

PORE WATER TRANSPORT MECHANISMS AND SOIL DIAGENESIS IN AN IMPACTED
ISOLATED WETLAND WITHIN THE LAKE OKEECHOBEE DRAINAGE BASIN:
IMPLICATIONS FOR INTERNAL NUTRIENT LOADING

By

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A DISSERTATION PRESENTED TO THE GRADUATE SCHOOL
OF THE UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

2009

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To my dearest parents-
I dedicate this degree to you both; thank you for all that you have done for me my entire life

ACKNOWLEDGMENTS

I wish to thank my advisor Dr. James W. Jawitz for his commitment towards my research and friendship during the process. I would like to thank the members on my committee: Dr. Willie Harris, Dr. Mark Clark, Dr. John Jaeger, and Dr. Mark Brenner for their help and support towards the completion on this research. I wish to thank my funding agency: The Florida Department of Agriculture and Consumer Services for supporting the research. I wish to thank the University of Florida Land Use and Environmental Change Institute Laboratory (Mr. William Kenney), Soil Pedology Laboratory, Environmental Hydrology Laboratory, Wetland Biogeochemistry Laboratory (Dr. Yu Wang), and the Florida Institute of Paleoenvironmental Research Laboratory for letting me use their facilities for analyses. I would like to thank my Department Chair (Dr. Ramesh K. Reddy), faculty and staff for their assistance and guidance whenever I needed it. I would also like to thank my colleagues (past and present) for their encouragement and help with field work. I wish to thank my good friends Miss Meghan O'Donoghue, and Dr. Melroy Borges for their constant support and many stimulating discussions regarding my research. Last but not the least I wish to thank my parents back home in India for their prayers and blessings.

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Abstract of Dissertation Presented to the Graduate School
of the University of Florida in Partial Fulfillment of the
Requirements for the Degree of Doctor of Philosophy

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August 2009

Chair: James W. Jawitz
Major: Soil and Water Science

The deteriorating water quality of Lake Okeechobee due to excess phosphorus (P) associated with beef cattle and dairy operations from surrounding basins have been an environmental concern for many decades. During this period, isolated wetlands within these basins have been extensively ditched and drained to improve farmlands and facilitate agriculture. Restoring the wetlands has been proposed as one of the strategies to reduce overland P loss by retaining it in the soils. Phosphorus fluxes associated with soils and shallow pore water from agricultural lands can contribute to internal loading which could undermine the effective use of these wetlands. Soil properties of deeper horizons within impacted isolated wetlands are rarely investigated due to the assumption that these wetlands are flooded, and that biogeochemical interactions occur at the soil-water interface. However, prolonged droughts and periodic draining can leave the wetlands dried for most of the year, and water tables can drop over a meter below the ground surface.

As part of my doctoral research, I investigated soil properties of surface as well as deeper horizons from an impacted isolated wetland located on a beef farm and its surrounding upland pasture. The upland soils (Alfisols) showed pedologically formed horizons compared to the

stratified wetland soils (Entisols). The soils were sandy up to a depth of 100 cm, and showed increasing clay content further down core (>100 cm). This can have implications for higher P sorption capacity, perched water tables and slower hydraulic conductivity. Net P reserves were highest at the surface 28 kg ha⁻¹ (46%), however, non-trivial quantities were also found in the deeper horizons associated with the clay horizons at 15 kg ha⁻¹ (25%). Due to the transient hydrology, one of the hypotheses tested was that internal loading of P from diffusive and advective processes was a significant component of the P budget to the wetland. Diffusive fluxes of SRP to the wetland water column were estimated at < 1 mg m⁻² d⁻¹, while advective fluxes associated to water table fluctuations were 8 (±10) mg m⁻² d⁻¹. The wetlands also showed very low annual hydroperiods with multiple drawdown events, this can have a negative effect on the P loading to the water column due to fast changes in soil redox conditions. In addition, P release and storage capacity of the soils was evaluated as a function of depth, based on batch equilibrium experiments, and amorphous Fe and Al content. There was a good correlation between S_{max} and Fe+Al (r = 0.84), and between P and Fe+Al (r = 0.91), suggesting that Fe and Al can be used as a good indicator for P sorption capacity and P content. The EPC₀ values at the wetland and upland surface (0-2 cm) was 1.8 (±1.3) mg L⁻¹ and 8.9 mg L⁻¹ respectively, suggesting that the surface horizons could behave as a potential source of P to the wetland. Based on the soil P storage capacity experiments both the wetland and the upland soils showed positive storage capacities. Results from this study adds to our overall understanding of P dynamics within impacted wetland soils in the Okeechobee basin, which will help develop sound P management strategies in the future.

CHAPTER 1 INTRODUCTION

Background and Motivation

Intensive agricultural practices in the United States have maintained a surplus of nutrients including phosphorus (P) within agricultural watersheds (Sharpley et al., 2001; Sims et al., 2005), and surface water export from such areas has resulted in eutrophication of surrounding fresh water bodies (Dougherty et al., 2004). In the state of Florida the problem of eutrophication in Lake Okeechobee has been largely attributed to excess P in runoff from agricultural lands within the drainage basin area (Flaig and Havens, 1995). The Lake Okeechobee Protection Act of 2000 set a total maximum daily load (TMDL) target of 140 Mg P yr⁻¹ for the watershed to be met by 2015 (SFWMD et al., 2004). Phosphorus management programs implemented within the watershed during the 1980s resulted in a decline in the P loading rate to the lake from a high of 2380 Mg P yr⁻¹ in 1985 to 1717 Mg P yr⁻¹ by 1990 (Hiscock et al., 2003). However, P loading to Lake Okeechobee has continued to remain approximately 100 Mg P yr⁻¹ over the legally mandated target primarily because of discharge from basins that have active beef cattle and dairy operations within the watershed (Havens et al., 1996; Hiscock et al., 2003). Such operations account for 12% of the land area in the Okeechobee basin, yet contribute a disproportionate amount of P (35%) to the Lake (Flaig and Reddy, 1995). In response to these issues, the agricultural industry is mandated to achieve P load reductions, and ranches used for dairy and beef cattle within the watershed are being targeted for a portion of these reductions. Concentrations of P in surface runoff tend to be lower from pastures than from holding areas or high intensity areas, yet the total P load from pastures is substantial due to the below-ground storage over vast acreage (Capece et al., 2007).

Over the past 50 years the hydroscape of South Florida has been severely altered by the construction of ditches and canals (Steinman and Rosen, 2000) that connect over 800 historically drained isolated wetlands within the Lake Okeechobee basin with major lotic systems such as the Kissimmee River and Taylor Creek, which ultimately drain into Lake Okeechobee. Among the P control and mitigation strategies being considered to achieve the TMDL target, is the physical restoration of historically isolated wetlands within the watershed that were drained by ditching. These drained isolated wetlands cover nearly 7% of the approximately 5160 km² Lake Okeechobee drainage basin area (Hiscock et al., 2003; McKee, 2005). The practical implications of restoring isolated wetlands would be to increase their flooding periods (hydroperiod), which would allow for greater P storage and retention within the soils. Increasing wetland hydroperiod would also involve an increase in wetland area, and this could facilitate greater P storage in above ground plant biomass. It has been suggested that hydrologic restoration of these wetlands may help retain P by up to 13 kg P ha⁻¹ yr⁻¹ (Dunne et al., 2007a).

The low nutrient retention capacity and hydrological setting of the agricultural soils of subtropical Florida can pose a nutrient management challenge. Categorized as the most widely distributed soil order in the state of Florida, Spodosols of this region form in sandy parent material on flatwood landforms that are usually poorly- or somewhat-poorly drained (Nair et al., 1998). The sandy nature of the soils in the Lake Okeechobee basin and the nearly level landscape (0-2% slope) aids in the rapid infiltration of water, resulting in significant subsurface flow (Capece, 1994). The P retention capacity within the A and E horizon in Spodosols is almost non-existent (Harris et al., 1996; Nair et al., 1998). The limited retention capacity of these soils is an important factor contributing to the high P load entering Lake Okeechobee. These poorly-drained soils can accumulate ground water that emerges as artificially drained surface water in

depression basins (Hiscock et al., 2003). Campbell et al. (1995) observed that in such low-relief landscapes, subsurface drainage is a significant mechanism for P transport. In a 120 ha field study in the Lake Okeechobee basin, Capece (1994) found no surface runoff, due to the combination of low topography (1.3% slope) and high infiltration, and estimated that all P export (averaging $25 \text{ kg P ha}^{-1} \text{ yr}^{-1}$) was via subsurface flow-paths. An estimated 60-70% of the P imported to the Okeechobee watershed is stored within the Bh horizon in upland soils (Reddy et al., 1998). Although these soils could still have up to 75% of their maximum P storage capacity remaining, Capece et al. (2007) suggested that they are already a significant source of non-point P, despite their total storage capacity.

A different set of challenges for P management in these soils is the presence of lower permeability argillic horizons (or lenses), composed of finer, P sorbing phyllosilicate minerals and quartz between 60 and 200 cm below ground surface (Villapondo and Graetz, 2001b). Argillic horizons with thicknesses varying between 20 to 200 cm could occur in Spodosols and Alfisols, another common soil order in subtropical Florida. The finer textured (loamy to clayey) horizons have the ability to sorb P, similar to the spodic-Bh horizon seen in Spodosols (Harris et al., 1996). Dissolved P moving downwards from the A horizon through the E generally accumulates in the Bh. However, the presence of loamy or clayey horizons below the Bh can impede the movement of water, thus promoting transport of P via surface runoff and lateral seepage to streams and canals, minimally sorbed and mitigated through A and E horizons (Allen, 1987). Further, alternating flooded (anaerobic) and drained (aerobic) conditions can significantly affect the distribution of P within impacted soils. Villapondo and Graetz (2001b) found that up to 50% of total P associated with clay horizons was readily leachable and released to pore water

under drained conditions. They concluded that the movement of P from such soils would be greater from rainfall events following the dry season than during the flooded wet season.

Many previous studies related to P retention in wetland soils within the Okeechobee drainage basin area have focused only on near-surface soil horizons (<30 cm) (for example, Richardson and Vaithyanathan, 1995; Pant et al., 2002; Pant and Reddy, 2003; Dunne et al., 2006, 2007a), and did not evaluate the effect of P-enriched horizons such as the Bh and Bt that usually exist below 30 cm. However, wetlands in the basin are hydrologically linked to deeper soil horizons by fluctuating water tables. In a three-year study of four isolated wetlands in the Okeechobee basin, Perkins (2007) recorded frequent water table fluctuations of 80 cm below ground surface to 50 cm of standing water in the wetlands. When the water table rises and the wetland re-floods following dry periods, there is the possibility of advection of P from the groundwater into the wetland (internal loading). In a laboratory column study, Villapando and Graetz (2001a) showed significant P leaching in impacted spodosols from the Lake Okeechobee basin due to a fluctuating water table. Maintaining the water table above (flooded) and below (drained) the Bh horizon resulted in substantial movement of P in the soil columns. Thus, it is suggested that in cases of fluctuating water tables, it may be important to assess the distribution of P deeper into a soil profile than the commonly studied surface horizons.

Internal Loading of Nutrients

The internal loading of nutrients from sediments (and/or soils) has been identified as a critical component of the nutrient budget, and can control the trophic conditions of aquatic systems such as lakes and wetlands (Berner, 1980; Håkanson, 2004). Within the Lake Okeechobee drainage basin, this internal release of nutrients from shallow aquatic systems can occur via two different mechanisms: (i) release at or below the sediment-water interface during hypoxic or anoxic conditions, and the subsequent *diffusion* of dissolved nutrients to the

overlying water column; and (ii) *advection* as a result of a fluctuating water table, bioturbation, and wind induced resuspension at the sediment surface (Moore et al., 1998; Fisher and Reddy 2001; Wu et al., 2001). The ability to quantify the nutrient flux within a system (from the ground to the water column) can be useful for ecosystem managers in determining the importance of internal versus external nutrient loading, thereby implementing strategies to mitigate them. The implementation of P control programs (PCPs) caused a decline in the loading to Lake Okeechobee from early 1980s to 1990 (Havens, et al., 1996), however P loads to the Lake have still remained over the legally mandated target primarily because of discharge from tributary basins such as Taylor Creek that has active beef cattle and dairy operations within its watershed. External nutrient loading from agricultural and cattle areas can be addressed through the implementation of Best Management Practices (BMPs), and interception strategies such as construction of storm-water treatment areas (STAs) and constructed wetlands in the state of Florida (Rice et al., 2002); however, internal loading from impacted soils and sediments has prevented the rapid improvement of water quality of numerous watersheds (Fisher and Reddy, 2001; Pant and Reddy, 2003). For example, studies conducted by Moore and Reddy (1994), and Reddy et al. (1995) in Lake Okeechobee estimated that mean P flux ($\text{mg m}^{-2} \text{d}^{-1}$) as a result of internal P loading from bottom sediments is approximately equal to the rate of external P loading ($\sim 1.0 \text{ mg m}^{-2} \text{d}^{-1}$). Based on their conclusions, the primary source of nutrients that constitutes an internal load is the organic matter within the upper sediments. With frequent drought conditions experienced in the state of Florida over the past decade, most of the wetlands within the Okeechobee drainage basin remain dry for 8-9 months throughout the year, and water levels are below the surface for prolonged periods (Perkins, 2007). This would allow for shallow ground

water to act as a potential source of nutrients that can affect internal loading as the water table fluctuates above and below the soil-water interface.

Besides drainage and other water management practices such as ditching, wetlands located on ranches are also affected by cattle activity (bioturbation) (Tollner et al., 1990; Sigua, 2003; Sigua and Coleman, 2006; Tweel and Bohlen, 2008). Grazing animals have been shown to affect the movement and uptake of nutrients through the soil and vegetation either directly or indirectly, thus affecting the chemical and physical characteristics of pasture soils. Standing cattle can facilitate soil compaction and the formation of vertical preferential flow paths (PFP) up to 50 cm within the soil profile (Dreccer and Lavado, 1993). Nutrients derived directly from manure can potentially seep through these PFPs, quickly altering the chemical equilibrium between the soil and surrounding pore water. Mulholland and Fullen (1991) showed that the magnitude of stress caused by animal hooves mainly depends on the soil water content. When dry soils are trampled upon, the main process is compression beneath the hoof, collapsing the larger soil pores by mechanical disruption of aggregates. However, when wet soils are trampled upon there is a plastic flow being generated around the hoof (Scholefield et al., 1985). Repeated treading under these conditions can produce deep hoof prints that coincide with the presence of surface water ponding up to depths of 5-20 cm (Taboada and Lavado, 1993).

It is believed that because of factors such as rapid changes in hydrology over short periods of time (months or even days), and the random movement of cattle in and out of the wetlands that these wetlands need to be perceived as very dynamic, transient systems, especially within the top meter of the soil profile.

Hypotheses and Objectives

The main theme of my dissertation deals with the potential for the wetland to act as a sink for nutrients under present hydrologic and management conditions on a cattle ranch. Through

detailed field sampling, laboratory experiments, analyses and modeling I tested the following three hypotheses:

1. Within a soil profile, certain horizons may behave as “hot-spots” that can act as a potential source of nutrients.
2. Nutrient fluxes across the soil-water interface associated with advective processes such as water-table fluctuations are significant compared to molecular diffusion.
3. Due to the transient hydrology, fast adsorption-desorption reactions between soil and water can only partially explain *in situ* pore water P concentration.

Three primary objectives of my research were to: (1) investigate the physical and chemical characteristics of surface and subsurface soil horizons (up to 160 cm) and their influence on the surrounding pore water P concentrations; (2) estimate nutrient fluxes across the soil-water interface within the wetland associated with internal loading based on advective and diffusive processes; (3) conduct laboratory experiments to evaluate soil P leaching and sorption capacities.

In the following three Chapters (2, 3, and 4) specific goals and set objectives will be discussed in detail, along with field (or experimental) results that were used to test the above hypotheses.

Study Area

The two wetlands selected for this study are historically isolated emergent marshlands located on an active beef ranch within the S-154 priority sub-basin of the Lake Okeechobee watershed, which has been identified as contributing relatively higher loads of nutrients to Lake Okeechobee, compared to the surrounding lake sub-basins. (Figure 1-1). These wetlands are located on the Dixie-Larson Ranch (27.24° N, 80.83° W) and are at the head of ditches that connect to the regional ditch network that ultimately drains into Lake Okeechobee. The two wetlands, Wetland 1 (or Larson East) and Wetland 2 (or Larson West) are about 1.1 and 2.2 ha, respectively.

Site Description

The majority of P export to Lake Okeechobee comes from four priority sub-basins (Hiscock et al., 2003). Approximately 21% of the total catchment area is comprised of depressional wetlands and other water features (streams, canals and ditches), with only 15% represented by wetlands alone (Boggess, et al., 1995). Nearly 45% of the wetlands today have been hydrologically managed by a network of ditches and canals that drain the landscape and divert the water off-site into rivers and streams that ultimately flow into Lake Okeechobee. The wetlands are typically less than one meter deep and exhibit a pan shaped morphology. They are remnants of historic sinkhole collapse features. They occur at a relatively small scale in comparison to the resolution of soil mapping units defined by the USDA Soil Survey for Okeechobee County (Lewis et al., 1997). Typical vegetation at these wetlands includes: *Juncus effuses*, *Panicum* sp., *Pontedaria cordata var. lancifolia*, *Ludwigia repens*, *Hydrocotyle ranunculoides* and *Andropogon glomeratus* (Dunne et al., 2006).

Hydrology

In the mid 1950s, an extensive network of ditches and canals was created throughout the Okeechobee drainage basin in an attempt to lower the regional water table and partially drain depressional wetlands so that more land could be used for grazing pasture (Flaig and Reddy, 1995). These ditches do not completely drain the depressional wetlands, as they were excavated to depths above the bottom of the wetlands. As a result, the water in the wetland must reach a critical height before water can exit via the ditch. However, with low topographic gradients, it is not uncommon for ditch flow rates to drop to undetectable levels. By limiting the water depth in the wetland throughout the year, these wetlands and the ditches serve as cooling ponds for the cattle. Such a strategy is advantageous for cattle productivity; however, the wetlands and ditches

that are hydrologically connected to the lake can create a rapid conduit for P-rich water to be transported off the pastures.

The effect of ditching on soils and shallow ground water is two-fold. First, it can create a recharge/discharge point for ground water in the landscape. Second, the ditch serves to drain the wetland quicker than natural conditions, thus producing a greater frequency of water table fluctuations. Ground water from the landscape surrounding the ditches can flow towards the ditch carrying water-soluble nutrients with it; conversely, water from the ditch can be transported laterally along the edges of the ditches to the surrounding watershed. Wetlands located within the Okeechobee basin remain dry for prolonged periods, and water levels are below the surface for months primarily due to periodic drought conditions experienced in the state of Florida (McKee, 2005; Perkins, 2007), and due to draining as a result of ditching. Prolonged dryness can lead to change in vegetation cover and erosion of the topsoil. Figure 1-2 shows the contrast in appearance of the wetland between the two extreme wet and dry periods.

