linear and Freundlich models for P modeling (DHI, 2007), these models may underperform as they are not field verified.

A pilot water storage PES program was started in 2007 in the Northern Everglades basin to reduce the excessive flows to Lake Okeechobee and associated estuaries and the Everglades. The program known as the Florida Ranchlands Environmental Services Project (FRESP) was a market-like program in which willing ranch owners can enter fixed-length contracts with the state to provide water and nutrient load reduction services exceeding the regulatory requirements in south Florida (Bohlen et al. 2009). The program was adopted by the state in 2010 as the Northern Everglades PES (NE-PES). The PES program focuses on water and nutrient retention by raising the spillage level at the ranch outlet to reduce surface flows and downstream damaging flows and to increase water storage and the time the ranch drainage spends in the ditches. Increased nutrient retention

because of increased residence time in ditches is one of the assumed benefits but this has not yet been verified.

Depending on the historic nutrient use in uplands and the sink or source function of drainage ditches, increased residence time can increase or decrease the nutrient loads. The objectives of this study were to 1) quantify short-term nutrient (P and N) fluxes resulting from changes in the solute concentration of the overlying water and evaluate the potential of drainage ditches as a P source or sink in a commercial cattle ranch, and 2) develop and evaluate empirical or semi-empirical models to simulate P adsorption/desorption between overlying water and ditch sediments.

2. Materials and Methods

2.1 Study Area

This study was conducted approximately 13 km northwest of the LO (27.28°N, 80.95°W), Florida at a low-density beef cattle (< animal unit per ha) ranch dominated by improved pasture laced with shallow ditches for drainage. The commercial ranch was considered in this study as it is one of the major P contributors in the Everglades. The region has a subtropical climate with a mean annual rainfall of 1385 mm (NOAA, 2010).

To evaluate the potential of drainage ditches as P sources or sink, we considered two different ditches that are common in the Everglades basin: a ditch with organic sediment (Site 1) and a ditch with mineral sediment (Site 2) (Figs. 1, 2). The P-rich runoff from the ranch first drains to ditches before exiting the ranch, so it is important to quantify

short-term nutrient fluxes to identify whether ditches are potential P sources or sinks. One ditch (Site 1) is dominated by *Pontederia cordata* (Pickerelweed) and drains a small wetland (25 ha), and the second ditch (Site 2) is dominated by *Eichhornia crassipes* (hyacinth) and *Lemna minor* (duckweed) and drains a large portion of the ranch (252 ha). Soils in these two basins consist primarily of Immokalee fine sand and Basinger fine sand. The sediment samples taken from the site are slightly acidic, so calcium or magnesium bound P will not be available. Phosphorus inputs to the ranch originate from pasture fertilization, cattle excrement, and animal supplements. The two ditches differ with regard to the drainage area fertilizer application history, forage types, sediments and ditch characteristics including water depth, channel size, and physical and chemical properties of the sediment. The P fertilizer rate (per unit area) applied in the drainage basin of Site 1 in 2003 and 2004 was more than double than that of Site 2. The sediment at Site 2 is mostly mineral, and the bulk density is much higher than Site 1 that has mostly organic sediment.

184

185

186 Figure 1. Photos of drainage ditches where nutrient additions and dilutions were performed
187 (left is Site 1, right is Site 2)

188

Figure 2. Ranch map showing study site drainage basins and upstream drainage.

Greater hydraulic residence time increases runoff contact with sediment which is likely to reduce N and P loads through increased P adsorption and denitrification. Considerably more retention is expected with greater hydraulic residence time. The median hydraulic residence time at each site was determined using velocity data measured using an Acoustic Doppler Velocimeter at each site from a series of approximately 70 monitored storm events from 2008 to 2014 (Shukla et al., 2014). The median storm velocity at Site 1 (3.34 cm/s) translates to a median hydraulic residence time of 0.46 ± 0.62 days to the ranch boundary, and the median storm velocity at Site 2 (5.98 cm/s) translates to a median hydraulic residence time of 0.11 ± 0.19 days to the ranch boundary.

2.2 Mesocosm Installation

Mesocosms consisted of 30, 208-liter steel open drums with a cross-sectional area of each being 0.27 m^2 . The drums were coated with non-reactive epoxy paint. Each mesocosm was pushed straight downward into 0.15 m of sediment without disturbing it using a backhoe. Visual inspection indicated that sediment was not suspended in this process. The mesocosms were positioned randomly such that they were at least 0.66 m from each other. The average minimum and furthest distances between mesocosms were 2.0 m and 37.7 m, respectively. Before treatments were applied, the water column P concentrations were not statistically different between the control and treatment mesocosms.

2.3 Treatments

The nutrient concentration of the water inside the field-situated benthic mesocosms was altered to evaluate the P flux across the sediment-water interface. The concentration of P in drainage water can vary from moderately high to very high, and to simulate it, we used two treatments for P flux analysis: a high P spike and a low P spike. The high P spike treatment was used to represent a high P concentration of overlying water column in a drainage ditch while the low P spike treatment was used to represent moderately high P concentration in drainage water. To simulate P flux in a drainage ditch with a low P concentration of overlying water column, a typical condition after successive rainfall events in the late wet season (June–October) when the P runoff within the ranch has already been washed away from earlier rainfall events, we conducted dilution treatments. For varying low P concentration of overlying water, we used two dilution treatments: low

and high dilution. In total, four treatments, representing two nutrient additions and two nutrient dilutions were tested in triplicate across two drainage ditches (Table 1 and 2). Treatments were assigned to random locations in the ditches. Two treatments were implemented by applying a fertilizer (KH_2PO_4) solution inside the mesocosm such that two increased P concentrations were represented (Table 1). Ammonium fertilizer (NH_4Cl) was also added to those mesocosms such that the N:P ratio in the water-column was maintained. The other two treatments involved diluting the water inside the mesocosm with different quantities of deionized water ($\text{SRP} = 0.0 \text{ mg L}^{-1}$) such that two reduced P concentrations were represented, approximately 50% (low dilution) and 75% (high dilution) (Table 2). A bromide (Br) tracer was added to all mesocosms to quantify potential gain or loss of water from or to the mesocosms. After spiking and dilution, four treatments were monitored over seven days (10/22/2004–10/29/2004) and compared with an experimental control (mesocosms installed, but no nutrient treatment) to determine if P uptake or release occurred. A one-week period was chosen because: (1) the typical hydraulic residence time of the ditches is shorter than one week (Shukla et al., 2011); (2) model results have shown that molecular diffusion alone can achieve 90% equilibration with porewater dissolved P in three days (Webster et al., 1998); and (3) it was believed that the majority of P adsorption, desorption, and biological assimilation would occur in less than a week. The average daily temperature during the study period was 23°C (min= 17°C and max= 29°C) with no rainfall and total reference ET (modified Penman method) of 18.1 mm.