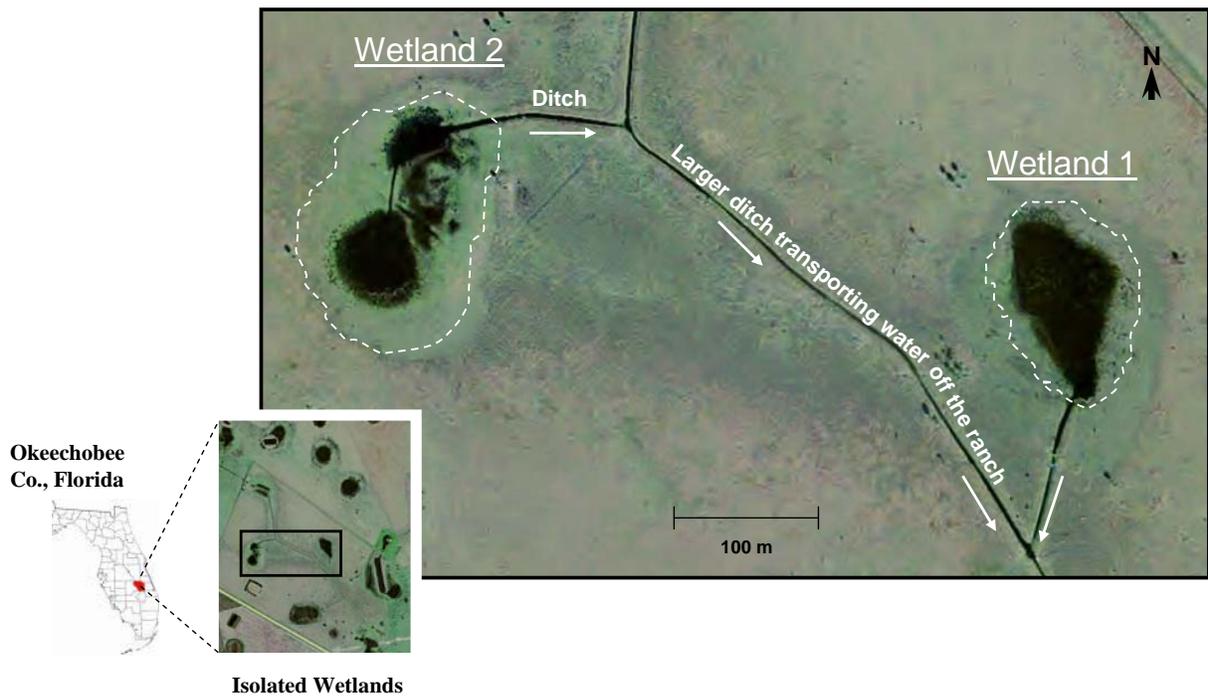


Figure 1-1. Map of study area showing the two wetlands. Dotted line represents the outer boundary of the wetlands. Water from these wetlands drains off into ditches that flow into a larger ditch transporting water off the ranch.



Figure 1-2. Contrast in the appearance of wetland hydrology and vegetation cover between wet and dry seasons.

CHAPTER 2 SOIL CHARACTERIZATION BASED ON PHYSICAL AND CHEMICAL PROPERTIES

Introduction

Over the past 50 years the Lake Okeechobee basin has been impacted as a result of ditching and cattle activity from beef and dairy farming. These operations account for only 12% of the land area in the Okeechobee basin, yet contribute a disproportionate 35% of the phosphorus (P) load to the Lake. Within this landscape, historically isolated wetlands are known to store water and nutrients such as phosphorus (P), and exist along the landscape continuum between the upland and the lake (Braskerud, 2000; Hiscock et al., 2003). At present, nearly 45% of the wetlands within the drainage basin are ditched and drained, surrounded by cow-calf pastures located on active beef or dairy facilities (SFWMD, 2004). Draining the isolated wetlands via ditches and canals was done to provide improved cow-calf grazing pastures, which have left the basin's hydroscape severely altered. One of the strategies recently proposed (Lake Okeechobee Protection Plan, 2004) to help mitigate P loss from improved pastures and reduce P loads to Lake Okeechobee was to restore the hydroperiod of these isolated wetlands located on beef and dairy farms, so as to facilitate water storage and P retention (Johns and O'Dell, 2004). An understanding of soil characteristics can help in planning future restoration work and implement sound management strategies.

Studies of wetland ecosystem functions have shown that soils are the most important long-term P storage compartment compared to litter or plant biomass (Dolan et al., 1981; Graham et al., 2005), and that their properties can influence wetland water quality. Most of the P stored in wetlands is in organic form derived from dead vegetation (Graham et al., 2005, Dunne et al., 2007a), typically concentrated in the surface horizons. Under flooded conditions biogeochemical cycling of P occurs within a few centimeters at or near the soil-water interface (Fisher and

Reddy, 2001; Debusk and Reddy, 2003), therefore previous studies have focused primarily on soil properties that relate to P storage capacity of surface soils (Reddy et al. 1998; Pant et al., 2002; Dunne et al., 2007a). However, due to the transient hydrologic conditions experienced by these wetlands there is a need to investigate the deeper horizons. It is common for water tables to drop below a meter in the ground during the dry season (Perkins, 2007), potentially transporting nutrients to the deeper horizons, in addition to causing sudden shifts in the soils redox conditions. Studies have shown that the P retention capacity of saturated soils that have undergone periodic drawdown diminish on re-flooding compared to continually flooded soils (Watts, 2000; Klotz and Linn, 2001). Bostic and White (2006) evaluated the behavior of periodically saturated marsh soils and found that up to 6% of total P (TP) from the soils was released from a single drawdown and reflooding event. The reason for observing this type of behavior is the sudden change in redox conditions which affects the iron oxide minerals in the soils, and its ability to retain P. Such episodic flooding and drying cycles are a common occurrence within the Okeechobee basin and could mobilize P from deeper horizons, releasing P to the water column on re-flooding (internal loading). Within soil profiles, clays typically accumulate in deeper horizons, below the E and within the B (Bh or Bt) horizons (Zhou, et al., 1997). In addition to the hydrologic impact of clay horizons, clay particles provide surface area for mineral-to-mineral and mineral-to-organic interactions (Rengasamy et al., 1984). Capece et al. (2007) reported clay layers below 60 cm near Lake Placid, FL., about 40 km west of our study site. They concluded that the accumulation of P in deep soils from historic fertilization had an overriding influence on P loads in surface runoff. Consequently, net P imports from deeper horizons would also need to be addressed in order to achieve mandated water quality targets in the long term.

Ditches and canals created artificially to drain the landscape can also have an impact on soil properties. Soil morphology has been used to evaluate a ditch's effectiveness, because morphology has been found to change when the hydrology is altered (Hayes and Vepraskas, 2000). For example, Daniels and Gamble (1967) showed that soils (ultisols) along stream-dissected edges of the Middle Coastal Plains (North Carolina) had redder colored Bt horizons than soils further from the edge. This "red-edge effect" was believed to have occurred after the Coastal Plain had been incised and drained by streams. Prior to the stream incision, restricted surface and subsurface drainage caused reduced conditions to persist for long periods. Stream incision resulting from lowered water tables and the subsequent oxidation of iron-aluminum minerals produced red and yellow soil horizons in areas of improved drainage. Such changes in redox conditions can have an overriding effect on P solubility and sorption mechanisms regardless of the soil/sediment mineralogy (Reddy et al. 1998b; Hayes and Vepraskas, 2000).

Isolated wetlands cover nearly 7% of the land within the Okeechobee basin, and nearly as much is covered by ditches and canals. (Hiscock et al., 2003; Gathumbi et al., 2005). With open access to wetlands and ditches, cattle can increase nutrient pollution by depositing manure into surface waters (Bottcher et al., 1999; Alloush et al., 2003), or by stimulating nutrient release from sediments stirred up by cattle activity (Line et al., 1998). Heavy stocking can also lead to reduction in vegetation cover and an increase in soil erosion (Capece et al., 2007). Cattle trampling can increase soil bulk density and decrease soil porosity (Tollner et al., 1990; Mulholland and Fullen, 1991; Bezkorowajnyj et al., 1993). Mature cattle can exert a static ground pressure of approximately 1.7 kg cm^{-2} of hoof-bearing area, which can affect bulk density up to 100 cm deep within a wet saturated soil profile (Rhoades et al., 1964; Bezkorowajnyj et al., 1993). In addition, cattle activity can also increase the physical breakdown of litter, stimulating

enhanced decomposition of organic matter (OM) at the surface (Klemmedson, and Tiedemann, 1995).

In order to evaluate the effectiveness of wetland restoration, a thorough understanding of pre-restoration soil characteristics is important. Soil characteristics of horizons deeper than a meter are not routinely investigated in impacted wetlands within the Lake Okeechobee drainage basin, and soil survey data for Okeechobee County only provide limited information because isolated wetlands in the Okeechobee drainage basin occur at a relatively small scale compared to the resolution of soil mapping units. The objectives of this study were to (i) determine differences in soils characteristics as a function of depth between an impacted isolated wetland and the surrounding upland, and (ii) determine the P status within deeper horizons that may be affected by water-table fluctuations. The physical properties described included color, texture (based on particle size distribution), bulk density, porosity and saturated hydraulic conductivity. Chemical analyses included soil organic matter (OM) content, total P (TP) concentration, and clay mineralogy.

Sampling and Analytical Methods

Four intact soil cores were collected in July 2006 using the vibracoring technique. Vibracoring works on the principle of liquefaction in fine-grained sediments by displacing sediment to allow passage of the pipe and retrieval of long (up to 10 m), continuous sections from unconsolidated saturated sediments (Smith, 1984). Vibracoring works best in saturated organic sediments, clays, silty clays, silts and fine sands, but is inefficient in firm clays and medium to coarse sands. Cores 1, 2, and 3 were collected from within the wetland basin, while core 4 was collected from a nearby upland site within 20 m from the ditch (Figure 2-1). These cores were 140, 144, 129 and 161 cm long, respectively. The water table was 6 to 10 cm below the ground surface at the time of coring, so the cores were virtually saturated. To ensure

saturation they were completely flooded with de-ionized water. The cores were transported to the laboratory where they were split lengthwise, described and photographed. Soil description was conducted on wet soil using USDA protocols (Soil Survey Staff, 2007).

One section of the split core was used to measure soil bulk density (BD) by gamma ray attenuation (Geotek Standard Multi-sensor Core Logger, MSCL-S) at 0.5 cm increments, and capture high-resolution digital images (Geoscan II, 40 pixels cm^{-1}) of the entire core lengthwise. The accuracy of the bulk density ($r^2 > 0.99$) was determined using a standard aluminum density calibration piece. Particle size distribution (PSD) was measured only on selected soil horizons extracted from core 2 (wetland) and core 4 (upland) based on morphological changes. The pipette-dispersion method was used to measure PSD (Gee and Bauder, 1986). Minerals in the clay fraction were identified by X-ray diffraction (XRD) using a computer-controlled X-ray diffractometer equipped with stepping motor and graphite-crystal monochromator. Oriented mounts were prepared by sedimentation on unglazed ceramic tiles under suction. Diagnostic cation saturation with MgCl and glycerol were performed to aid phyllosilicate identification (Harris and White, 2008).

The remaining halves of all four split soil cores were sectioned at 2-cm intervals, weighed, freeze-dried, and re-weighed prior to chemical analyses. Freeze-drying the samples was preferred over conventional oven-drying (2 h at 105 °C), because the process sublimates the moisture content, with minimal physical or chemical alteration (McClymont et al., 2007). The samples were stored in air-tight containers to prevent any rehydration. Wet and dry soil weights were used to determine water content for each 2-cm section. Soil porosity was calculated using measured BD and a fixed particle density of 2.65 g cm^{-3} (quartz sand).

Soil samples were also analyzed for TP and organic matter (OM) content. Total P was analyzed colorimetrically (Bran-Luebbe Autoanalyzer) using the acid persulfate digestion for soil TP (Nelson, 1987). Organic matter content was measured using the loss on ignition (LOI) technique (Dean, 1974) where 2.0 g of dry mass (freeze-dried) sample were oxidized at 550°C in a muffle furnace for two hours. The weight loss on ignition represents the OM content of the sample. Note that the LOI method used in this study may overestimate the OM content in clayey material due to dehydroxylation reactions of secondary phyllosilicates in the temperature range of OM combustion. Analytical precision for TP and OM was assessed using duplicates every tenth sample, and reported as relative percent difference (RPD, 3.3% for TP and 5.2% for OM content).

Saturated hydraulic conductivity was measured using the slug test method (slug-out technique) from five fully penetrating onsite wells extending approximately 1.5 m below the ground; one well located in the wetland, and four in the surrounding upland. The Hvorslev method (Fetter, 1994) was used to analyze the slug test data for fully penetrating wells with well-length more than eight times the well-radius.

Results and Discussion

Soil Description and Classification

The soil texture in all four cores was sandy down to a depth of 100 cm (Figure 2-2). The top of upland core 4 showed a distinct Ap horizon with high OM, underlain by an eluvial E horizon (10-40 cm depth), a Bt horizon (40-80 cm), a sandy loam Btg1 horizon (80-140 cm), and a sandy clay Btg2 horizon (140-161 cm). While the upland core comprised horizons Ap, E, Bt and Btg formed by pedogenesis, all three wetland cores showed stratified C horizons. Deposition of surface sediments eroded from surrounding uplands may have given rise to the stratified morphology observed in all three of the wetland cores. Below 100 cm, there were finer-textured

horizons (sandy loam and sandy clay), in which fine stratification was not as prominent as in the overlying horizons. In upland core 4, I observed what may be a result of the “red-edge effect” within the Bt horizon, where a well defined yellow to red coloration (high chroma) is visible between 75-83 cm. Being close to the ditch, it is possible that following ditch incision, lowering of the water table due to surface and subsurface drainage may have caused oxidizing conditions, conducive for formation of iron oxides.

The upland soil is classified as an Alfisol, while the wetland soils are classified as Entisols by virtue of having > 50 cm of recent material (stratification). The genesis of Alfisols involves the translocation of clay from the upper to lower soil zones, ultimately forming thick argillic horizons. Such horizons have the ability to sorb P, similar to the spodic-Bh horizons seen in Spodosols. Dissolved P moving vertically downwards from the A and O horizon through the E, generally accumulates in the B horizon. However, the presence of clay within the B horizon can impede the movement of water, thus promoting transport of P via surface runoff and lateral seepage to the ditches through A and E horizons.

The texture of the wetland soils below the stratified horizon became loamier, gradually transitioning to clay at the core bottom. Particle size distribution analysis of cores 2 and 4 showed that the sand fraction (0.05-2.0 mm) gradually decreased with depth, while the clay fraction (<0.002 mm) increased, up to 36% in core 2 and up to 38% in core 4 (Figure 2-3). The sandy clay layer observed in all four cores will subsequently be referred to as “clay horizons”. The top of the clay horizon was encountered at approximately 120 cm in all three wetland cores. The clay thickness is unknown, but it extended all the way to the bottom of the soil cores. A similar 15-cm clayey horizon was seen around 85-100 cm in core 2. Such clay horizons could

establish a perched water table, and separate it from underlying aquifers, and reduce the loss of P through leaching.

The porosity of all four cores was higher (0.49 ± 0.05) within the top 20 cm (Figure 2-4). This is probably due to the presence of the loosely bound OM associated with plant roots within the top 20 cm (Justin and Armstrong, 1987). Below 20 cm, the porosity gradually decreased to less than 0.45 in the wetland cores. The small range in porosity (± 0.006) between 50-160 cm in upland core 4 reflects uniform grain size. Bulk density increased with depth in all four cores: in the wetland soils from $1.33 \pm 0.15 \text{ g cm}^{-3}$ in the top 20 cm to $1.56 \pm 0.03 \text{ g cm}^{-3}$ in the bottom 20 cm, and in the upland soil from $1.39 \pm 0.11 \text{ g cm}^{-3}$ in the top 20 cm to $1.70 \pm 0.01 \text{ g cm}^{-3}$ in the bottom 20 cm (Figure 2-4). Cattle poaching, which is the penetration of the soil surface by the hooves of grazing animals (Mulholland and Fullen, 1991), may be responsible for the increase in BD observed at 10 cm depth within the soil profile. The sharp increase in BD from 1.45 to 1.70 g cm^{-3} in the upland core 4 at the E-Bt horizon interface is because of the change in soil texture due to pores being filled during illuviation.

Saturated hydraulic conductivity within the wetland based on slug test measurements from the wetland well was 1.62 m d^{-1} , while the hydraulic conductivity in the surrounding upland pastures was $0.82 \text{ m d}^{-1} (\pm 0.21)$. These values are comparatively lower than those reported by Soil Survey Staff (2007) for the Basinger and Valkaria fine sands of this region (3.7 to 12.2 m d^{-1}). The discrepancy in values may be because the 1.5 m long screened wells intercept the clay horizons that could lower the integrated conductivity for the soil unit down to the well depth.

The XRD analyses on four selected soil horizons from core 2 showed that smectite was the dominant mineral in the clay-size fraction, and that smectite enrichment gradually increased with depth, as evidenced by the smectite:kaolinite ratio (based on peak areas) of 1.16, 1.38, 3.07, 2.23

from samples collected at 45, 60, 92 and 144 cm depth respectively (Figure 2-5). Smectites are typically considered to have minimal P sorption capacity given their low edge to face ratio and permanent negative charge. They impart a higher cation exchange capacity than kaolinite, suggesting less retention of species such as orthophosphate than kaolinite (Pant et al., 2002).

Soil Total Phosphorus and Organic Matter Content

Characterizing P storage in wetland soils is often accompanied by OM characterization, as the TP pool within wetland ecosystems is often dominated by organic P, which can comprise > 50% of soil TP (Reddy et al., 1998b). High concentrations of OM in the form of manure and decomposed vegetation can drastically increase the availability of P within surface soils since organic anions formed by the decomposing OM can compete with P for the same adsorption sites such as clays and iron-alumino minerals (El-Dewiny et al., 2006). Except for core 1, OM concentrations in the cores were greatest within the top 2 cm (Figure 2-6). The OM content within the top 6 cm was 38% ($\pm 14\%$) and 48% ($\pm 2\%$) for the wetland and upland soils respectively. The high OM content at the surface is believed to be associated with decomposing vegetation and cattle manure. Below 6 cm, the OM concentrations steadily dropped to < 2% at the top of the clay horizon. Due to the presence of finer clay material OM content in those zones may be slightly overestimated, because small quantities of finer inorganic minerals could have also been lost by the incineration process. An irregular decrease in OM with depth was consistent with the observed fine stratification within the wetland soils.