Table 1. Summary of P spike treatments at two drainage ditches to assess P sorption.

Site	Treatment	Number of replicates	Soluble reactive P (SRP) mass before treatment (mg)	SRP mass added (mg)	SRP mass measured after treatment (mg)
Site 1	High P spike	3	44	255	300
	Low P spike	3	56	145	200
Site 2	High P spike	3	23	255	280
	Low P spike	3	21	130	155

Table 2. Summary of dilution treatments at two drainage ditches to assess P release.

Site	Treatment	Number of replicates	Dilution attempted (%)	Dilution achieved (%)
Site 1	High dilution	3	75	85
	Low dilution	3	50	63
Site 2	High dilution	3	75	74
	Low dilution	3	50	50

2.4 Sampling

Five water-column samples were taken from each mesocosm and two from each ditch over the course of seven days ($t = 0, 1, 2, 4$, and 7) (total samples = 170). Samples were collected manually using 40 mL syringes. Samples were analyzed for soluble reactive P (SRP), total P (TP), total Kjeldahl N (TKN), nitrate/nitrite (NO_x), ammonium (NH_4), and Br. Bromide was used as a conservative tracer to quantify potential dilution from water outside the mesocosms. Water quality samples to be analyzed for SRP, NO_x , and NH_4 were passed through 0.45 μm filter papers and acidified in the field by adding one drop of concentrated H_2SO_4 for every 20 mL of sample water. Samples for TP and TKN were acidified but not filtered. All samples were analyzed at the University of Florida Analytical Research Laboratory (ARL) for SRP, TP, TKN, NO_x , NH_4 , and Br. Soil cores were taken from inside each mesocosm to determine the bulk density, water content, soil pH, organic matter, water-extractable P, TP, and oxalate-extractable P, Al, and Fe contents.

2.5 Nutrient Concentration Adjustments

Several techniques were used to adjust the raw nutrient concentration data from the water samples. The nutrient data were adjusted to compensate for evapotranspiration (ET) (calculated using on-site weather station data) and dilution from outside the mesocosm (quantified with Br content which was used as a conservative tracer). Evapotranspiration increases the concentration of all dissolved solutes in the mesocosms to the same degree. Because the amount of ET was known, the extent to which the measured nutrient and Br concentrations would increase could be determined accurately. Dilution from water outside the mesocosm would cause Br concentrations to decrease, because no Br was present in water outside of the mesocosms. The measured nutrient concentrations were adjusted to remove the effect of ET and dilution. Because the effects of these processes were known, compensating the raw data was logical and provided precise results.

2.6 Phosphorus Modeling

Phosphorus dynamics were modeled by (1) comparing net uptake/release over the course of the 7-day experiment to initial SRP concentrations, and (2) examining the SRP trends over time for each treatment individually. The former models quantify the net uptake and release, but the latter kinetic P models can estimate the uptake/release as a function of time and initial condition in an aquatic system before an equilibrium is reached. Kinetic P modeling is useful when the hydraulic residence time of wetlands, streams, and other waterways limits the amount of contact time between sediment and the water column. The net P flux data were used to calibrate the Freundlich and a linear model (Barrow 1978; Mead 1981; Reddy et al. 1995). Because soil-solution systems vary widely,

a single kinetic model may not be universally valid (Pavlatou and Polyzopoulos, 1988), so the kinetic P flux data were used to calibrate the Parabolic Diffusion and Boundary Layer models (Pavlatou and Polyzopoulos, 1988; Barlow et al., 2004).

3. Results and Discussion

3.1 Phosphorus Retention

Considerable P retention was observed in mesocosms from both sites after the mesocosm was spiked with a KH_2PO_4 solution (Fig. 3). Because the influences of ET, dilution, and water loss were considered and accounted for, adsorption, diffusion, and biotic uptake were the remaining potential processes causing the reduction of P in the water column. The last data point at seven days (Fig. 3a) appears to be reaching an asymptote, indicating that SRP concentrations in the mesocosm are close to achieving a new equilibrium, and further P retention after seven days will be much slower. The decline in water column SRP load in both the low and high spike treatments were rapid during the first four days followed by a gradual decline (Fig. 3a,b).

Figure 3. Average cumulative phosphorus sorption measurements and predictions using kinetic models for the high (a) and low P spike (b) treatment at Site 1 and the high (c) and low P spike (d) treatment at Site 2. Error bars represent $\pm$ one standard deviation. The median measured hydraulic residence time from the site to the ranch boundary (for 70 storm events from 2008–2014) is shown as a vertical gray line.

Sorption at Site 2 was less dramatic than that observed at Site 1. The adsorption at Site 2 was significant only after seven days (Fig. 3c, d). The difference in P retention between two sites is largely due to differences in sediment characteristics. The water content of the mostly organic peat sediment at Site 1 is over twice that of the mostly mineral sediment at Site 2. An index of aluminum and iron not associated with P ($\text{free}[\text{Al}_{\text{ox}} + \text{Fe}_{\text{ox}}]$) (Patrick and Khalid, 1974) indicates that Site 1 sediments possess over three times more capacity to retain P than Site 2 sediments which resulted in higher P retention in Site 1. Additionally, more than twice as much P fertilizer per unit area was applied to the drainage basin at Site 1 in 2003 and 2004 compared to the drainage basin at Site 2. P retention capacity was greater at Site 1 compared to Site 2 despite increased P loading, which shows that sediment characteristics are an important control on P retention.

Though the P retention of high and low P spikes and control differ at Site 1 (Fig. 3a,b) and Site 2 (Fig. 3c,d) as expected, with greater retention in the high spike treatments,

the relative trends, normalized by initial measured load, are nearly identical (not shown). Therefore, it may be possible to infer the uptake rates for other potential starting loads as long as they are within the range of SRP concentrations studied at Site 1 (0.5, 3.0, 4.9 mg L⁻¹) and Site 2 (0.2, 1.6, 2.9 mg L⁻¹). P concentration data from the ranch in the LO basin are observed to be within this SRP concentration range.

Over the relatively short hydraulic residence times for storm events measured (2008–2014) at these sites (Site 1: 0.46±0.62 days, Site 2: 0.11±0.19 days), some P sorption may be expected at Site 1 (Fig. 3), but little is expected at Site 2. Phosphorous retention is significant (p=0.035) after one day, a residence time greater than measured at the ranch, but both sites have the potential for much greater P retention if hydraulic residence time is increased (Fig. 3).

3.2 Phosphorus Release

The P release to the water column from sediment at Site 1 was rapid and occurred immediately after dilution and then slowed after two days for both dilution treatments (Fig. 4a). The P release measured in this study was mostly due to sediment porewater diffusion and desorption from the sediment. Though the magnitude of P release was greater for the high dilution treatment than for the low dilution treatment, the water column SRP load returned to a similar value (110 mg m⁻², data not presented) under both dilution treatments at Site 1, which indicates that a single equilibrium will be reestablished in the mesocosms after dilution regardless of the extent of the dilution. Results from the two dilution treatments also show that the magnitude of P release is proportional to the starting load at Site 1 (Fig. 4a; the high dilution treatment had a lower initial P load than the low dilution

treatment). Phosphorus release at Site 2 (Fig. 4b) was less dramatic compared to Site 1. Some P flux was measured, but it was not significantly different from initial treatment conditions (Fig. 4b). For the current residence time of Site 1, P may be released after large storms with excessive dilution or small successive events late in the wet season (September–October) when most water soluble P has been flushed out of the watershed. For example, the average daily P flow weighted concentration after Hurricane Wilma (October 24, 2005) at Site 1 was 1.12 mg L^{-1} , 37 % lower than the annual average of that year (2005) (Shukla, et al., 2014), increasing the potential for P release. Therefore, sites like Site 1 that have P rich sediment can become a P source after a large rainfall event.

Figure 4. Average cumulative phosphorus release observed for the high and low dilution treatments at Site 1 (a) and Site 2 (b). Error bars represent $\pm$ one standard deviation. Predicted phosphorus release at Site 1 was fitted to data from days 0 through 4 using the Boundary Layer model, but the model could not fit the data at Site 2. The median measured hydraulic residence time from the site to the ranch boundary (for 70 storm events from 2008–2014) is shown as a vertical gray line.

3.3 Modeled Net P Flux

The difference between the first and the last (7th day) SRP load was used as the net P flux for each treatment. The SRP reduction or release rate (mg m^{-2}) was proportional to the SRP concentration in the water column (Fig. 5). At Site 1, the net P uptake and release (P flux, mg m^{-2}) was related to the initial SRP concentration (mg L^{-1}) in the water column and is given by the linear relation:

$$\text{P flux} = 134.0(\text{P solution concentration}) - 61.45 \quad (r^2 = 0.98) \quad (1)$$

At Site 2, the linear relation is:

$$\text{P flux} = 47.7(\text{P solution concentration}) + 11.62 \quad (r^2 = 0.96) \quad (2)$$

Figure 5. Measured net P flux versus initial SRP concentration at Site 1 (a) and Site 2 (b). P uptake is positive, and release is negative. Error bars represent $\pm$ one standard deviation. Fitted models are shown as lines.

The fitted linear model, also used by Reddy et al. (1995), indicates that the P release potential of the sediment under ambient conditions is 61.5 mg m^{-2} at Site 1. There is some uncertainty in the ambient release potential, because the fitted Freundlich model with an extra term (ETF, $r^2 = 0.99$) (Barrow, 1978) indicates that 111 mg m^{-2} of surface-sorbed SRP is present under ambient conditions at Site 1. The P release potential at Site 2 is low by comparison, 19 mg m^{-2} , which may be because of high organic content and high P fertilizer loadings at Site 1 compared to Site 2 (Table A.1, Figure 5).

The X-intercept of 0.458 mg L^{-1} for the linear model (Table A.1) represents the EPC_w , the water column SRP concentration at which P flux does not occur at Site 1. An SRP concentration of 0.458 mg L^{-1} is approximately equivalent to a TP concentration of 0.597 mg L^{-1} in the ditch water column. At Site 1 an EPC_w of 0.458 mg L^{-1} (or 0.416 mg L^{-1} predicted from the ETF model) is less than the average annual SRP concentration (Shukla et al, 2014), but the water column concentration has dropped below 0.458 mg L^{-1} after some summer storms (unpublished data). Therefore, ditches with high organic

sediments like Site 1 are a P sink for most of the year, but they may be a P source after large storms.

The predicted EPC_w at Site 2 is -0.243 from the linear model and 0.041 mg L^{-1} from the ETF model, indicating that P sorption occurs at either all or most water column SRP concentrations. Because P concentration of ditch water in Site 2 is always higher than 0.041 mg L^{-1} , P release after a seven-day water retention is unlikely.

The ETF model or the linear model are good choices for simulating the P sorption for both sites based on goodness of fit and interpretability. The observations were also used to fit other models commonly used in P adsorption studies, and parameters from these fits are included in the Appendix (Table A.1).

3.4 Kinetic Modeling of P Retention

Kinetic models, which consider P flux over time as opposed to total P flux, were fitted to the data to test their applicability to drainage ditches. The Boundary Layer and Parabolic Diffusion models successfully fitted the measured kinetic P sorption for both high and low P spikes at Site 1 (Table A.2, Fig. 3a, $r^2 = 0.94$ to 1.00), and model fits of other kinetic P sorption models are included in the Appendix. Good performance of the parabolic diffusion model indicates that the sorption is a diffusion-controlled process (Toor and Bahl, 1999). The Boundary Layer model can predict short-term sorption potential, and we observed that only the Boundary Layer model can predict the maximum sorption (Table A.2) making it more useful than the Parabolic Diffusion model. The maximum sorption predicted from the Boundary Layer model for the high P spike treatment is 660 mg m^{-2} (Table A.2), though maximum sorption is not expected to occur for 20 days.