Similar to OM, clays can also influence the P storage capacity with depth, because of the ability to sorb P. Except for core 1, soil TP concentrations were also highest within the top 2 cm of the soil profile (Figure 2-7). In the wetland soils, these concentrations gradually decreased with depth to about 100 cm, but then increased again as the clay content increased. In comparison, the upland core showed a sharper increase in TP concentrations below 120 cm. This

increase in TP concentrations below a meter in the soil profile is also associated with the clay fraction within and below the Btg1-horizon at those depths. Depth-averaged soil TP concentrations between 0-20 cm were 62.8 mg kg^{-1} (± 28), 182.6 mg kg^{-1} (± 241), 166.1 mg kg^{-1} (± 104), and 124.2 mg kg^{-1} (± 172) for cores 1, 2, 3, and 4, respectively. The high degree of variability is primarily because of the high concentration of TP within the top 2 cm of the soil profile. The increase in P concentration between 40-60 cm seen in core 4 corresponds to the affinity for iron-bearing minerals for P present within the Bt horizon in the upland.

Based on the BD values and average concentration of soil P for a given thickness of soil horizon, the net P reserve within wetland and upland soil horizons was estimated (Figure 2-8). While the majority of the P is accumulated in the upper 10 cm (46-49%), up to 25% is also present in the deeper argillic horizons of the upland, and 17% in the deep, finer-textured layers of the wetland. The increasing trend of TP observed at the bottom of core 2 and 4 indicates that there may still be more P in horizons deeper than the core bottom; this would further decrease the relative proportion of net TP reserves estimated in the upper 10 cm of the wetland and upland soils. The low-permeability clay horizons could impede vertical movement, thereby forcing the flow laterally, potentially transporting P to nearby ditches, a process previously addressed by Allen (1987). Under such conditions ground water could be short-circuited rapidly along preferential flow paths and emerge as surface water (Kadlec and Wallace, 2008).

The TP concentrations within the soil profiles followed OM trends in all four cores ($r = 0.89$, Figure 2-9). The regression was dominated by the surface horizon ($r = 0.90$), because TP concentrations at the surface were nearly two orders of magnitude higher than in the rest of the soil profile. Correlations in other horizons were all much weaker: for example, root-zone (10-20 cm) $r = 0.56$, mixed zone (20-100) $r = 0.65$, and finer textured zone (>100 cm) $r = 0.6$. The

strong OM to P correlation within the top 10 cm likely corresponds to P in cattle manure and decaying vegetation deposited at the soil surface. This is because both OM and P would tend to accumulate at the surface, whether they are chemically associated or not. The slope of the regression for surface soils corresponded to 10.3 mg kg⁻¹ of TP for every 1% increase in OM. In comparison, Dunne et al. (2007a), estimated an increase of 4.2 mg kg⁻¹ of TP for every 1% increase in OM ($r^2 = 0.86$) in surface soils (0-10cm) from adjoining wetlands including this one located on the same pasture land. An inverse correlation between OM and P was observed between 10-20 cm within the root-zone (rhizosphere). This is not unusual, because at this depth C:P ratios are typically elevated, and virtually all the P is sequestered within the rooted macrophytes, responding to the increase in soil P concentrations (Davis, 1991). The P within the clay horizons is primarily associated with the increase in clay content, and its ability to retain P on reaction sites. This deep pool of TP could be critical for understanding soil P retention dynamics associated with clayey horizons, especially if the water table intercepts those depths during the dry periods.

Summary and Conclusions

Soils recovered from the wetland are classified as Entisols by virtue of un-obliterated stratification seen throughout the entire soil profile, possibly resulting from upland soil erosion. The upland soils are classified as Alfisols, because of a distinct argillic horizon and the Bh does not meet the taxonomic criteria for a spodic diagnostic horizon. All four soil cores recovered from the site included clayey material below 120 cm in the soil profile. The two dominant phyllosilicate minerals present within the wetland soils were smectite and kaolinite. These minerals can lower hydraulic conductivity by impeding subsurface flow, however, kaolinite can increase P sorption capacity due to its lower cation exchange capacity and a higher edge to face ratio than smectite. The high-chroma reddish-yellow horizon within the Bt-horizon in the upland

soil may have resulted from the altered hydrology as a result of ditching (the “red-edge effect”). The effect of cattle trampling is evident within the top 10 cm of the wetland soils causing an increase in soil BD.

Organic matter and P within the top few centimeters of the soil profile were highest compared to the rest of the soil profile; both were at least partially derived from manure inputs. Restricting the cattle from entering the wetland could help control the high P concentrations seen at the surface. Although not supported by measured data, moderation of cattle stocking ratios is probably the most effective means of decreasing the effect of overgrazing and erosion, in addition to reducing P inputs from cattle activity at the surface in the uplands. Significant amounts of P were also found within the deeper Btg1 and Btg2 horizons (upland), and in the clay horizons below 100 cm in the wetland. The vertical translocation of P due to infiltration may result in further accumulation of P at those depths. Net TP reserves within the deeper horizons are nontrivial, and cannot be ignored when computing P budgets. The clay horizon accounts for nearly 25% of TP ha⁻¹ of the measured soil profile in the upland, and 17% of TP ha⁻¹ of the measured soil profile in the wetland. Further investigation of soil characteristics in the deeper horizons on neighboring wetlands is encouraged to improve our understanding of below-ground soil P dynamics and in delineating soil properties in response to ditching and surrounding land-use practice.

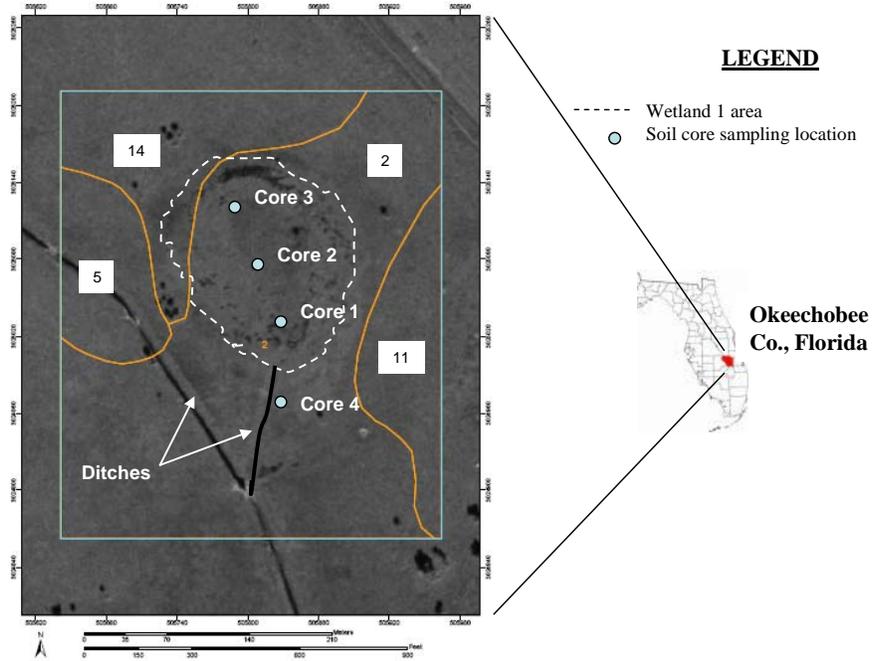


Figure 2-1. Location of four soil cores collected from Wetland 1. Soil survey map units for the area: [2] Basinger fine sand; [5] Valkaria fine sand; [11] Imokalee fine sand; [14] Myakka fine sand.

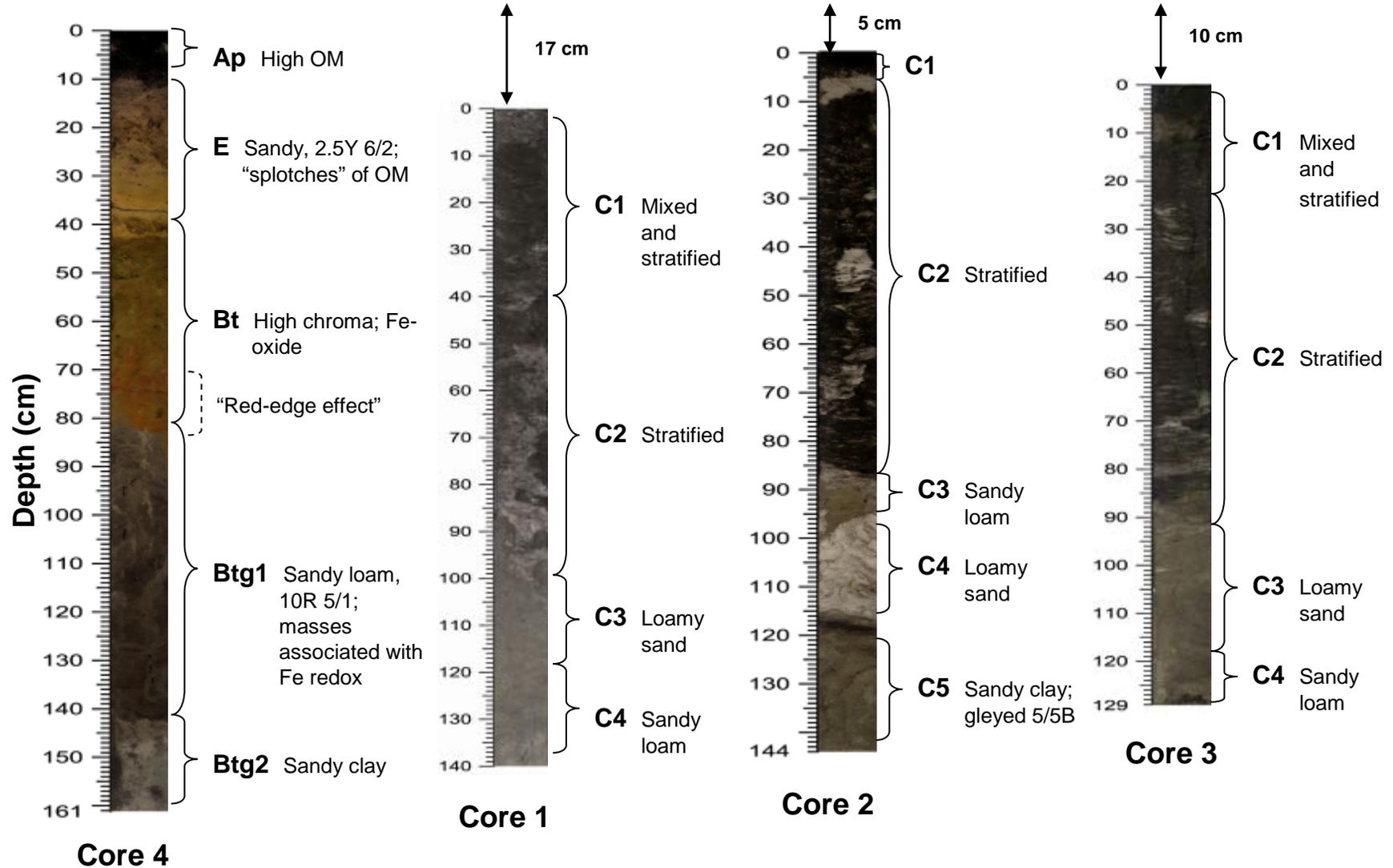


Figure 2-2. Soil description. Cores 1, 2, and 3 were collected from the wetland, while Core 4 was collected from the upland < 20 meters from the ditch. Relative difference in elevation from the upland shown on the top.

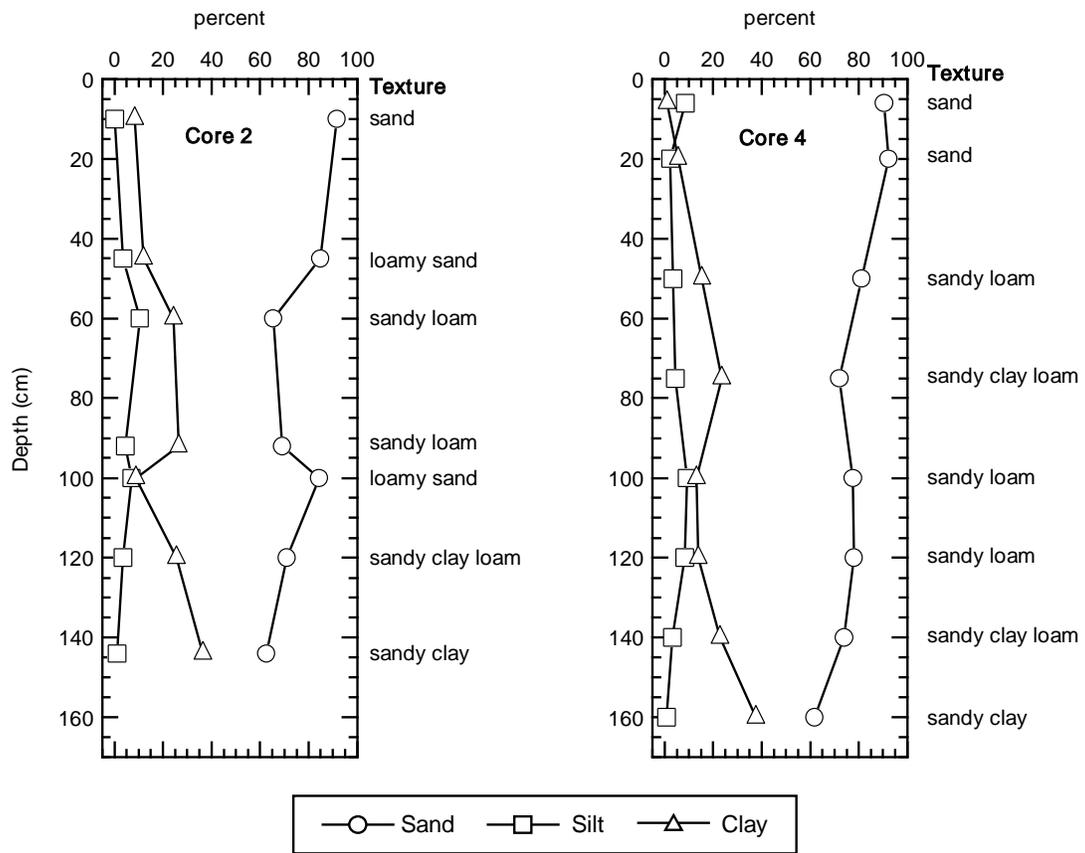


Figure 2-3. Particle size distribution and soil texture based on the soil texture triangle for Core 2 (wetland) and Core 4 (upland).

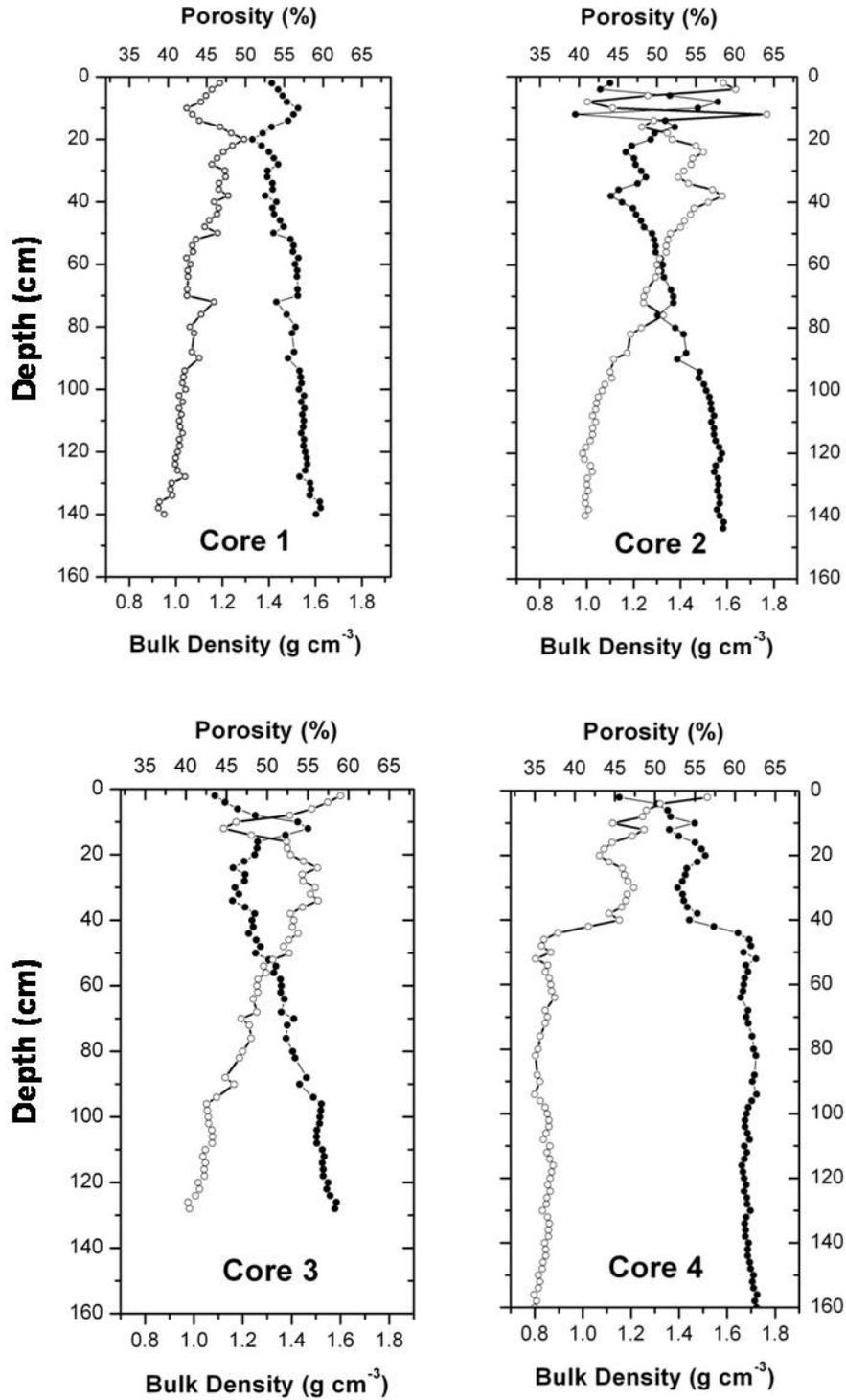


Figure 2-4. Changes in soil bulk density (solid circles), and porosity (empty circles) with depth.