Hence, for the high P spike treatment, 47%, 72%, and 90% of the predicted maximum sorption occurred after two, four, and seven days, respectively at Site 1. For the median residence time of 0.46 days for Site 1, P sorption of only 14% (94 mg m^{-2}) was predicted from the Boundary Layer Model.

At a measured load of 457 mg m^{-2} (low P spike treatment), the Boundary Layer model predicts that the system reaches equilibrium in over 30 days, though 77% of the predicted maximum sorption occurs in seven days (Fig. 3b). After 0.46 days, the median measured hydraulic residence time for storms, only 9 to 14% of the maximum predicted sorption has occurred, depending on water column P concentration (Initial P spike treatment TP concentrations ranged from 3.21 to 5.60 mg L^{-1} , which correspond to high water column concentrations measured in the water columns (unpublished data)). If hydraulic residence time is increased to 1 day, almost 100% more P retention is expected, and considerably more P retention is expected with greater hydraulic residence times.

Modeling P retention kinetics for the high P spike treatment (Table A.3) for Site 2 was difficult compared to Site 1 because of the apparent occurrence of both sorption and release during the 7-day period. Fig. 3c shows that a small quantity of P was released before P uptake was observed, however kinetic P models do not account for P release. Although the observed P flux after seven days was net P sorption, the kinetic models did not fit data well (Fig. 3c).

In contrast to the high P spike treatment, the data for the low P spike treatment for Site 2 (Fig. 3d) did not exhibit early P release. The kinetic models had poorer fits ($r^2 = 0.74$ to 0.89) compared to Site 1, because P retention rate was slow at Site 2. The diffusion or

adsorption models work best in conditions where P flux response is rapid after a change in the floodwater nutrient load. Similar to the high P spike treatment, the shape of the Boundary Layer model response was nearly linear. For the low P spike treatment at Site 2, the Boundary Layer model indicates that increasing the hydraulic residence time to one day could result in an 800% increase in P retention. Though reasonable kinetic P model fits were only achieved in three (high and low P spike at Site 1 and low P spike at Site 2) of four treatments, considerable P retention is expected if hydraulic residence time can be increased regardless of ditch type.

3.5 Kinetic Modeling of Desorption

The data from the four dilution treatments were too scattered to successfully apply kinetic models. If the last data point (day 7) was omitted, the Boundary Layer model represented P release from the high dilution treatment at Site 1 ($r^2 = 1.00$), but it did not reasonably represent the data for the low dilution treatment at Site 1 (Fig. 4a, Table A.4). For Site 2, the Boundary Layer model failed to fit the data (Fig. 4b). This is because, as can be seen in Fig. 4, measured desorption was not significant for any elapsed time.

3.6 Nitrogen

The data do not illustrate specific N transformation processes in this study (Fig. 6a,b). The measured nitrate and nitrite concentrations of all water samples taken during the experiment were negligible. The lack of soluble nitrate indicates that nitrification is severely hampered, or that biotic uptake, volatilization, and denitrification processes are much more significant. If the sediment-water interface were anoxic, nitrification would be

severely reduced (Kemp et al., 1990), and optimal conditions would exist for denitrification. In warm south Florida most nitrate is denitrified in the presence of an energy source (White and Reddy, 1999). In a cattle fencing BMP study at the same ranch, Shukla et al. (2011) observed denitrification to be the main avenue of N loss from the drainage ditches. The TKN concentrations are nearly unchanged with time (data not shown), and dilution treatments at both sites showed no effect on TKN concentration.

Figure 6. High and low nutrient addition and experimental control ammonium loads over the course of the experiment at Site 1 (a) and Site 2 (b). Error bars represent $\pm$ one standard deviation.

Variability between replicates also clouds the effect of dilution on NH₄-N in ditches. However, Fig. 6a shows that elevated ammonium loads drop dramatically in two days at Site 1. The same was not observed at Site 2 where the elevated ammonium loads

462 did not change considerably over time (Fig. 6b). The rapid ammonium decline at Site 1
463 may be attributable to biotic uptake either from emergent macrophytes, duckweed, algae,
464 or bacteria, or ammonium adsorption due to cation exchange with highly decomposed
465 organic matter present at Site 1.

466 **4. Conclusions**

467 The capacity of ditches to retain or release P and N differed significantly with the
468 sediment characteristics. The P uptake was greater and release was more rapid at the
469 drainage ditch with organic sediment (Site 1) compared to the drainage ditch with mostly
470 mineral sediment (Site 2). The nutrient addition treatments showed significant P adsorption
471 after one day at Site 1 while the adsorption was significant only after seven days for Site 2.
472 Promoting the development of wetland sediment by planting wetland vegetation in ditches
473 can enhance P adsorption. Plant establishment may be done after canal and field ditch
474 cleaning which has been recommended as a P-reduction BMP (Diaz et al. 2006). Dilution
475 treatments for Site 1 suggest that P release or uptake is affected by the residence time.
476 Significant desorption was measured at Site 1 after the high dilution treatment which
477 indicates that if the sediment has high P content and the runoff P concentration is very low,
478 there will be a net release of P. Such condition is possible after successive rainfall events
479 or a large tropical storm, a typical condition of late summer (August–October). Nutrient
480 addition treatments for Site 2 indicate that P release is possible if the residence time in the
481 ditches is less than four days. However, net P uptake is expected once the residence time is
482 extended beyond four days. To eliminate the risk of P discharge in such a case, water in the
483 ditch needs to be retained for at least four days before discharging downstream. Each P

flux model showed proportional increase in net P flux with initial SRP concentrations with significant retention when initial SRP exceeds 1 mg L^{-1} for both sites. Fitted kinetic P flux models indicate considerable P retention if the hydraulic residence time exceeds one day.

The median hydraulic residence time for both sites is shorter than one day (0.46 and 0.11 days for Site 1 and Site 2, respectively), so only a BMP that holds the water in the ditch for a longer time can make these sites serve as P sinks. Currently, water retention on ranchlands is encouraged through water retention BMP and the NE-PES water storage program in the Northern Everglades to reduce downstream flows. To achieve increased water storage on ranchlands, the spillage levels are raised using culverts fitted with riser boards (Goswami and Shukla, 2014), which is expected to increase the hydraulic residence time. Results show that depending on the actual increase in residence time, additional P retention may be achieved within the ranch and downstream regional canals that discharge to the Lake Okeechobee. Similar benefits may be expected for other agricultural systems (e.g. dairy, citrus, and sugarcane) within the greater Everglades and beyond with similar environmental conditions. The models developed in this paper can be applied to design and evaluate BMPs and payment for water storage and treatment programs which require simpler models for wider acceptability.

Acknowledgements

This research was made possible by funding from the Florida Department of Agriculture and Consumer Services, the South Florida Water Management District, and the Florida Department of Environmental Protection. Many thanks to Christy Sackfield and Vibhuti Pandey for providing field work assistance, Yu Wang, Gavin Wilson, Ed Dunne, Atanu

Mukherjee, Chris Martinez, and Jaehyun Cho for assistance with sediment and water analysis, and Roger McGill, Bob Tonkinson, Dale Hardin, Ann Summeralls, Mark Clark, Ralph Hoffman, Billy Duckworth, and Gary Barfield for providing insight and help constructing and installing mesocosms.

References

- Agbenin, J.O. and H. Tiessen, 1995. Phosphorus sorption at field-capacity and soil ionic-strength: Kinetics and transformation. *Soil. Sci. Soc. Am. J.* 59: 998-1005.
- Alvarez-Cobelas, M., R. Sanchez-Andres, S. Sanchez-Carrillo and D.G. Angeler, 2010. Nutrient contnet and export from stream in semiarid catchments of central Spain. *J. Arid Environ.* 74(8): 933-945.
- Barlow, K., D. Nash and R. Grayson, 2004. Investigating phosphorus interactions with bed sediments in a fluvial environment using a recirculating flume and intact soil cores. *Water Res.* 38: 3420-3430.
- Barrow, N., 1978. The description of phosphate adsorption curves. *J. Soil Sci.* 29: 447-462.
- Boggess, C.F., E.G. Flaig and R.C. Fluck, 1995. Phosphorus budget-basin relations for Lake Okeechobee tributary basins. *Ecol. Eng.* 5: 143-162.
- Bohlen, P.J. and O.R. Villapando, 2011. Controlling runoff from subtropical pastures has differential effects on nitrogen and phosphorus loads. *J. Environ. Qual.* 40(3): 989-998.
- Bohlen, P.J., S. Lynch, L. Shabman, M. Clark, S. Shukla and H. Swain, 2009. Paying for environmental services from agricultural lands: an example from the northern Everglades. *Front. Ecol. Environ.* 7: 46-55.
- Bottcher, A. B., B. J. Whiteley, A. I. James, and J. H. Hiscock. 2012. Watershed assessment model (WAM): Model use, calibration, and validation. *Trans. ASABE* 55(4): 1367-1383.
- Chien, S. and W. Clayton, 1980. Application of Elovich equation to the kinetics of phosphate release and sorption in soils. *Soil. Sci. Soc. Am. J.* 44: 265-268.
- Crank, J., 1964. *The Mathematics of Diffusion*. Oxford University Press, London.

534 DeBusk, T.A., K.A. Grace, F.E. Dierberg, S.D. Jackson, M.J. Chimney and B. Gu, 2004.
535 An investigation of the limits of phosphorus removal in wetlands: a mesocosm
536 study of as shallow periphyton-dominated treatment system. *Ecol. Eng.* 23(1): 1-
537 14.

538 DHI, 2007. MIKE SHE user manual, volume 2: Reference Guide.

539 Diaz, O.A., Lang, T.A., Daroub, S.H. and Chen, M, 2006. Best management practices in
540 the Everglades Agricultural Area: controlling particulate phosphorus and canal
541 sediments. EDIS Publication# SL228. University of Florida, IFAS Extension,
542 Florida, USA.

543 Engstrom, D.R., S.P. Schottler, P.R. Leavitt and K.E. Heavens, 2006. A reevaluation of the
544 cultural eutrophication of Lake Okeechobee using multiproxy sediment records.
545 *Ecol. App.* 16(3): 1194-1206.

546 Fisher, M.M. and K.R. Reddy, 2001. Phosphorus flux from wetland soils affected by long-
547 term nutrient loading. *J. Environ. Qual.* 30: 261-271.

548 Goswami, D. and S. Shukla, 2014. Effects of passive hydration on surface water and
549 groundwater storages in drained ranchland wetlands in the Everglades Basin in
550 Florida. *J. Irrig. Drain. Eng.* 141(1), 04014046.

551 Heatwole, C.D., K.L. Campbell and A.B. Bottcher, 1987. Modified CREAMS hydrology
552 model for coastal-plain flatwoods. *T. ASAE.* 30: 1014-1022.

553 House, W.A. and F.H. Denison, 2002. Exchange of inorganic phosphate between river
554 waters and bed-sediments. *Environ. Sci. Technol.* 36: 4295-4301.

555 House, W.A., F.H. Denison and P.D. Armitage, 1995. Comparison of the uptake of
556 inorganic phosphorus to a suspended and stream bed sediment. *Water Res.* 29: 767-
557 779.

558 Hurlbert, S.H., 1984. Pseudoreplication and the design of ecological field experiments.
559 *Ecol. Monogr.* 54: 187-211.

560 Kelly, M.H. and J.A. Gore, 2008. Florida river flow patterns and the Atlantic multidecadal
561 oscillation. *River Res. App.* 24: 598-616.

562 Kemp, W.M., P. Sampou, J. Caffrey, M. Mayer, K. Henriksen, and W.R. Boynton, 1990.
563 Ammonium recycling versus denitrification in Chesapeake Bay Sediment. *Limnol.*
564 *Oceanogr.* 35(7): 1445-1563.

565 Kroger, R., M.M. Holland, M.T. Moore, and C.M. Cooper, 2008. Agricultural drainage
566 ditches mitigate phosphorus loads as a function of hydraulic variability. *J. Environ.*
567 *Qual.* 37:107-113.