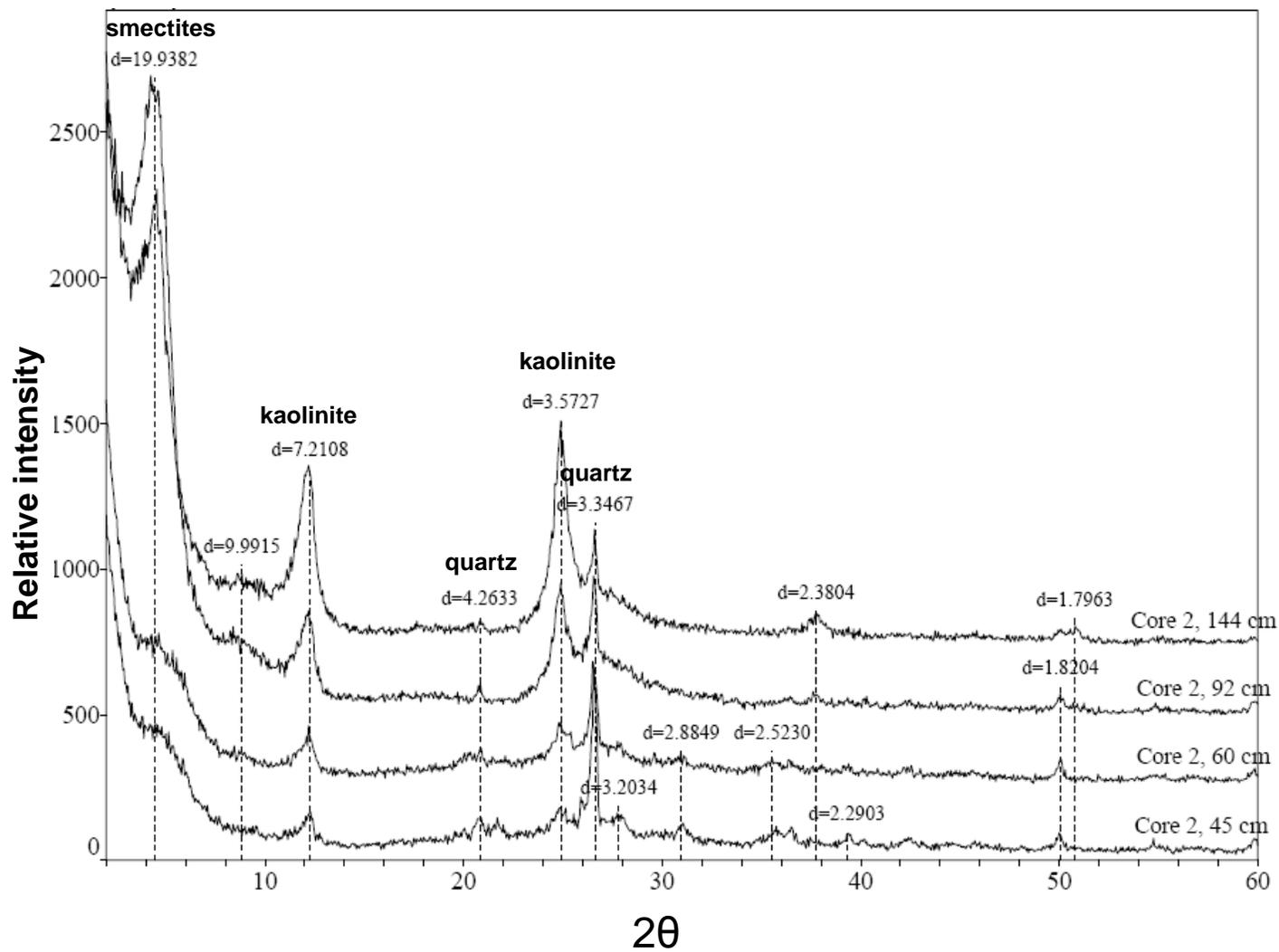


Figure 2-5. Sequences of X-ray diffraction patterns for soil clays from Core 2 at four different depth intervals, and scanned at 25°C after cation-saturation of MgCl and glycerol.

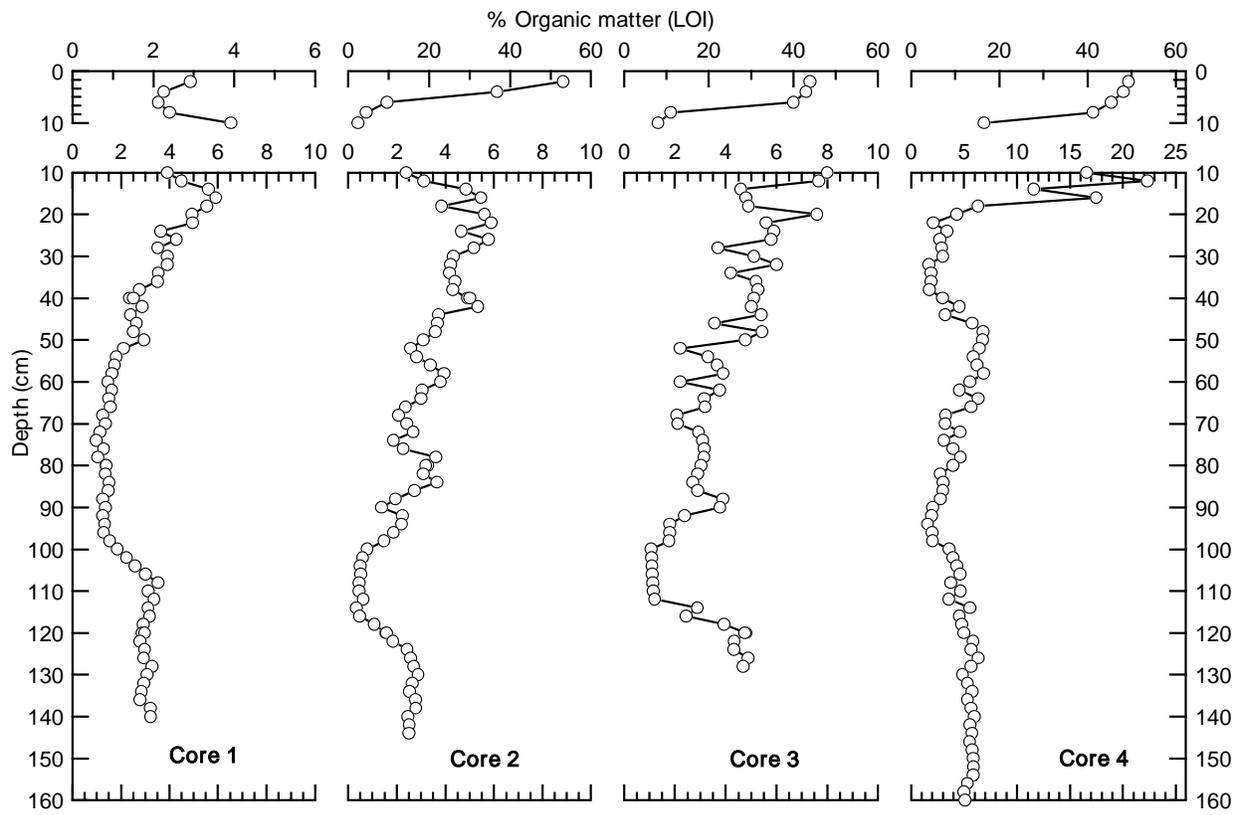


Figure 2-6. Changes in soil organic matter content with depth.

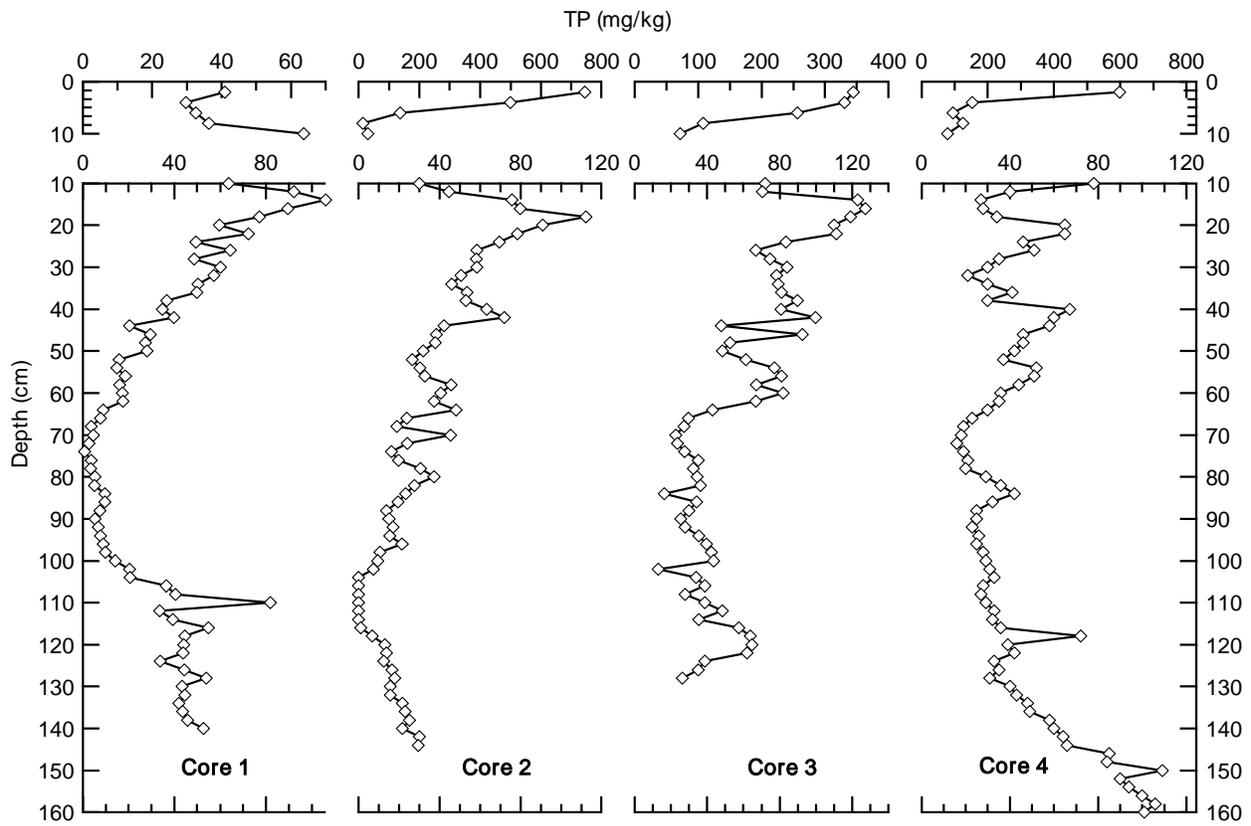


Figure 2-7. Changes in soil total phosphorus with depth.

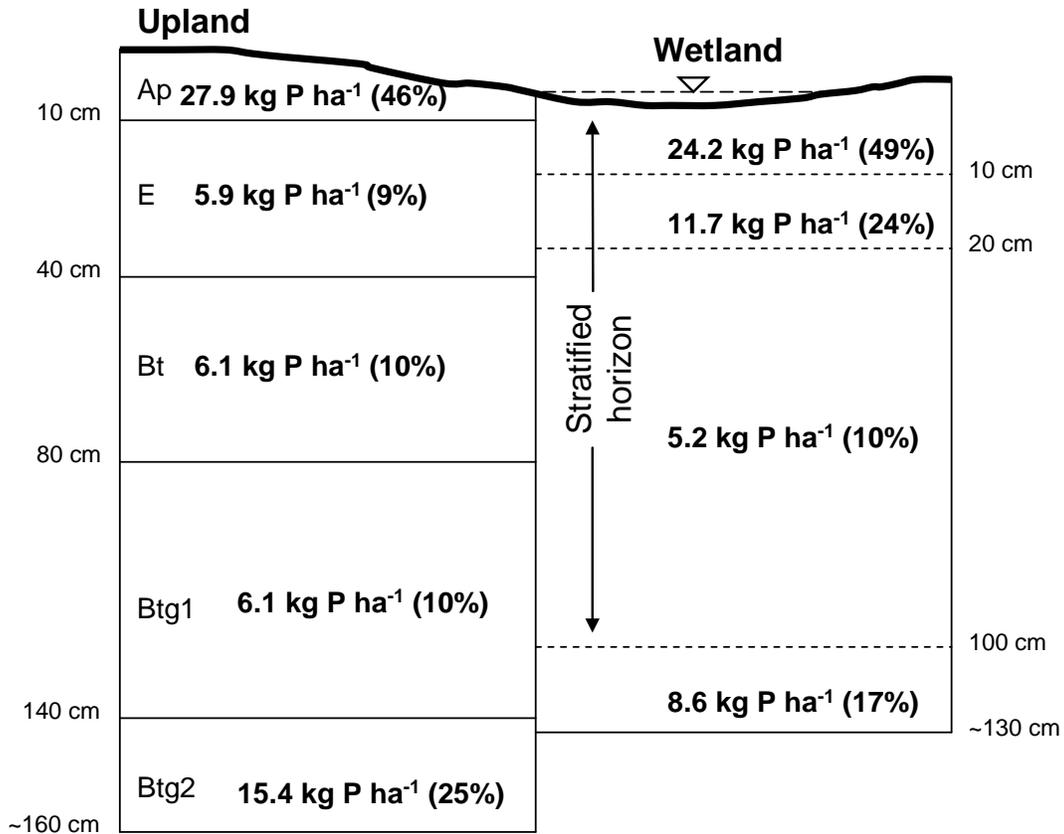


Figure 2-8. Amount of TP (kg ha⁻¹) estimated within various soil horizons in the upland and wetland.

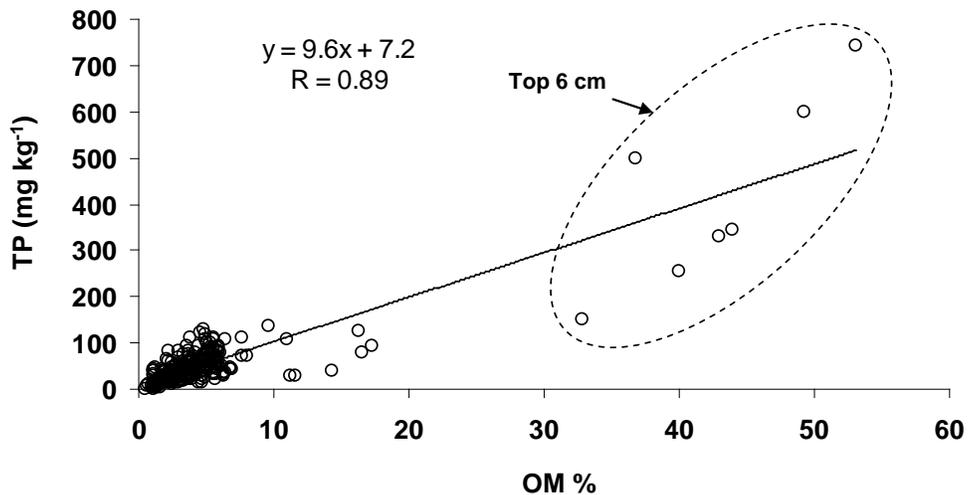


Figure 2-9. Correlation between soil TP (mg kg⁻¹) versus % OM compared using 280 samples from all four cores. Every 1% increase in OM corresponds to a 10.3 mg kg⁻¹ increase in TP within surface soils (0-10 cm).

CHAPTER 3
PHOSPHORUS FLUXES AND MASS BALANCE CALCULATIONS BASED ON SURFACE
AND GROUND WATER CHEMISTRY

Introduction

The internal loading of P from sediments and soils has been identified as a critical component of the nutrient budget that can control the trophic conditions of aquatic systems such as lakes and wetlands (Berner, 1980; Håkanson, 2004). Within the Lake Okeechobee drainage basin, this internal release of P from shallow aquatic systems can occur via two different mechanisms: (i) release at or below the sediment-water interface during hypoxic or anoxic conditions, and the subsequent *diffusion* of dissolved P to the overlying water column (Moore et al., 1998; Fisher and Reddy, 2001; Pant and Reddy, 2003); and (ii) *advection* as a result of a fluctuating water table (Corstanje and Reddy, 2004). Studies conducted by Moore and Reddy (1994), and Reddy et al. (1995) in Lake Okeechobee have shown that the mean P flux ($\text{mg m}^{-2} \text{d}^{-1}$) as a result of internal P loading from bottom sediments is approximately equal to the rate of external P loading ($\sim 1.0 \text{ mg m}^{-2} \text{d}^{-1}$). Based on their conclusions the primary source of P that constitutes an internal load is the organic matter within the topmost sediments.

The implementation of P control programs in the Okeechobee basin resulted in a decline in P loading from early 1980s to 1990 (Havens, et al., 1996), however P loads to Lake Okeechobee still remain over the legally mandated target primarily because of discharge from tributary basins such as Nubin Slough and Taylor Creek that have active beef cattle and dairy operations within their watersheds. External loading of P from agricultural and cattle areas has been addressed through the implementation of best management practices (Bottcher et al., 1997), and interception strategies that involve the restoration of isolated wetlands in the state of Florida (Rice et al., 2002). Internal loading through impacted soils, however, has prevented the rapid improvement of water quality within the basin. In addition, wetlands that are exposed to less than

100% hydroperiods can also be affected by drawdown events that increase soil oxidation and subsequent mobilization of P during reflooding (Bostic and White, 2006).

In the past, P fluxes from wetland soils have been routinely estimated using a general procedure that involves exposing a soil core to a layer of P-free water (Olila et al., 1997; Fisher and Reddy, 2001; Pant and Reddy, 2003; Dunne et al., 2006); concentration gradients between the water column and pore water were measured over time to generate a flux (mass area⁻¹ time⁻¹). However, these are typically abiotic experiments, in which plants are absent, and transport via groundwater flow is non-existent. Hence, such experiments place a limit on how much labile P can be released under low flooding conditions, and it is dangerous to extrapolate the results to full-scale field scenarios as they fail to capture P fluxes associated with the advective mode of transport (Kadlec and Wallace, 2008). Wetlands within the Okeechobee basin remain dry for prolonged periods, and water levels can remain below the land surface for months due to periodic drought conditions in Florida (McKee, 2005; Perkins, 2007), and draining as a result of ditching. This would allow shallow ground water (pore water) to act as a potential source of P that can advect internally as the water table rises above the soil-water interface and mix with the water column. Zhang et al. (2006) showed that up to a 20% P load reduction from beef cattle ranch facilities within the Okeechobee drainage basin could be achieved by maintaining a fixed surface water detention depth of 0.5 inches on the landscape. It is hypothesized that under fluctuating water table conditions, the internal load of P from an impacted isolated wetland may be significant compared to diffusion. The ability to estimate the load depends on measuring the flux accurately. Figure 3-1 represents a conceptual model of surface and ground water hydrology based on a fluctuating water table. Quantifying diffusive and advective P fluxes from these

wetlands can be useful for ecosystem managers to determine the importance of internal versus external P loading, enabling them to develop strategies to mitigate such loads.

When dealing with a shallow-water system such as a wetland, a simple one-dimensional (depth) diagenetic model such as Fick's first law of diffusion is often used to estimate the vertical flux based on close-interval estimation of pore water nutrient concentration gradients (Berner, 1980; Harper et al., 1997). Such models assume microbial-mediated processes are uniform horizontally (American Society of Limnology and Oceanography, 1998). Nutrient gradients can be measured from pore water samples using equilibration devices such as peepers (Pardue and Jackson, 2001) or multisamplers (Martin et al., 2003). Quantifying nutrient fluxes via advective modes is slightly more difficult, as they depend on transient processes that are harder to calibrate and measure, such as wind effects, wave action, and fluctuating water tables. Some of the techniques used in the past to quantify advective fluxes include chemical tracers (Rama and Moore, 1996), ground water modeling (Pandit and El-Khazen, 1990), and seepage meters (Micheal et al., 2003).

In this chapter I present results from a field study that was done to estimate P fluxes inside and outside of the wetland. The objectives of the study were to: (i) calculate diffusive and advective fluxes of soluble reactive P (SRP) based on *in-situ* measured pore water concentrations; (ii) develop a P budget that will help evaluate the importance of diffusion and advection from wetlands affected by flooding and drying cycles.

Sampling and Analytical Methods

The location of sampling sites is shown in Figure 3-2, and the various sampling techniques and analytical methods used are described below.

Pressure Transducers

The wetland surface water elevation was monitored for a three year period between 2003-2006 (Perkins, 2007). For this study, an 11-month period between May 2005 and March 2006 was selected for monitoring work, sampling, and testing water quality. An internally-logging pressure transducer (Mini-troll STP, In-situ, Inc.) was deployed in a 0.032 m diameter fully-screened, PVC well in the deepest location of Wetland 1. The wetland monitoring well was 3.0 m deep below ground surface, and the above-ground portion of the monitoring well was housed inside a larger diameter PVC casing (0.051 m diameter) to provide structural protection. Wetland water surface elevations were recorded at half-hour intervals and were subsequently averaged on daily time intervals. A simple input/output hydrologic budget was used to estimate daily changes in stage (cm) in wetland water elevation, that was later used to calculate the velocity (v) at which the ground water fluctuated with time (cm d^{-1}) (Perkins, 2007).

Multi-level Samplers

Surface and pore water sampling was conducted on six occasions from Wetland 1 during the monitoring period (July-05, September-05, October-05, January-06, February-06, March-06). On each of these occasions surface water samples were collected by the simple dip and grab method in 100 ml polypropylene bottles. Depth variable groundwater (pore water) samples were collected using a multisampler, which is simply a multilevel piezometer (Figure 3-3 A). Three such multisamplers (MS1, MS2, and MS3) were deployed in the wetland 60 meters apart. A peristaltic pump was used to extract water from sampling ports located at 10 cm depth increments up to 110 cm below the soil-water interface. Approximately 100 ml of pore water was purged prior to sampling, so as to discard any residual water remaining in the tubes from previous sampling. Water samples were acidified, preserved, and transported to the University of Florida where they were analyzed for soluble reactive phosphorus (SRP) using a Technicon

AAII autoanalyzer. Standard EPA method 365.3 was used for analyzing SRP. Analytical precision was calculated by analyzing duplicates every tenth sample, and calculating relative percent difference (RPD) for each sampling event ($RDP < 5\%$).

Pore Water Equilibrators (peepers)

In addition to the multisamplers, in August 2008 three pore water equilibrators (peepers) were deployed in Wetland 1 and 2 to capture vertical changes in solute concentrations at every 1 cm depth interval near the soil water interface. Using peepers helps identify the precise depth (± 1 cm) below the soil-water interface where ground water concentration is highest. In contrast to the multisampler, peepers can provide a much finer resolution in concentration gradients but limit the pore water volume to 8 ml, only enough for analysis of a single analyte. For this study I was only interested in SRP concentration. The three peepers in each wetland were deployed strategically, one near the head of the wetland (or entrance of the ditch), the second in the center of the wetland, and the third at the boundary of the wetland. This provides insight into the spatial variability of the of pore water concentrations within the wetland.

The peepers used in this study were similar in design to the device described by Hesslein (1976). It consisted of a $2 \times 10 \times 60$ -cm laths of acrylic into which are milled 8-cm^3 cells that were spaced vertically 1 cm apart (Figure 3-3 B). The cells were filled with deionized water, covered by a sheet of $0.2 \mu\text{m}$ polyethersulfone membrane with a $300 \mu\text{m}$ sheet of silk netting placed over it. An acrylic cover was tightly screwed on to the lath, and the entire set-up was placed in containers, sealed, and purged of O_2 using a N_2 gas line for 48 hours prior to field deployment. On site, the peepers were pushed into the wetland soil so that 10 cells (10 cm) were in the water column, and the remaining cells were buried below ground. Equilibrium studies have shown that between 2-3 weeks is sufficient time for the solution inside the cells to

equilibrate with pore water P (Carignan et al., 1985). The equilibration period for this study lasted for 19 days, and during this time tropical storm Fay passed directly over the wetlands. After the equilibration period, the peepers were retrieved from the soils, and the water samples drawn out of individual cells using a syringe, acidified, and stored at 4 °C until analysis.

Flux Calculations

Diffusive fluxes were calculated using Fick's first law (Berner, 1980):

$$J_D = -\phi D_s \frac{\partial C}{\partial z} 8.64 \times 10^5 \quad (3-1)$$

where J_D is the vertical diffusive flux ($\text{mg m}^{-2} \text{d}^{-1}$), ϕ is the porosity ($\text{cm}^3 \text{cm}^{-3}$), D_s is the bulk soil diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$), $\partial C/\partial z$ is the concentration gradient with respect to depth z (cm), and 8.64×10^5 is a units conversion. Porosity of soil for each location was depth averaged from an intact core study up to 10 cm depth. Li and Gregory (1974) reported the diffusion coefficients of HPO_4^{2-} and H_2PO_4^- in pure water as 7.34×10^{-6} and $8.46 \times 10^{-6} \text{cm}^2 \text{s}^{-1}$, respectively. An average of the two values was used for our calculations ($7.9 \times 10^{-6} \text{cm}^2 \text{s}^{-1}$). The diffusion coefficient was modified for the restrictive effect of soil structure by dividing it by the square of the soil tortuosity Θ . Where $\Theta^2 = 0.47\phi + 1.91$ (Berner, 1980; Sweerts et al., 1991).

Ground water advective fluxes were estimated using the hydraulic loading rate (q) of ground water moving in and out of the wetland (cm d^{-1}) derived from hydrologic budget calculation (Perkins, 2007), and multiplying it by either the pore water concentration (C_{pw}) of SRP for fluxes into the wetland, or multiplying by the surface water concentration (C_{sw}) of SRP for fluxes out of the wetland.

$$J_{in} = qC_{pw} \quad (3-2)$$

$$J_{out} = -qC_{sw} \quad (3-3)$$

This would suggest that at times the advective flux (J_{in}) would be positive (+) and move up from

the pore water into the water column, and at other times the flux (J_{out}) would be negative (-), i.e., when the water table drops below the soil-water interface carrying dissolved P with it. Advective fluxes (+/-) were computed for times when the water table drove solutes in and out of the wetland between May 05 to March 06. Diffusive fluxes were calculated for all six sampling periods. While diffusion can occur at all times when the wetland is flooded, advection from groundwater to the wetland is limited only to times when the water table rises across the soil-water interface, based on the hydraulic loading rate (q). The process can be considered as a single event-based process that occurred five times during the monitoring period. The downward advection from the water column back into groundwater was calculated for times when the wetland stage drops due to infiltration into the ground.

Using the Damköhler Number to Evaluate Pore Water Concentration (C_{pw})

The Damkohler number (D_a) is a unit less parameter that has been used to evaluate the rate of change by a reaction over the rate of transport by advection (Kadlec, 2000; Carleton, 2002).

Defined as:

$$D_a = k_v L / u \quad (3-4)$$

where k_v is the volumetric rate constant (s^{-1}) used to evaluate the sorption reaction between the soil and pore water as the front moves upwards within the soil profile; L is the soil length; and u is the pore water velocity ($m\ s^{-1}$). Chen et al. (1996) estimated rate coefficients for a two-site kinetic model reaction through columns of dry sandy spodic soils (Myakka) ranging from 1.2×10^{-3} to $4.4 \times 10^{-3}\ s^{-1}$. Using this range of k_v and different velocities of the wetting front (ranging between 3 and 30 $cm\ d^{-1}$) I was able to estimate D_a for different scenarios of high and low velocities. The use of pore water concentrations measured at 10 cm depth for all times when calculating J_{in} was justified by a large D_a (>10) ranging between 35-1294, meaning that the soil

and pore water were in equilibrium based on the residence time of the slow-moving wetting front.

Using Peclet Number to Evaluate Magnitude of Diffusive Versus Advective Flux

The Peclet Number is a dimensionless number (P_e), which works out to be the product of system length (L) and fluid velocity (U), divided by diffusivity (D); such that, $P_e = LU/D$.

It is the measure of the relative importance of advection to diffusion processes in the system. For any given system, the higher the Peclet number ($P_e \gg 1$), the more important is advection. Similarly, smaller the Peclet number ($P_e \ll 1$), diffusion become the more important mode of solute transport in the system. This approach can be used to evaluate whether P fluxes across the soil-water interface into the wetland water column are dominated by advective or diffusive processes. Clearly, the bigger the L the higher the P_e . Hence it is important to set spatial and temporal boundary conditions because P_e will vary with varying boundary conditions.

To calculate the P_e within a 1 m² soil domain, we assumed steady state conditions with a velocity of 3 cm d⁻¹. The diffusivity of diffusion coefficient was 10⁻⁶ cm² s⁻¹ (0.0864 cm² d⁻¹, Li and Gregory, 1974). Based on the above values $P_e = 3472$, suggesting that advection would be the dominant mode of solute transport. If we were to reduce the soil domain to just 10 cm, the P_e would still be $\gg 1$, and advection would still be dominant. Using this simple calculation we can come up with a good first estimate that advective processes are more dominant than simple molecular diffusion at the wetland sites.

Phosphorus Budget

The P budget was based on a simple input versus output equation, comprising parameters whose cumulative P mass loads (kg) were estimated over the eleven-month monitoring duration:

$$C = A + R + GW_{in} - GW_{out} - D \quad (3-5)$$

where C is the amount of P in the wetland generated from input parameters such as atmospheric

loading (A), surface runoff (R), and ground water loading into the wetland water column associated with diffusive and advective fluxes (GW_{in}), and output parameters such as ground water load out of the wetland water column related to the advective flux (GW_{out}), and load exiting the wetland via ditch flow (D).

Ahn and James (2001) estimated atmospheric P concentration in the Okeechobee drainage basin area to vary between 6.8 to 32.6 $\mu\text{g L}^{-1}$ depending on wet and dry seasons respectively, with an annual average of 0.112 $\text{mg P m}^{-2} \text{d}^{-1}$. Using this estimate we calculated atmospheric loading to the wetland based on the periodicity of rain events. Concentration of P from pasture runoff was not measured as part of this study; however, Capece et al. (2007) reported concentrations of P from pasture runoff ranging between 0.15-0.63 mg L^{-1} based on a six year average (1998-2003) from a nearby ranch (Buck Island, Florida). For this study runoff P concentration of 0.6 to 1.0 mg L^{-1} (reported in Reddy et al. 1999) was used as a range of best estimate values based on review of water quality data provided by the South Florida Water Management District related to a beef cattle density of 1.2 cow ha^{-1} and improved pasture as the land type. Phosphorus load exiting the wetland via the ditch was calculated using the volumetric loss of water via the ditch times the concentration of surface water in the wetland for periods when the wetland stage is greater than the bottom of the ditch elevation (0.3 m).

Results and Discussion

Wetland Hydrography and Hydroperiod

Both wetlands 1 and 2 are situated at the head of a ditch, with no ditch inflows, thus sources of inflow to the wetland are only from rainfall, surface runoff and ground water input mechanisms. These inflows should account for surface water storage, evapo-transpiration (ET), ditch flow out of the wetland, and groundwater discharge. Based on the stage data from wetland 1, the wetland remained flooded for 230 days out of the 335 days of monitoring; the remaining

105 days the water table remained below the ground surface (Figure 3-4). One of the key controls on ground water nutrient cycling processes in seasonally flooded wetlands is the alternation between flooded and dry conditions. During the monitoring period wetland 1 exhibited this type of seasonal variation on six occasions: thrice when the wetland was dry and the water table rose up past the soil surface and flooded the wetland, and thrice when the stage of water in the wetland gradually dropped below the soil surface. The maximum water table fluctuation was between 56 cm above ground and 88 cm below ground surface. The average yearly rainfall in Okeechobee County is between 1.3 and 1.6 m (Lewis et al., 2001). During the monitoring period, precipitation was just below the annual average at 1.16 m. Severe drought conditions rendered these wetlands dry for prolonged periods and since April 2006, the wetland remained dry until July 2008, except for a few days between July and October 2007. In July 2008, the wetlands were flooded once again and the water level in the wetland was 120 cm above ground after tropical storm Fay (08/19/2008).

The U.S. Geological Survey (U.S.G.S.) has been involved in monitoring real-time surface and ground water data for over two decades. The data are accessible to the public (<http://waterdata.usgs.gov/nwis/rt>). I used five-year stage data from one of the U.S.G.S. monitoring sites (Cypress slough, near Basinger, FL), which is within 30 km from the wetland sites to estimate the yearly hydroperiod of our study site. The calibration was based on the same 335-day monitoring period of our study. The relationship between our wetland measurement and the U.S.G.S. stage data was fitted using a sixth order polynomial curve ($r^2 = 0.58$) (Figure 3-5, top). Using the equation of the line represented by the fit between the U.S.G.S. stage data and the wetland, I was able to estimate the average yearly hydroperiod of the wetland from the beginning

of 2004 to the end of 2008. Results show that from 2004 to 2008 the wetlands have only been inundated for short periods (Figure 3-5, bottom).

Ground Water Chemistry

Ground water chemistry was evaluated based on the pore water samples collected using multisamplers (during the 2005-2006 monitoring period), and peepers (in August 2008). During the 2005-2006 monitoring period, wetland 1 pore water concentrations of SRP showed both spatial and temporal variability (Figure 3-6). Concentration of SRP was highest at 10 cm depth for all six sampling periods; the mean values were $3.9 \text{ mg L}^{-1} (\pm 2.1)$ at MS1, $3.4 \text{ mg L}^{-1} (\pm 1.4)$ at MS2, and $2.2 \text{ mg L}^{-1} (\pm 0.4)$ at MS3. It is not unusual for pore water P concentrations to be high in the surface horizons due to inputs from plant-associated P during senescence and manure inputs from cattle activity. With depth, SRP concentration drops to $< 0.02 \text{ mg L}^{-1}$ below 80 cm depth at MS2 and MS3, however, SRP concentrations increased below 70 cm at MS1. This could be a result of the upward diffusion of P from the deeper horizons that could have transported water from high concentration zones to get intercepted at those depths. At all three sampling locations the lowest concentrations at the surface (10 cm depth) were measured during the February (winter) sampling event, while the highest concentrations were observed between July-October (hurricane season) sampling events.

Pore water SRP concentrations were also measured at three locations from wetlands 1 and 2 during a one time sampling event using peepers in August 2008 (Figure 3-7). Results show that in wetland 1 pore water concentration of SRP at P1 is highest at 11 cm below the surface (12.5 mg L^{-1}). At P2 and P3 SRP concentrations are highest at 9 cm (6.7 mg L^{-1}) and 8 cm (6.2 mg L^{-1}), respectively. In wetland 2 pore water concentrations of SRP at P4 is highest at 17 cm (7.2 mg L^{-1}) below the surface. At P5 and P6 SRP concentrations are highest at 8 cm (4.6 mg L^{-1}) and 7 cm (7.0 mg L^{-1}), respectively. The concentration of pore water SRP analyzed from the peepers

nearest to the ditch were relatively higher than those from either the center of the wetland or its boundary. Regardless of the sampling locations SRP pore water concentrations measured using the peepers in August 2008 were significantly ($p < 0.01$) greater than those measured using multisamplers during the 2005-2006 sampling events. It is believed that this increase in pore water concentrations may be directly related to an event-based phenomenon associated to tropical storm Fay. While it is also possible that P loading to the wetland in 2008 was greater than in 2005-2006, Olila et al. (1997) showed that dissolved reactive P from drained soils that were rapidly reflooded were four times higher compared to controlled, continuously flooded soils.

While the shallow ground water P concentrations are useful in calculating diffusive fluxes to the wetland water column, concentrations deeper in the profile provide insight into the below ground dissolved P repository that could potentially advect to the surface driven by a fluctuating water table.

Diffusive Fluxes of P Based on Fick's First Law

Based on the concentration gradients between the pore water and the surface water the direction of the diffusive fluxes was always from the ground (pore water) to the water column (positive). The upward flux of SRP from the soil into wetland 1 was estimated for all six sampling events, with highest rates observed at MS1 (Figure 3-8). Out of the six sampling events the highest rate of SRP flux to the water column was $0.97 \text{ mg m}^{-2} \text{ d}^{-1}$ recorded during the September 2005 sampling period, while the lowest flux was observed for the month of February 2006 from all three sites (MS1, MS2, and MS3). The high degree of variability in measured fluxes is reflective of the spatial distribution of the multisamplers, and also the temporal variations between surface and pore water concentrations because diffusive fluxes are highly redox sensitive. Malecki et al. (2004) and Sen et al. (2007) were able to show that soluble

reactive P flux released from sediments under anaerobic conditions are significantly greater than the flux under aerobic conditions. For our study, the wetlands are only seasonally flooded, hence ground water concentrations (and therefore the fluxes) are highly influenced by changing redox conditions. Nearly 78% (± 18) flux reduction was observed between September (high-flux) and February (low-flux) months from sites MS1, MS2, and MS3.

Diffusive fluxes of SRP were also calculated using the pore water concentration gradients collected from all six peepers that were deployed in wetlands 1 and 2 (Figure 3-9). The diffusive fluxes of SRP calculated using peepers in 2008 were only slightly greater than the ones calculated using multisamplers during 2005-2006, even though the concentration in the shallow pore waters was significantly higher during the August 2008 sampling event. This is primarily because there is relatively little change in the concentration gradients between the two sampling events. The average SRP fluxes calculated using peepers from both wetlands 1 and 2 was $0.84 \text{ mg m}^{-2} \text{ d}^{-1}$ (± 0.31). Several studies have been performed on P fluxes in a variety of aquatic systems using intact soil incubation (Table 3-1). While the diffusive fluxes calculated from this study are lower than those estimated from the peat soils within the Everglades Water Conservation Area (WCA) 2A (Fisher and Reddy, 2001), they are slightly higher than those from within the sandy zones from within Lake Okeechobee (Moore et al., 1998). The concentration gradient is greater between pore water and surface water when the water column is underlain by P-rich peat soils as compared to sandy sediments. It is evident that while the accretion of P-rich material at the soil-water interface could increase the diffusive fluxes, an increase in surface water concentrations from runoff inputs can reduce ground water fluxes from shallow soils (Dunne et al., 2006). However, diffusive fluxes of SRP alone do not account for the total fluxes from shallow soils in the wetland associated with internal loading. Advection plays an integral

role in driving soluble P in-and-out of the wetland, and needs to be accounted for when computing net internal loads.