568 Lai, D.Y.F., and K.C. Lam, 2008. Phosphorus retention and release by sediments in the
569 eutrophic Mai Po Marshes, Hong Kong. *Mar. Pollut. Bull.* 57: 349-356.

570 Liu, F., Xiao, R., Wang, Y., Li, Y., Zhang, S., Luo, Q., Wu, J. 2013. Effect of a novel
571 constructed drainage ditch on the phosphorus sorption capacity of ditch soils in an
572 agricultural headwater catchment in subtropical central China. *Ecol. Eng.* 58: 69-
573 76.

574 Lookman, R., D. Freese, R. Merckx, K. Vlassak and W.H. Vanriemsdijk, 1995. Long-term
575 kinetics of phosphate release from soil. *Environ. Sci. Technol.* 29: 1569-1575.

576 McCormick, P.V. and M.B. O'Dell, 1996. Quantifying periphyton responses to phosphorus
577 in the Florida Everglades: a synoptic-experimental approach. *J. N. Am. Benthol.*
578 *Soc.* 15(4): 450-468.

579 McGechan, M.B. and D.R. Lewis, 2000. Watercourse pollution due to surface runoff
580 following slurry spreading, part 2: Decision support to minimize pollution. *J. Agr.*
581 *Eng. Res.* 75: 429-447.

582 Mead, J.A., 1981. A comparison of the Langmuir, Freundlich and Temkin equations to
583 describe phosphate adsorption properties of soils. *Aust. J. Soil. Res.* 19: 333-342.

584 Nguyen, L. and J. Sukias, 2002. Phosphorus fractions and retention in drainage ditch
585 sediments receiving surface runoff and subsurface drainage from agricultural
586 catchments in the North Island, New Zealand. *Agr. Ecosyst. Environ.* 92: 49-69.

587 NOAA, 2010. National Centers for Environmental Information, National Oceanic and
588 Atmospheric Administration. Available at [https://www.ncdc.noaa.gov/climate-](https://www.ncdc.noaa.gov/climate-monitoring/)
589 [monitoring/](https://www.ncdc.noaa.gov/climate-monitoring/). Accessed in 28 May 2014.

590 O'Connor, B.L., M. Hondzo and J.W. Harvey, 2010. Predictive modeling of transient
591 storage and nutrient uptake: Implication for stream restoration. *J. Hydraulic Eng.*
592 136(12): 1018-1032.

593 Pavlatou, A. and N.A. Polyzopoulos, 1988. The role of diffusion in the kinetics of
594 phosphate desorption - The relevance of the Elovich equation. *J. Soil Sci.* 39: 425-
595 436.

596 Pollman, C.D. and R.T. James, 2011. A simple model of internal loading of phosphorus in
597 Lake Okeechobee. *Lake Reservoir Manage.* 27: 15-27.

598 Reddy, K.R., O.A. Diaz, L.J. Scinto and M. Agami, 1995. Phosphorus dynamics in
599 selected wetlands and streams of the Lake Okeechobee Basin. *Ecol. Eng.* 5: 183-
600 207.

601 Sakadevan, K. and H.J. Bavor, 1998. Phosphate adsorption characteristics of soils, slags
602 and zeolite to be used as substrates in constructed wetland system. *Water Res.* 32:
603 393-399.

604 Schulz, M., H. Kozerski, T. Pluntke and K. Rinke, 2003. The influence of macrophytes on
605 sedimentation and nutrient retention in the lower River Spree (Germany). *Water*
606 *Res.* 37, 569-578.

607 Shrestha, R.K. and Alavalapati J.R.R, 2004. Valuing environmental benefits of
608 silvopasture practice: A case study of the Lake Okeechobee watershed in Florida.
609 *Ecol. Econ.* 49: 349-359.

610 Shukla, S., G. Hendricks, and N.K. Shrestha. 2014. Effectiveness of Ranchland Water
611 Retention BMP with Regards to Nutrient Discharges in the Northern Everglades.
612 Technical Report LO-FDACS-2013-02 -FDACS 19027. Office of Agricultural
613 Water Policy Florida Department of Agricultural and Consumer Services
614 Tallahassee, FL, University of Florida, Immokalee, FL.

615 Shukla, S., D. Goswami, W.D. Graham, A.W. Hodges, M.C. Christman and J.M. Knowles,
616 2011. Water quality effectiveness of ditch fencing and culvert crossing in the Lake
617 Okeechobee basin, southern Florida, USA. *Ecol. Eng.* 37: 1158-1163.

618 Simon, S.M., 2003. Phosphorus retention and release of soils in a constructed wetlands for
619 wastewater treatment. Masters thesis, University of Florida.

620 Smith, D.R., B.E. Haggard, E.A. Warnemuende, C. Huang, 2005. Sediment phosphorus
621 dynamics for three tile fed drainage ditches in northeast Indiana. *Agric. Water*
622 *Manage.* 71(1): 19-32.

623 Staes J., Rubarenzya M.H., Meire P., Willems P. 2009. Modeling hydrological effects of
624 wetland restorations: a differentiated view. *Water Sci. Technol.* 59, 433-441.

625 Steinman, A.D. and P.J. Mulholland, 1996. Phosphorus limitation, uptake, and turnover in
626 stream algae. In: F.R. Hauer and G.A. Lamberti (Eds), *Methods in stream ecology*,
627 Academic Press, San Diego, CA, pp. 161-189.

628 Steinman, A.D. and B.H. Rosen, 2000. Lotic-lentic linkages associated with Lake
629 Okeechobee, Florida. *J. N. Am. Benthol. Soc.* 19: 733-741.

630 Steinman, A.D., K. E. Havens, H. J. Carrick, and R. VanZee. 2002. The past, present, and
631 future hydrology and ecology of Lake Okeechobee and its watershed. J. Porter and
632 K. Porter (Eds.). The Everglades, Florida Bay, and coral reefs of the Florida Keys,
633 an ecosystem sourcebook, CRC Press, 2002 pp 19-37.

634 Stream Solute Workshop, 1990. Concepts and methods for assessing solute dynamics in
635 stream ecosystems. J. N. Am. Benthol. Soc. 9: 95-119.