Advective Fluxes of P Based on Ground Water Fluctuations

During the eleven-month monitoring period the stage of the water in the wetland fluctuated almost daily. Thrice the water level dropped below the soil surface, rendering the wetland completely dry, and then rose, filling the wetland once again. Each fluctuation is indicative of the head difference between the water level in the wetland and the upland. This corresponds to a pulse of P driven in or out of the wetland controlled by the velocity (hydraulic loading rate) of water across the soil-water interface. Once the front crosses the interface ground water can still advect in and out of the wetland carrying with it soluble P (i.e., even under flooded conditions advection via ground water can occur based on the hydraulic loading rate). The net volumetric rate of ground water into and out of the wetland was evaluated based on a hydrologic budget that accounts for changes in precipitation, ET, and surface runoff (Perkins, 2007). Based on the hydrologic budget calculations, during the eleven month monitoring period ground water into the wetland occurs five times for a few of days per month, generating a positive (+) advective flux. During the same period, water from the wetland was drawn down into the ground (ground water out) on eleven occasions (every month), generating a negative (-) advective flux associated with seepage/infiltration (Figure 3-10).

The advective fluxes of P to the wetland via ground water were greater than the diffusive fluxes for all sampling events. Positive advective fluxes were greatest during the month of May 2005, when the water table rose >80 cm in just two days resulting from ~13 cm of rainfall. Ground water flux of SRP to the wetland for that month was $27.4 \text{ mg m}^{-2} \text{ d}^{-1}$, primarily driven by the higher hydraulic loading rate of 1.37 cm d^{-1} (Table 3-2). Negative fluxes were greatest during September 2005 at $45.9 \text{ mg m}^{-2} \text{ d}^{-1}$. During the eleven-month monitoring period, the net

advective P fluxes leaving the wetland were far greater than those entering it via ground water. Nevertheless, the positive advective flux of SRP were nontrivial and indicate that while diffusion temporally dominates the wetland's hydrologic regime (230 days out 335), it accounts for smaller total fluxes than advection via ground water movement.

Phosphorus Budget Estimation From May 2005 - March 2006

The internal loading of P to the wetland water column is primarily associated with the two modes of transport - diffusion and advection. Based on diffusion alone, the cumulative P load to the wetland water column was 5.2 kg (± 1.4), accounting for 52% of the total P load entering the wetland. In comparison, the cumulative P load associated with advection to the wetland was 0.93 kg, accounting for 9% of the total load. The cumulative P load entering the wetland via runoff was estimated at 3.8 kg, accounting for 38% of the total load to the wetland (Figure 3-11). During the monitoring period the cumulative load of P from the atmosphere (dry + wet) was 0.15 kg, accounting for only 1% of the total P loads entering the wetland water column, and was by far the smallest input. The cumulative load of P exiting out of the wetland water column via infiltration was 10.6 kg; by far the dominant component of the P budget, 81% of total P load leaving the wetland water column. The cumulative P load exiting the wetland via the ditch flow was estimated at 2.5 kg during the monitoring period, accounting for only 19% of the P load out of the wetland. It is important to note that wetland vegetation is a vital component of the P budget that can sequester dissolved P by incorporating it into non-labile above and below ground biomass (Dunne et al., 2007a; Kadlec and Wallace, 2008). Conversely, plant colonization during dry periods in P-enriched soils, is a significant mechanism for P release from the soil at the time of flooding (Bostic and White, 2006). This component of the wetland P budget was not evaluated in this study. My calculations suggest that about 3 kg of P was contained within the wetland water column over the eleven-month monitoring period.

Summary and Conclusions

Both advective and diffusive processes need to be evaluated when calculating total P fluxes from wetlands that are affected by flooding and drying cycles. Results indicate that advective fluxes associated with ground water fluctuations are greater than diffusive fluxes based on concentration gradients between surface and pore water. During the monitoring period between May 2005 and March 2006 the wetland hydroperiod was 230 days, and diffusion occurred for the entire period generating a maximum flux of $0.97 \text{ mg m}^{-2} \text{ d}^{-1}$ recorded in September 2005 at sites MS1 and MS2. During the same monitoring period advection occurred for only 21 days, yet generated a maximum flux of $27 \text{ mg m}^{-2} \text{ d}^{-1}$ in the month of May 2005. This pulse of high P flux was a direct effect of a single two-day rain event that caused the ground water to rise rapidly across the soil-water interface. Similar upward movement of ground water was observed on four other occasions during the monitoring period, however, the hydraulic loading rates associated with those events were much slower, hence the fluxes associated with them were much smaller ($2.2\text{-}4.0 \text{ mg m}^{-2} \text{ d}^{-1}$).

Using the online U.S.G.S stage data we were able to calibrate the stage of the water in our wetland, allowing us to extrapolate its hydroperiod over five years. Results indicated that the wetland has been fairly dry for prolonged periods over the last five years. It also shows the number of times the wetlands undergo “drawdown events”; this could have a negative effect on nutrient loading, and also on the ability of the soil to retain P. In the future the wetland stage can be monitored using a 31.5 ft threshold value for the U.S.G.S. site above which the wetland starts to fill assuming the input of water remains the same, and the local topography does not change.

Based on the P budget calculations the internal loading of P to the wetland water column via advection and diffusion accounted for nearly 61% of the total P entering the wetland. By far the greatest sink of P within the wetland was the GW_{out} component via advection as surface

water seeps into the soil. This type of advective transport accounted for nearly 81% of P loss to the wetland. The P budget calculations for this study do not consider all possible sources and sinks, and do not include functions such as plant uptake/release, or the effect of cattle on wetland hydrodynamics.

From a management standpoint maintaining prolonged flooded conditions by increasing the hydroperiod in the wetland may be considered as a strategy to reduce advection and suppress nutrient loading associated with it. Dunne et al. (2007a) proposed a strategy whereby increasing the wetland area by 20% could potentially increase wetland P storage by up to 13 kg ha⁻¹ within plant biomass. Both these strategies could be implemented in the future if wetland restoration work involves either deepening the wetland basin, raising the ditch elevation, or simply damming it.

Table 3-1. Diffusive flux of soluble P from sediments to overlying water in selected aquatic systems

Aquatic System	Diffusive Flux (mg P m ⁻² d ⁻¹)	Reference
<i>Wetland 1 (multisamplers)</i>	0.06-0.97	<i>This study (2005-2006)</i>
<i>Wetland 1 (peepers)</i>	0.61-1.1	<i>This study (2008)</i>
<i>Wetland 2 (peepers)</i>	0.53-1.2	<i>This study (2008)</i>
Lake Apopka, Florida	1.0-5.3	Reddy et al., 1996
Lake Apopka, Florida	0.3-0.7	Olila et al., 1997
Lake Okeechobee, Florida		Moore et al., 1998
Mud zone	0.1-1.9	”
Peat zone	0.2-2.2	”
Sand zone	0.1-0.5	”
Littoral zone	0.6-1.5	”
Indian River Lagoon, Florida	1.6	Reddy et al., 1999
Lower St. Johns River Estuary, Florida	0.13-4.55	Malecki et al., 2004
Everglades (Water Conservation Area-2A), Florida	1.5-6.5	Fisher and Reddy, 2001
Beaver Reservoir, Arkansas	0.01-1.77	Sen et al., 2007
Lake Eucha, Oklahoma	1.03-4.4	Haggard et al., 2005

Table 3-2. A summary of wetland hydroperiod, duration of events, ground water flow, wetland size, and water chemistry on a monthly basis during the monitoring period (May 2005-March 2006). NA = not applicable

	Wetland hydroperiod (d)	Number of days out of 335					GW flow in (cm d ⁻¹)	GW flow out (cm d ⁻¹)	Wetted wetland area (m ²)	Surface water conc. (mg SRP L ⁻¹)	Pore water conc. (mg SRP L ⁻¹)
		Rained	Ditch flow	Runoff	GW _{in}	GW _{out}					
May	6	8	0	2	2	2	1.37	6.06	831	0.40	2.0
Jun	30	19	27	8	8	4	0.15	0.13	18044	0.40	2.0
Jul	31	14	16	2	0	15	NA	0.69	15176	0.49	3.1
Aug	31	15	0	8	0	31	NA	1.53	5529	0.40	2.0
Sep	13	27	0	7	0	12	NA	8.45	1065	0.54	4.6
Oct	16	17	7	5	4	15	0.05	2.07	12618	0.72	4.3
Nov	30	8	14	5	4	26	0.2	0.70	13725	0.40	2.0
Dec	31	6	0	6	0	31	NA	1.06	8728	0.40	2.0
Jan	6	4	0	2	0	6	NA	5.56	2281	0.62	3.2
Feb	25	6	2	4	3	22	0.25	0.83	13021	0.61	1.3
Mars	11	3	0	2	0	10	NA	1.53	6669	0.32	2.6
Total	230	127	66	51	21	174					

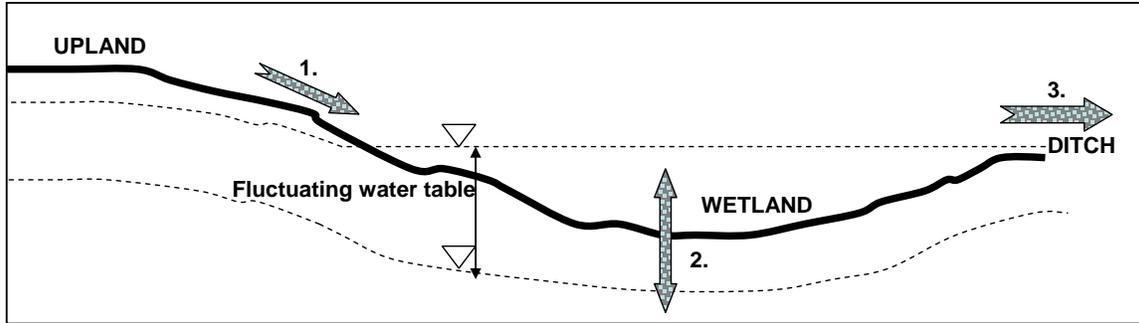


Figure 3-1. Conceptual model of the wetland P-budget shown by arrows representing 1. external load entering the wetland, 2. internal loading (diffusive and advective fluxes) within the wetland, 3. total load exiting the wetland via ditch. Due to seasonal fluctuation of the water table, groundwater is an important source of P to the wetland.

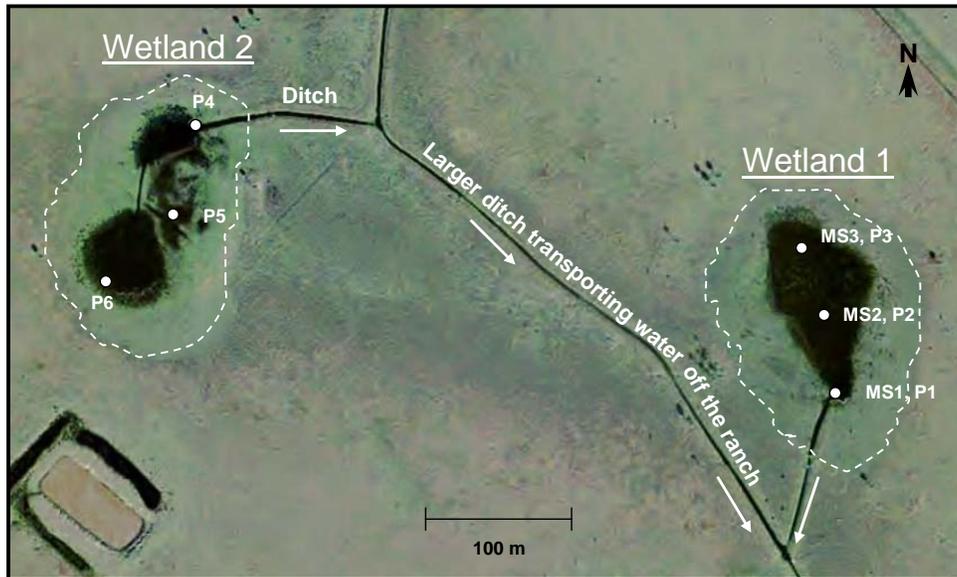


Figure 3-2. Map of ground water sampling locations. Three multisamplers (MS1, MS2, and MS3) and three peepers (P1, P2, and P3) used to sample pore water from Wetland 1, and three peepers (P4, P5, and P6) used to sample pore water from Wetland 2.

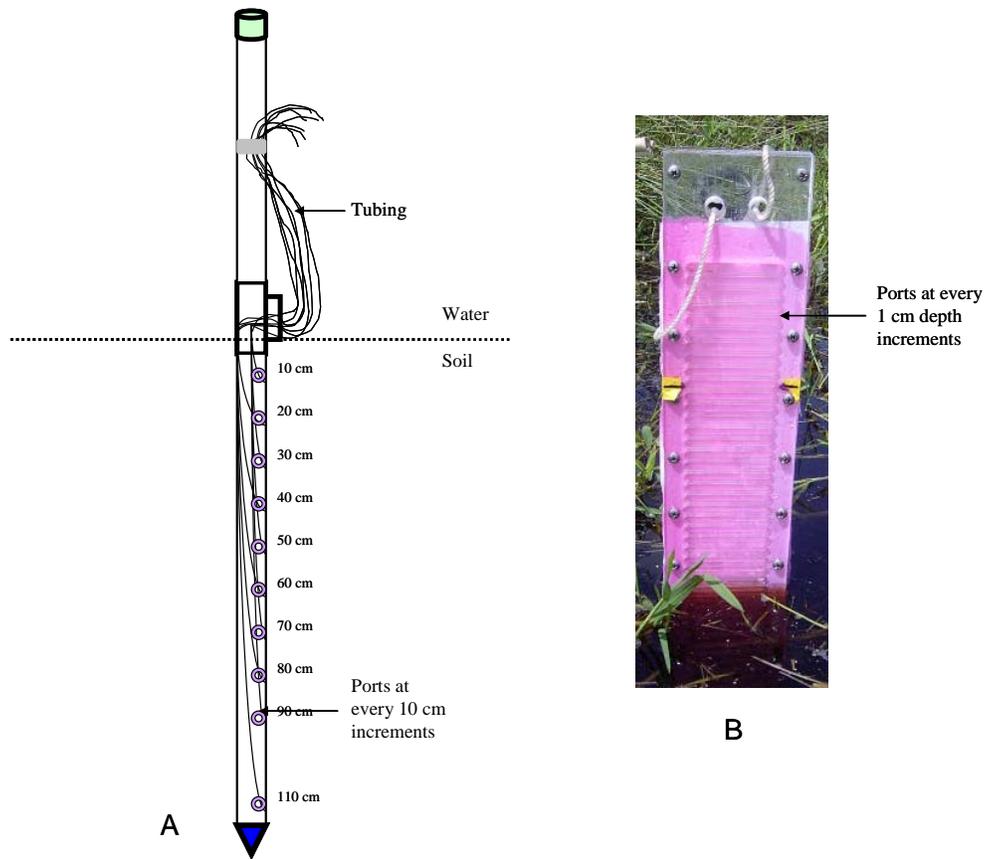


Figure 3-3. Pore water sampling devices. A) Multisampler consisting of sampling ports at 10-cm depth increments. B) Pore water equilibrator (peeper) consisting of sampling port at 1-cm depth increments.

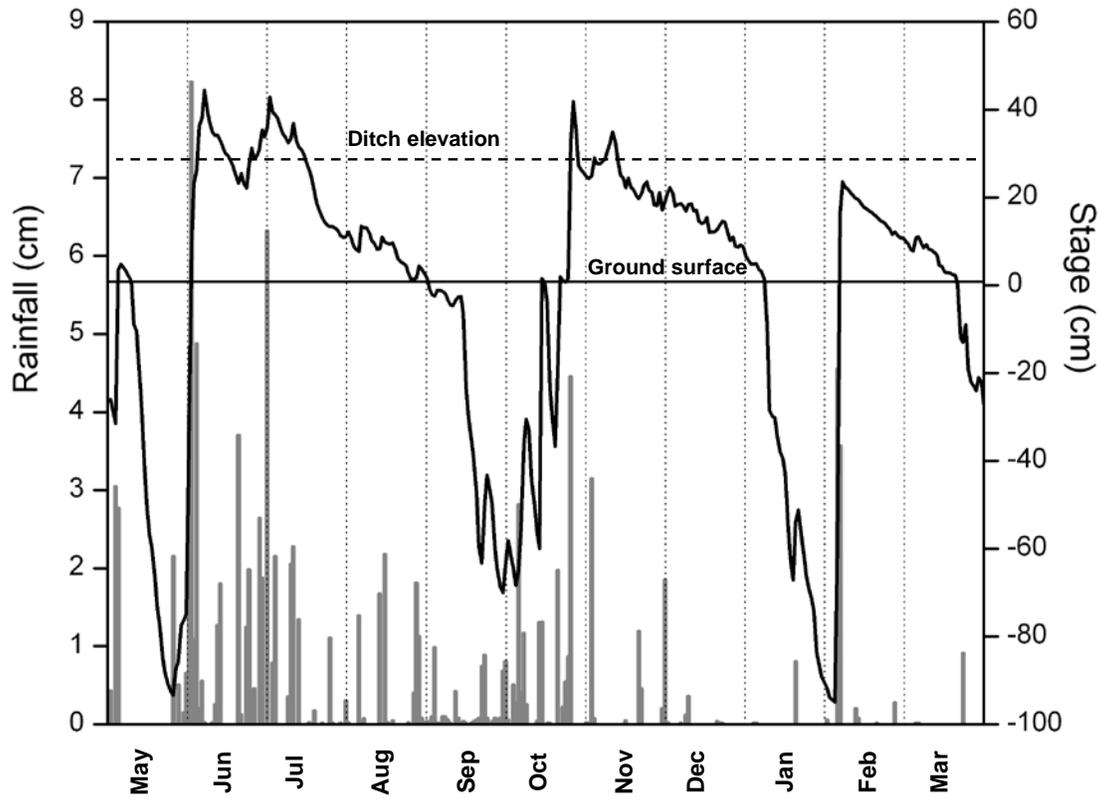


Figure 3-4. Rainfall represented in grey bars and water table (stage) fluctuation in solid black line during the monitoring period between May 2005 and March 2006.