636 Tanner, C.C., M.L. Nguyen, J.P.S. Sukias, 2005. Nutrient removal by a constructed
637 wetland treating subsurface drainage from grazed dairy pasture. Agric. Ecosyst.
638 Environ. 105(1-2): 145-162.

639 Tolhurst, T.J., R. Riethmuller and D.M. Paterson, 2000. In situ versus laboratory analysis of
640 sediment of sediment stability from intertidal mudflats. Contin. Shelf Res. 20(10-
641 11): 1317-1334.

642 Toor, G.S. and G.S. Bahl, 1999. Kinetics of phosphate desorption from different soils as
643 influenced by application of poultry manure and fertilizer phosphorus and its
644 uptake by soybean. Bioresource Technol. 69: 117-121.

645 Triska, F.J., V.C. Kennedy, R.J. Avanzino, G.W. Zellweger and K.E. Bencala, 1989.
646 Retention and transport of nutrients in a third-order stream: Channel processes.
647 Ecol. 70(6): 1877-1892.

648 Tweel, A.W. and P.J. Bohlen, 2008. Influence of soft rush (*Juncus effusus*) on phosphorus
649 flux in grazed seasonal wetlands. Ecol. Eng. 33: 342-251.

650 US EPA, 2008. Total maximum daily load (TMDL) for biochemical oxygen demand,
651 dissolved oxygen, and nutrient in the Lake Okeechobee tributaries Osceola,
652 Okeechobee, Highlands, Glade, and Martin, Florida.

653 Vanriemsdijk, W.H., A.M.A. Vanderlinden and L.J.M. Boumans, 1984. Phosphate
654 sorption by soils: III. The P diffusion-precipitation model tested for three acid
655 sandy soils. Soil. Sci. Soc. Am. J. 48: 545-548.

656 Van den Berg, L.J.L., H.B.M. Tomassen and J.G.M. Roelofs, 2005. Effects of nitrogen
657 enrichment on coastal dune grassland: a mesocosm study. Environ. Pollut. 138(1):
658 77-85.

659 Wagner, B.J. and J.W. Harvey, 1997. Experimental design for estimating parameters of
660 rate-limited mass transfer: Analysis of stream tracer studies. Water Resour. Res.
661 33: 1731-1741.

662 Webster, I.T., P.R. Teasdale and N.J. Grigg, 1998. Theoretical and experimental analysis
663 of peeper equilibration dynamics. *Environ. Sci. Technol.* 32: 1727-1733.

664 Whalen, J.K. and C. Chang, 2002. Phosphorus sorption capacities of calcareous soils
665 receiving cattle manure applications for 25 years. *Commun. Soil Sci. Plan.* 33:
666 1011-1026.

667 White, J.R. and R. Reddy, 1999. Influence of nitrate and phosphorus loading on
668 denitrifying enzyme activity in Everglades Wetlands Soils. *Soil Sci. Soc. Am. J.*
669 63: 1945-1954.

670 Yuan, T.L. and D.E. Lucas, 1982. Retention of phosphorus by sandy soils as evaluated by
671 adsorption-isotherms. *Soil Crop Sci. Soc. FL*, 41: 195-201.

672 Zedler, J. B, 2003. Wetlands at your service: reducing impacts of agriculture at the
673 watershed scale. *Front. Ecol. Environ.* 1(2): 65-72.

674 Zhuan-xi, L., Bo, Z., Jia-liang, T., Tao, W. Phosphorus retention capacity of agricultural
675 headwater ditch sediment under alkaline condition in purple soil area, China. *Ecol.*
676 *Eng.* 35(1): 57-64.

677 Zhou, A., Tang, H., Wang, D. 2005. Phosphorus adsorption on natural sediment: Modeling
678 and effects on pH and sediment composition. *Water Res.* 39: 1245-1254.

679

Appendix

Empirical model background and fitted model parameters

Research has shown two distinct phosphorus sorption processes: 1) fast, reversible sorption of P on the particle surface-sites, and 2) time-dependent, irreversible deposition and burial of P. The latter process is frequently termed as a slow sorption. These two processes have different P assimilation rates, and desorption only readily occurs from the fast-sorbed surface-bound P pool.

Many studies have used the Freundlich, Langmuir or other isotherm equations to model instantaneous P sorption. Kinetic versions of these isotherms and other kinetic models have been used to fit P sorption data. Most of the models included in this study are empirical or semi-empirical. Though mechanistic models may be physically justified, the parameters are difficult to estimate at best (Crank, 1964; Vanriemsdijk et al., 1984; House and Denison, 2002).

The linear model and the Freundlich model with an extra term are included in Figure 5, though model fits for the Temkin, Langmuir, linear Freundlich, and Michaelis-Menton models are also included in this Appendix. The Temkin model has been used for modeling data for the batch incubation studies (Barrow, 1978; Mead, 1981; Whalen and Chang, 2002). The Langmuir model assumes completely mixed conditions and can estimate the maximum sorption capacity (sorption index) (McGechan and Lewis, 2000). The Freundlich model has been used to fit the sorption data for most soils. The linear Freundlich model, which has been used in several studies, describes the P sorption better

than the Langmuir model for Florida's sandy soils (Yuan and Lucas, 1982; McGechan and Lewis, 2000). The Michaelis-Menton model has been frequently used to describe the hyperbolic relation between the water column nutrient concentration and the algal uptake rate (Steinman and Mulholland, 1996). This model is similar to the Langmuir model used for instantaneous sorption with soil. The linear model is valid under aerobic and anaerobic conditions, and Reddy et al. (1995) observed a linear relation between the P sorption and solution P concentration for soil and sediments in the LO basin.

The Parabolic Diffusion and Boundary Layer kinetic P models are included in Figure 3, though model fits using the power function and Elovich equation are also included in this Appendix. The Parabolic Diffusion model has been used to model phosphorus diffusion in sediments (Pavlatou and Polyzopoulos, 1988; House et al., 1995). Applicability of the Parabolic Diffusion model is generally considered evidence for rate-limited diffusion (Pavlatou and Polyzopoulos, 1988). This model can also be presented as a function of concentration instead of uptake (Barlow et al., 2004). Similar to the Parabolic Diffusion model, applicability of the power function is indicative of diffusion kinetics with a slow chemical reaction (Agbenin and Tiessen, 1995). The power function has produced reasonable agreement with data from an outdoor experimental flume (House et al., 1995). The Elovich equation is a semi-empirical rate model and assumes that the P uptake rate is related to the degree of sediment saturation and the associated activation energy required for P sorption (Barlow et al., 2004). Several studies involving the interaction of phosphorus with agricultural soils have used the Elovich equation (Chien and Clayton, 1980; Pavlatou and Polyzopoulos, 1988), and House et al. (1995) found that the SRP influx

723 to stream bed and suspended sediments was best described by the Elovich equation. The
724 Boundary Layer model (Barlow et al., 2004), which has been used for modeling P flux
725 kinetics (Lookman et al., 1995), can estimate the equilibrium P load per unit area in the
726 solution.

727 Table A.1. Best-fit parameters and goodness of fit for the six models fitted to net P flux at Site 1 and Site 2¹

Model		r ²	SSR	Site 1 Parameters	Intercept	r ²	SSR	Site 2 Parameters	Intercept
Freundlich	$Q=k_F C^{b_I}$	0.974	12230	$k_F = 82.825$ $b_I = 1.244$	0.000	0.983	264	$k_F = 70.566$ $b_I = 0.680$	0.000
Freundlich with extra term (ETF)	$Q=k_F C^{b_I} - Q_o$	0.988	3959	$k_F = 212.973$ $b_I = 0.739$ $Q_o = 111.35$	0.416	0.986	206	$k_F = 95.245$ $b_I = 0.503$ $Q_o = 19.07$	0.041
Langmuir	$Q=Q_{max}(k_L C/(1+k_L C))$	0.984	15465	$Q_{max} = 34181$ $k_L = 0.003$	0.000	0.964	912	$Q_{max} = 15247$ $k_L = 0.004$	0.000
Linear	$P_r = AC - P^I$	0.984	5280	$A = 134.030$ $P^I = 61.452$	0.458	0.963	553	$A = 47.739$ $P^I = -11.623$	-0.243
Michaelis- Menton	$V=V_m(S/K_s+S)$	0.984	321	$V_m = 3.477E+16$ $K_s = 2.036E+15$	0.000	0.989	3	$V_m = 251.375$ $K_s = 2.234$	0.000
Temkin	$Q=k_{T1}\ln(k_{T2}C)$	0.930	22762	$k_{T1} = 179.811$ $k_{T2} = 3.372$	0.297	0.957	638	$k_{T1} = 38.120$ $k_{T2} = 11.463$	0.087

728 ¹ Q is quantity of P sorbed, C is concentration of P in the solution, b_I , k_F , k_L , k_{T1} , k_{T2} are coefficients, Q_o is surface-sorbed P in
729 the soil prior to sorption test, Q_{max} is maximum sorption capacity, P_r is phosphorus assimilated by soils or sediments, A is
730 phosphorus retention coefficient, P^I is phosphorus release potential of the soil or sediment under ambient conditions, V is
731 nutrient uptake rate, V_m is maximum nutrient uptake rate, K_s is half-saturation constant, and S is concentration of the nutrient.

732 Table A.2. Best-fit parameters and goodness of fit statistics for four kinetic models fitted to the P sorption data for the high and
733 low P spike treatment at Site 1 where $n(t)$ is mass of P uptake per unit area at time t , and A' , B' , α' , k' , R , b , K_b , and ν are
734 constants.

Model		High P Spike				Low P Spike			
		r ²	SSR	Parameters		r ²	SSR	Parameters	
Elovich	$n(t)=B'\ln(1+te^{A'})$	1.00	443	$B' = 296.25$	$A' = -0.034$	0.98	1807.35	$B' = 282.35$	$A' = -1.003$
Boundary Layer	$n(t)=\alpha'(1-e^{-k't})$	1.00	35	$\alpha' = 660.10$	$k' = 0.333$	0.99	1311.26	$\alpha' = 457.33$	$k' = 0.212$
Parabolic Diffusion	$n(t)=Rt^{1/2}+b$	0.99	2127	$R = 234.88$	$b = 13.604$	0.94	4664.32	$R = 140.89$	$b = 30.376$
Power	$n(t)=K_Bt^v$	0.99	1886	$K_b = 213.88$	$v = 0.544$	0.97	2893.89	$K_b = 93.24$	$v = 0.700$

735

736

737 Table A.3. The best-fit parameters and goodness of fit statistics for four kinetic models fitted to the P sorption data for the high
738 and low P spike treatment at Site 2 where $n(t)$ is mass of P uptake per unit area at time t , and A' , B' , α' , k' , R , b , K_B , and ν are
739 constants.

		High P Spike				Low P Spike			
Model		r^2	SSR	Parameters		r^2	SSR	Parameters	
Elovich	$n(t)=B'\ln(1+te^{A'})$	0.80	7782.73	$B' = 52702.40$	$A' = -8.170$	0.87	912.07	$B' = 34049.8$	$A' = -7.812$
Boundary Layer	$n(t)=\alpha'(1-e^{-k't})$	0.80	7785.04	$\alpha' = 35899.52$	$k' = 0.000$	0.87	912.48	$\alpha' = 24411.1$	$k' = 0.001$
Parabolic Diffusion	$n(t)=Rt^{1/2}+b$	0.51	9766.88	$R = 50.860$	$b = 48.323$	0.74	1744.07	$R = 35.7$	$b = 12.685$
Power	$n(t)=K_B t^\nu$	0.96	1564.72	$K_B = 0.044$	$\nu = 4.190$	0.89	810.78	$K_B = 8.1$	$\nu = 1.302$

740

741

Table A.4. Best-fit parameters and goodness of fit for the Boundary Layer model applied to high and low dilution treatment data sets at Site 1 and 2. The last data point (day 7) was omitted from the analysis.

	Site 1		Site 2	
	~75% dilution	~50% dilution	~75% dilution	~50% dilution
r^2	1.00	0.52	0.11	0.64
SSR	0.67	49.86	129.30	39.80
Parameters	$\alpha = 76.589$	$\alpha = 8.815$	$\alpha = -4.58$	$\alpha = 986.64$
	$k = 1.629$	$k = 1.886$	$k = 80.631$	$k = 0.002$