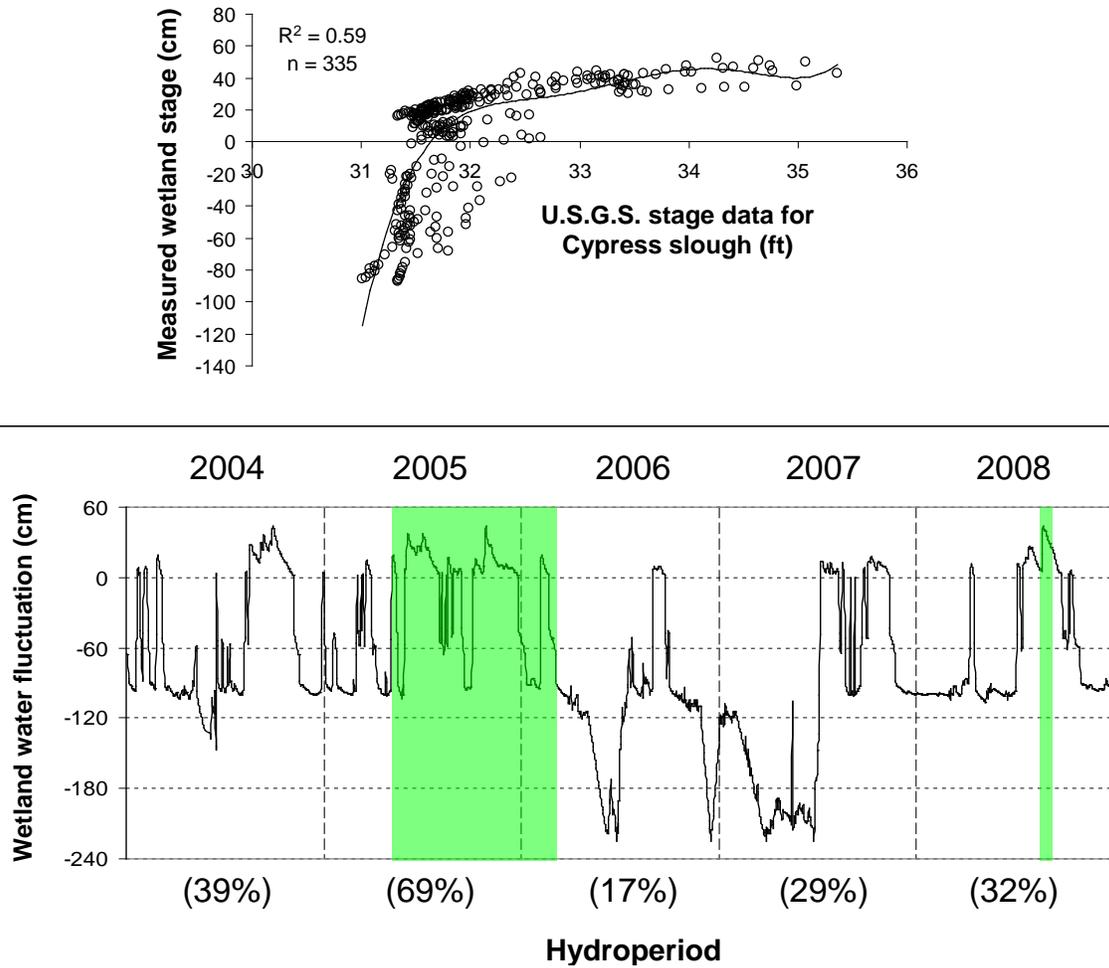


Figure 3-5. (top) Relationship between U.S.G.S. stage data (Cypress slough, near Basinger, FL) and measured wetland stage data for 335 days. Trendline represents a polynomial fit used as a calibration for extrapolating wetland hydroperiod. (bottom) Wetland hydroperiod (%) estimated for five years from 2004 to 2008. The two shaded areas represent the monitoring duration used for this study.

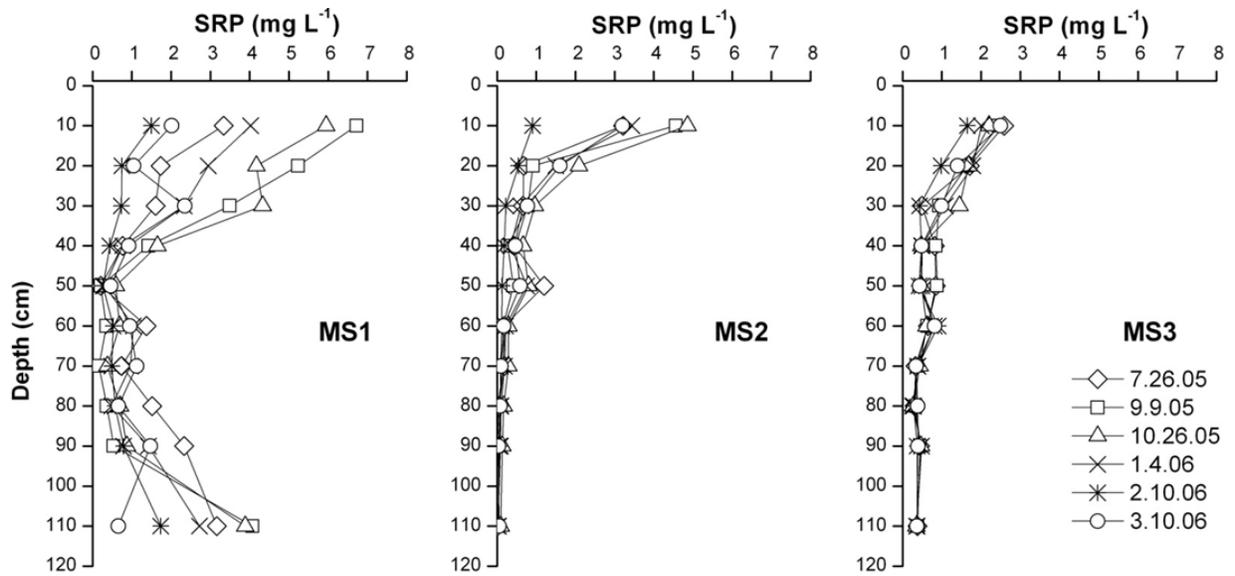


Figure 3-6. Pore water concentration of soluble reactive phosphorus (SRP), measured at three separate locations (MS1, MS2, and MS3) within Wetland 1 using a multisampler. Concentrations were measured for times throughout the monitoring period. Dates are month.day.year.

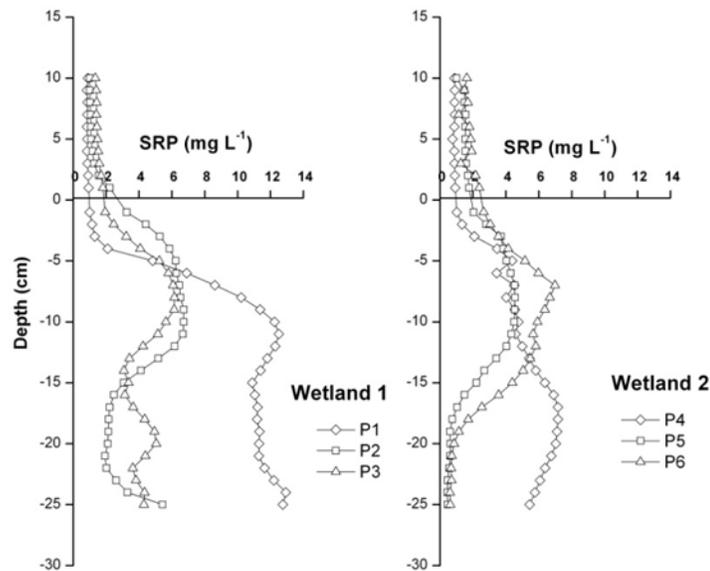


Figure 3-7. Pore water concentrations of SRP measured using peepers from Wetlands 1 and 2 in August 2008.

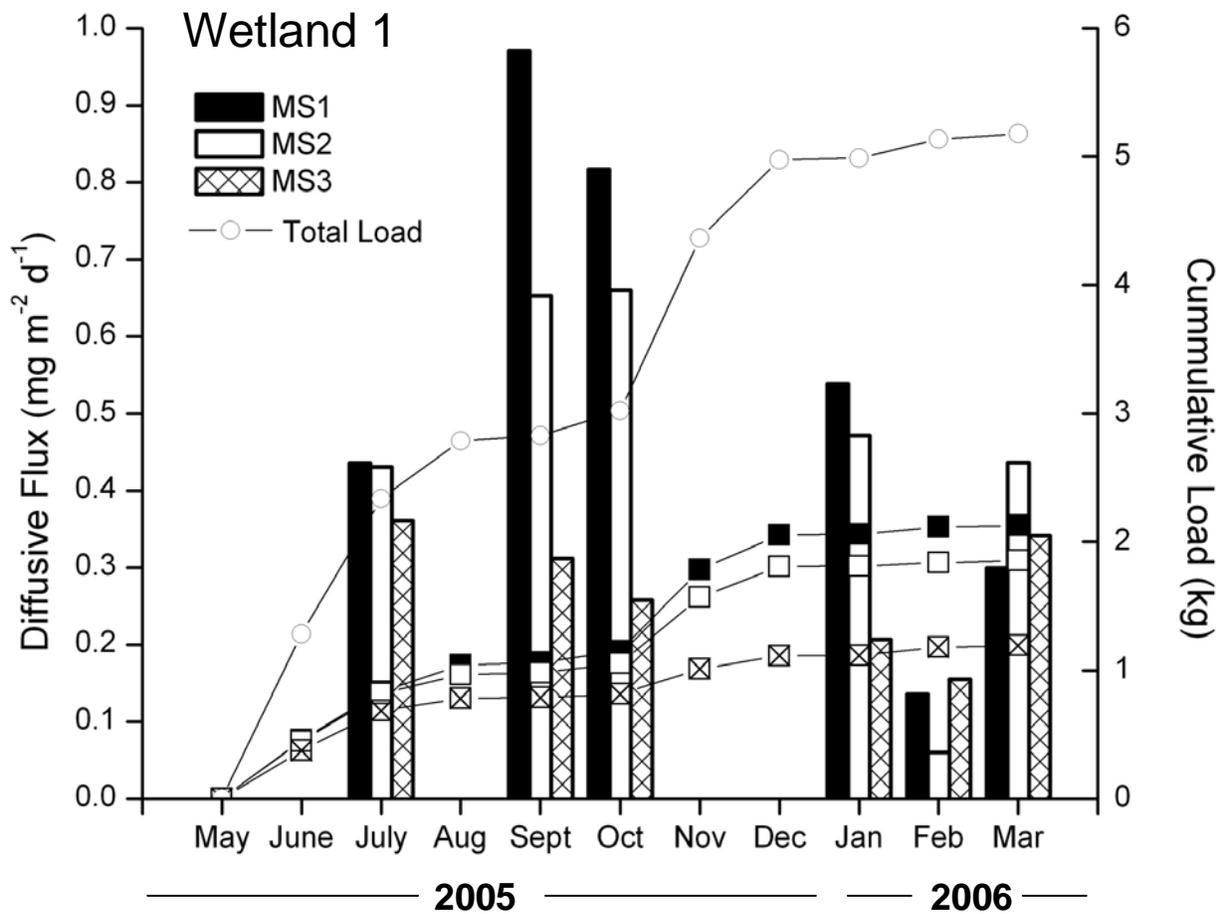


Figure 3-8. Diffusive flux ($\text{mg m}^{-2} \text{d}^{-1}$) of SRP calculated for the three sampling locations represented by the vertical bars, and their corresponding cumulative load (kg) over time (May 2005-March 2006) represented by the line with tiny square boxes.

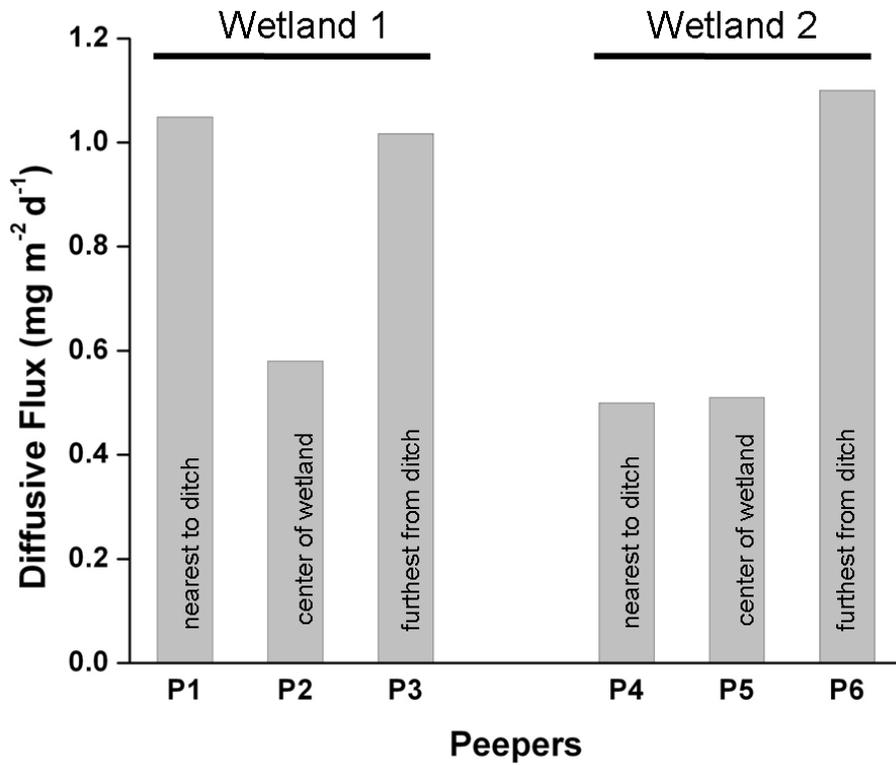


Figure 3-9. Diffusive flux (mg m⁻² d⁻¹) of SRP calculated using peepers from Wetlands 1 and 2 during August 2008.

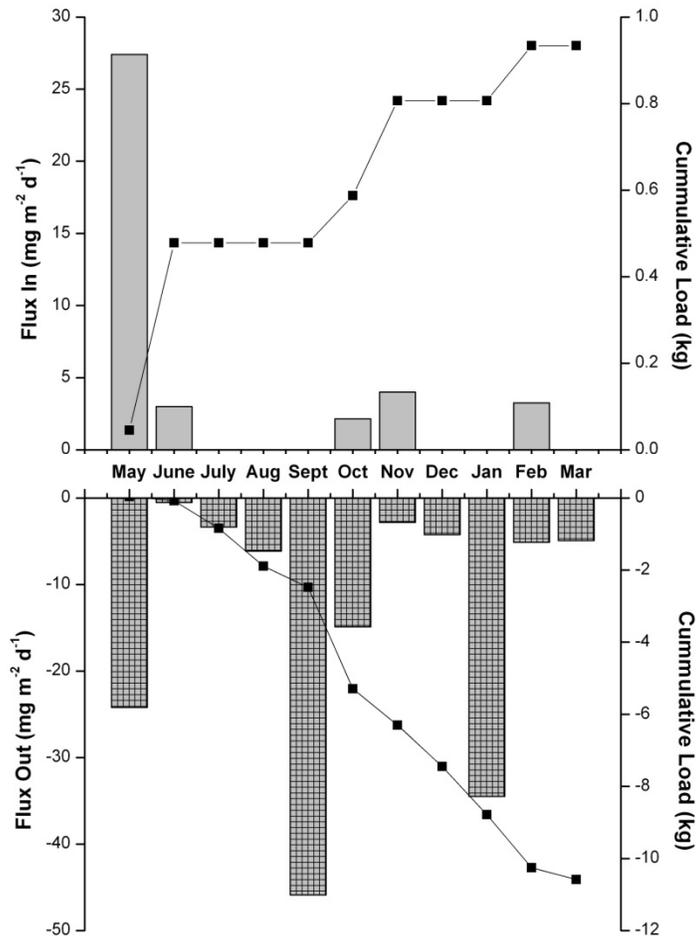


Figure 3-10. Advective flux ($\text{mg m}^{-2} \text{d}^{-1}$) of SRP represented by vertical grey bars calculated for times when ground water moved in (+) and out (-) of wetland 1 between May 2005 and March 2006 monitoring period. Corresponding cumulative load (kg) represented by the line with square boxes.

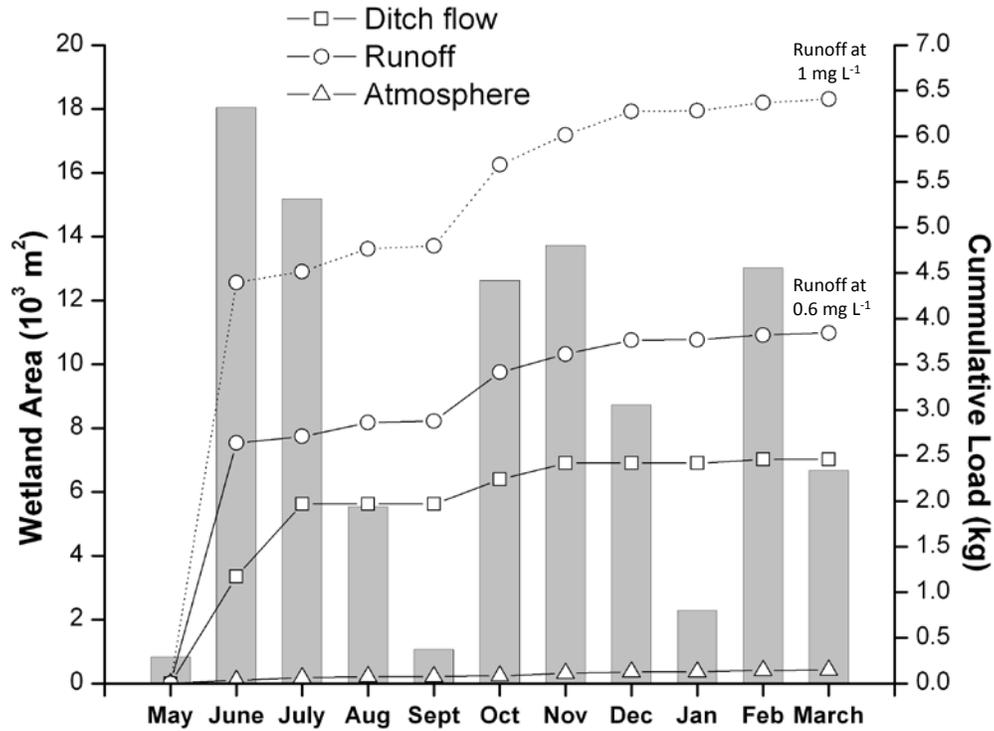


Figure 3-11. Cumulative load (kg) of P exiting the wetland via ditch flow, and entering it via surface runoff and atmospheric deposition during the monitoring period (May 2005-March 2006). Average wetted wetland area for individual months represented by vertical grey bars.

CHAPTER 4
SOIL PHOSPHORUS RELEASE AND STORAGE CAPACITY BASED ON
EXPERIMENTAL AND FIELD DATA

Introduction

Years of intensive agricultural practices associated with the beef and dairy industries have maintained a surplus of P within the Lake Okeechobee watershed (Boggess, 1995). The lateral transport of P from manure-impacted surface soils to adjacent streams is facilitated by seasonally high water tables, and this has been attributed as a major source of P loading to the Lake (Havens et al., 1996). Historically isolated wetlands within the landscape have been used to intercept surface runoff thereby increasing water storage and P retention (Braskerud, 2002). However, ditching the landscape to provide greater expanses of improved pasturelands has left the wetland soils drained and exposed for extended periods. Generally, at the soil-water interface when inorganic P is present at concentrations considerably greater than the interstitial (pore) water P is sorbed to the soil, whereas at low P concentrations, wetlands can release P (Pant et al., 2001; Dunne et al., 2006). However, changes in redox conditions associated with drying events can significantly alter P solubility and sorption mechanisms. Investigations have found that more P is released from dried soils upon reflooding than from perpetually flooded soils and sediments (Baldwin et al., 2000; Watts, 2000; Klotz and Linn, 2001). This could pose a serious concern for managing P from wetlands within the Okeechobee basin that are exposed to prolonged dry periods primarily due to droughts, and partly due to ditching practices.

Soils within the Lake Okeechobee drainage basin are typically sandy, and retain less P than finer textured soils because of a lack of mineral components such as metal oxides and phyllosilicates that have surface affinity for orthophosphate (o-P) (Sample et al., 1980). In addition, desiccation and consequent oxidation have been shown to cause significant changes to soil (and sediment) mineralogy (Sah et al., 1989; De Groot and Van Wijck, 1993; Klotz and

Linn, 2001), which in turn can affect P solubility and sorption capacity of the soil. Repeated drying and wetting cycles have been shown to cause an irreversible “aging” of the mineral phases in the soil (Baldwin et al. 2000). Dried mineral phases become more crystalline making them difficult to reduce (Lovely and Phillips, 1986). Over time, the increase in crystallinity reduces the soil’s ability to sequester o-P or release it under both oxidizing and reducing conditions. For example, De Groot and Van Wijk (1993) showed that when anoxic wetland soils were exposed to air the ferrous sulfide previously present was rapidly oxidized to amorphous ferric oxyhydroxide. These ferric (oxy)hydroxides have both a large surface area and high affinity for o-P; however, extended periods of desiccation lead to a significant reduction of the o-P binding capacity of ferric hydroxides in both flooded and drained soils (Sah et al., 1989).

Phosphorus sorption by aluminum (Al) does not involve oxidation-reduction reactions, and thus is not affected by aerobic or anaerobic conditions (Reddy et al., 1998a). The P sorption by Al compounds is regulated by pH and organic matter. The availability of o-P in solution is controlled by the magnitude of organic acid production derived from detrital organic matter within the soil profile (Traina et al., 1986). The chemical basis for this observation appears in the hydrolysis of exchangeable aluminum (Al^{3+}) and the subsequent reaction of the newly formed surface hydrolytic species with o-P from the soil solution. The presence of organic acids such as citric, formic, and tartaric can inhibit the Al^{3+} hydrolysis reaction. Characterizing P storage in wetland soils is often accompanied by organic matter (OM) measurement, because the total phosphorus (TP) pool within wetland ecosystems is often dominated by organic-P, which can comprise >50% of soil TP (Reddy et al., 1998b). High concentrations of OM in the form of manure and decomposed vegetation can drastically increase the availability of P within surface soils since organic anions formed by the decomposing OM can compete with P for the same

adsorption sites such as clays and iron-aluminum (Fe-Al) minerals (El-Dewiny et al., 2006). Goh and Huang (1984) showed that elevated concentrations of citric acid in solution can displace Al^{3+} in favor of the formation of soluble Al^{3+} -citric acid complexes. Metal-complexing organic acids tend to reduce exchangeable Al^{3+} by inhibiting hydrolysis, which in turn increases o-P solubility.

Standard soil test methods have been used to evaluate the environmental risks of P loss from agricultural soils (Maguire and Sims, 2002). As concerns of excess P in soils arose, the concept of “saturation index” was introduced to assess the potential risk of soluble forms of P. The degree of P saturation (DPS) was expressed as the molar ratio extractable P to the sum of extractable Fe and Al, expressed as a percent and incorporating a factor which made it approximate the percent of total P sorption capacity (Breeuwsma et al., 1995). The simple molar ratio of extractable P to extractable Fe plus Al is referred to as the phosphorus saturation ratio (PSR) (Nair and Harris, 2004). The relationship between measures of P desorption (e.g., water soluble P, WSP) and the DPS or PSR show a “change point” at which water extractable P starts to increase.

Pautler and Sims (2000) have shown that Fe and Al can control P sorption capacity by contributing to P retention. This occurs mainly because of the formation of chemical bonds between orthophosphates and Fe-Al at the soil surface, a ligand exchange reaction producing an orthophosphate-surface complex (Pierzynski et al., 2005). While PSR is often used to make environmental risk assessments, it does not give information about how much more P can be added to the soil without creating an environmental problem. Hence, the concept of soil P storage capacity (SPSC) was introduced, which refers to the mass of P that can be added to a mass of soil before the soil becomes an environmental concern (Nair and Harris, 2004; Chrysostome et al., 2007). This information is important to this study as it will identify soil

horizons (surface and subsurface) that are capable of storing P, and predict the amount of additional P that can be accommodated by a given soil horizon before the added P becomes an environmental concern.

Under inundated conditions, the P release from soil and sediments has only been evaluated within the top few centimeters or even millimeters, that are considered to be important for most biological and chemical activity (Boström et al., 1982). However, wetlands are hydrologically linked to deeper soil horizons by fluctuating water tables. Periodic drying of soils has been shown to chemically and physically alter soil horizons up to 40 cm (De Groot and Van Wijck, 1993). During the dry season, the receding water table can transport dissolved P from surface horizons into deeper zones, while subsequent flooding can potentially mobilize P from shallow horizons (Kleinman et al., 2003). The fact that wetland soils below the surface may be active in the process of P release has implications for the prediction of internal loading to the wetland water column, and deserves additional investigation. An evaluation of P release and storage capacity of surface and subsurface soil horizons can be useful in the design of future wetland restoration and management programs with long-term goals. Thus, this study was conducted with the following objectives: (i) to determine the maximum P sorption capacity (S_{max}) of surface and subsurface soil horizons (up to 160 cm) based on a batch equilibrium isotherm experiment, (ii) determine the equilibrium P concentration (EPC_0) values from the experiment, and evaluate the effect of changing soil:solution ratio on EPC_0 values (iii) to determine soil P storage capacity (SPSC) based on oxalate-extractable Fe, Al, and P concentrations.

Sampling and Analytical Methods

In this study I conducted two separate experiments on soil samples derived from cores 1, 2, 3, and 4. Only selected sub-sections were used for analyses and experimental purposes. Soil

samples used for the experiments were selected starting at the surface (0-2 cm), and then at 10 cm depth increments (10-12cm, 20-22cm, 30-32cm, and so on) until the bottom of the core.

Batch Incubation and EPC₀ Calculations

Soil samples were freeze-dried and ground to pass a 0.8-mm (20-mesh) sieve for use in the EPC₀ experiment. Incubation was performed under aerobic conditions, where 1 g of soil was placed in a 50-ml centrifuge tube and treated with 20 ml of 0.01 M KCl solution containing several concentration levels of P (0, 0.1, 0.5, 1.0, 5.0, and 10.0 mg P L⁻¹) as standard phosphate solution. The tubes were placed on an automatic shaker for a 24-h equilibration at low speed. Following equilibration, soil samples were centrifuged for 10 minutes at 6000 rpm, and filtered through a 0.45 µm membrane filter. Filtrates were analyzed for soluble reactive P (SRP) using a Technicon Autoanalyzer (Standard EPA method 365.3). Phosphorus not recovered in the solution was assumed to be retained by the soil. Water soluble P (WSP) was calculated based on the concentrations recovered from samples that contained 0 mg P L⁻¹. Analytical precision was calculated based on 5% duplicates of the entire batch experiment, and calculating relative percent difference (RPD) for individual concentration levels (RDP ≤ 3%).

Phosphate retained by the soils and the EPC₀ was calculated as follows:

$$S' = [(C_0 \times V) - (C_{eq} \times V)] / M \quad (4-1)$$

where S' = P sorbed by soil (mg kg⁻¹); C_0 = concentration of P added (mg L⁻¹); V = volume of liquid (L); C_{eq} = concentration of P in solution after 24 h (mg L⁻¹); M = mass of dry soil (kg).

Calculations expressed in equation (4-1) do not account for the native soil P in the sorbed phase, because it is primarily used to calculate P adsorbed or desorbed with regard to the P added. The total amount of P retained by the soil can be calculated as:

$$S = S' + S_0 \quad (4-2)$$

where S = total amount of P sorbed (mg kg^{-1}); S_0 = initial soil P present in adsorbed phase (mg kg^{-1}). The S_0 can be estimated using a least squares fit of S' measured at low equilibrium concentrations C_{eq} . At these concentrations the relationship between S' and C_{eq} is typically linear (Rao and Davidson, 1979) and described by the following equation:

$$S' = K_d C_{eq} - S_0 \quad (4-3)$$

where S_0 = the y-axis intercept representing the initial soil P present in the adsorbed phase (mg kg^{-1}); K_d = linear adsorption coefficient (L kg^{-1}).

The EPC_0 is defined as the concentration of P in solution where adsorption equals desorption (i.e., $S' = 0$). Thus,

$$C_{eq} = S_0 / K_d \quad (4-4)$$

where $C_{eq} = \text{EPC}_0$ (mg L^{-1}).

For individual depth intervals the P sorption data were fitted to the Langmuir model to help characterize the isotherms. Quantitative fitting parameters such as maximum P sorption capacity (S_{max}), and an affinity constant related to the bonding energy (k) were derived using the linearized form of the Langmuir equation:

$$C_{eq} / S = 1 / (k S_{\text{max}}) + C_{eq} / S_{\text{max}} \quad (4-5)$$

By regressing C_{eq}/S against C_{eq} , the slope corresponds to $1/S_{\text{max}}$ and the y-intercept equals to $1/(k S_{\text{max}})$.

Effect of Soil:Solution Ratio on EPC_0

The rationale for selecting a particular soil:solution ratio (SSR) in studies relating to sorption of inorganic P is rarely, if ever given (Hope and Syers, 1976), except for the choice of a wide ratio to simulate runoff environments (Ryden et al., 1972). The fact that variation in SSR

can influence the final concentration of P in solution (Hope and Syers, 1976; Nair et al., 1984) requires additional investigation if P management strategies are based on EPC values derived using sorption isotherms. The purpose of this exercise was to try to determine the EPC₀ values based on SSR that are representative of field conditions, so that EPC₀ values could be used to predict pore water concentrations if the soil and pore water were under equilibrium conditions.

To determine the effect of SSR at equilibrium which represent natural field conditions, without measuring the equilibrium isotherms, we used the data from the isotherm experiment performed on a 1:20 SSR and recalculated S₀ and K_d based on the new SSR. The rationale Hope and Syers (1976) used to evaluate the effect of SSR on P remaining in solution was, that if the final solution concentration (C_{eq}) after 24 h equilibrium using a 1:40 SSR was x, and the soils adsorbed P, then at a 1:1 SSR the C_{eq} should be x/40; if however, the soils desorb P, then the final solution concentration (C_{eq}) at 1:1 SSR should be 40x. They used four separate SSR (1:1, 1:5, 1:10; 1:40) to test the effect of SSR on P sorption by soils. We used the same rationale to evaluate the degree of change in EPC₀ values by adjusting the SSR to represent field conditions. Calculations were done on all four cores at the same depth increments (0-2, 10-12, 20-22, and so on) as those done for the EPC₀ experiment using the 1:20 SSR. In order to estimate the SSR under field conditions, we converted the mass of 1 g of soil to volume based on the bulk density, then using changes in soil porosity with depth we calculated the new SSR at individual depth increments. Using the new SSR we estimated EPC₀ values representing field conditions.

Oxalate Extraction, Analyses, and SPSC Calculations

Oxalate-extractable (ox) P, Fe, and Al were determined at the surface (0-2 cm) followed by every 10 cm depth interval for all four cores, using 0.1 M oxalic acid + 0.175 M ammonium oxalate solution, equilibrated at a pH of 3.0. Phosphorus, Fe and Al in the oxalate solution were

determined using inductively coupled argon spectroscopy (Thermo Jarrell Ash ICAP 61E). The degree of P saturation (DPS) and phosphorus saturation ratio (PSR) were calculated as:

$$DPS = \frac{ox(P)}{\alpha[ox(Fe + Al)]} \times 100 \quad (4-6)$$

$$PSR = \frac{ox(P)}{ox(Fe + Al)} \quad (4-7)$$

where P, Fe, and Al are molar concentrations of these elements and α is a dimensionless P saturation factor whose value is often assumed to be 0.5 (Schoumans and Groenendijk, 2000; Daly et al., 2001). Nair et al. (2004) used a statistical approach in identifying a 0.15 PSR threshold for Florida soils as corresponding to an approximate P solution concentration of 0.10 mg L⁻¹. Soil P storage capacity (SPSC; Nair and Harris, 2004) can be calculated based on this threshold PSR, as follows:

$$SPSC = (0.15 - PSR) \times ox(Fe + Al) \times 31 \quad (4-8)$$

where Al and Fe concentrations are expressed as mol L⁻¹ and SPSC is a calculation of how much additional P (mg kg⁻¹) can be added before reaching the PSR threshold.

Results and Discussion

Phosphorus Sorption and Equilibrium Concentrations

The soil phosphorus sorption characteristics for all four cores were well described ($r^2 \geq 0.88$) using the Langmuir model for $C_0 \leq 10$ mg P L⁻¹ (Figure 4-1). At zero initial concentration level ($C_0 = 0$ mg P L⁻¹) the soils from every horizon desorbed P after 24 h equilibration. The surface horizons by virtue of having higher P released the highest amount of P (S_0) at the zero concentration level, which may also account for the higher EPC₀ concentrations at the surface. At the highest initial concentration level ($C_0 = 10$ mg P L⁻¹) soils at every horizon adsorbed P after equilibration. The S_{10} values only provide a relative indication of the maximum sorption

capacity (S_{\max}) at different depths, because S_{\max} were higher than the S_{10} for all soil horizons ($S_{\max} = 1.9 \times S_{10}$); however the correlation was weak ($r = 0.61$) suggesting that the feasibility of using a single point isotherm for a data set should be done using $C_0 > 10 \text{ mg P L}^{-1}$. The amount of P adsorbed at the high initial concentration level (typically at $C_0 = 100 \text{ mg L}^{-1}$) is usually a good indication of the soil's maximum adsorption capacity based on a single point isotherm (Harris et al., 1996; Reddy et al., 1998a). The highest maximum sorption capacities (S_{\max}) calculated using linearized fits were observed at the surface (0-2 cm), at 588, 250, and 260 mg kg^{-1} for cores 2, 3, and 4 respectively. Periodic drying of the surface soils may have oxidized ferrous iron to amorphous ferric oxides, and increased the P sorption capacities at the surface. There was a positive correlation between S_{\max} and amorphous metal concentrations of Fe and Al that were best fit using a linear regression ($r = 0.84$) (Figure 4-2). This type of positive effect is not uncommon (Reddy et al., 1998a; Pant et al., 2002; Kang et al., 2009), implying that the presence of non-crystalline Fe and Al is a good proxy for P sorption capacities regardless of soil depth. To evaluate the effect of OM, the relationship between $\text{ox}(\text{Fe}+\text{Al})$ and S_{\max} was divided into two groups: low OM ($< 4\%$, $n = 33$) and high OM ($>4\%$, $n = 28$). There was a 10% diminishing effect of $\text{ox}(\text{Fe}+\text{Al})$ at the higher OM content based on the change in linear regression from $r = 0.90$ for low OM, to 0.80 for high OM content. Similar findings were also observed by Kang et al. (2009), suggesting that the contribution of oxalate-extractable Fe and Al tends to be less effective in soils with relatively higher OM. The OM content at the surface was 38% (± 14) from the wetland, and 48% (± 2) from the upland, and $< 2\%$ at depths beyond a meter (Chapter 2). Values of S_{\max} were also generally elevated (but not always) in the deepest horizons, i.e., below 120 cm in cores 1, 2, and 3, and below 140 cm in core 4. This increase in S_{\max} may be associated with the higher clay content (up to 38%) present in those zones. Similar significant

direct effects between clay content, Al, and Fe on the S_{\max} have also been observed in the North Carolina Coastal Plain soils that ultimately resulted in a good regression model (Kang et al., 2009).

The EPC_0 determined from sequential P sorption isotherm data is often used as an estimate of wetland floodwater P concentration, where adsorption equals desorption between soil-water interactions (Reddy et al., 1998). The EPC_0 values in all four cores were greatest at the surface (0-2 cm), compared to the deeper horizons (Figure 4-3). The values were between 0.81-3.28 mg L^{-1} from the three wetland cores, and are well within the range of estimates calculated by Pant and Reddy (2003) for a series of surface agricultural soils from a proposed storm water treatment site located in the Lake Okeechobee basin (1.3 to 3.4 mg L^{-1} SRP). Greatz and Nair (1995) reported EPC_0 values for four different soil horizons (A, E, Bh, and Bw) from a pasture located on an active dairy operation. They found decreasing EPC values with depth ranging from A = 5.3 (± 3.5), E = 2.2 (± 2.7), Bh = 0.1 (0.3), and Bw = 0.0; similar in behavior to our findings. Dunne et al. (2006) reported EPC values of 1.08 (± 0.063) mg L^{-1} for these soils based on a 28 d incubation experiment on 20 cm soil cores that were initially spiked at 1 mg L^{-1} . They found that completely flooded cores corresponded to lower P flux than partially flooded cores. This would imply that changes in wet and dry conditions have the potential to affect EPC_0 values depending on the time of year and the environment (flooded or completely drained) from which soil samples are collected. The 0-2 cm surface soil layer from upland core 4 is unique from the other cores because it has a very high EPC_0 value of 8.99 mg L^{-1} based on non-linear (polynomial) fit using the six point isotherm ($r^2 = 0.94$, Figure 4-3). The high EPC_0 value of upland soil surrounding the wetland would imply that the surface horizon (0-2 cm) of the uplands consists of labile P that could potentially behave as a source of P to the wetland if the concentration of P in

the incoming waters (runoff) is lower than 8.99 mg L^{-1} . However, overland sheet flow runoff is uncommon in this region due to the low relief and sandy nature of the soils, but, it is quite possible for a hurricane or a severe storm to induce runoff over short durations. It is more common for P to move laterally along the A and E horizons before ultimately being intercepted by the wetland or ditches (Allen, 1987). Below 40 cm the EPC_0 values were $<0.004 \text{ mg L}^{-1}$, implying that the deeper horizons do not pose an imminent threat to wetland water quality resulting from vertical (upward) P loading of ground water. However, the downward diffusion, and advection associated with water table fluctuations may be responsible for the redistribution of P from the surface to deeper (Bh or Bt) horizons.

Effect of Soil:Solution Ratio on EPC_0 Values and Pore Water Concentrations

Trying to translate EPC_0 values to pore water concentrations is a challenging task because of the transient hydrologic conditions which allow for the constant redistribution of soluble P within the soil profile. Additionally, biotic transformations of P by plants and microbes could significantly alter pore water concentrations regardless of EPC_0 values of the soils (Kadlec and Wallace, 2008). The EPC_0 values calculated using 1:20 SSR from cores 1, 2, and 3 were compared to *in situ* pore water SRP concentrations and total P from the soils up to 110 cm below the soil-water interface (Figure 4-4). Pore water P concentrations at all times were exponentially elevated compared to the EPC_0 values based on a regression fit ($r^2=0.64$) between EPC_0 and pore water. The regression was as: $\text{EPC}_0 = 8 \times 10^{-4} \exp(1.65 \times \text{pore water})$.

The effect of adjusting the SSR from 1:20 (used in the experiment) to those of field conditions based on soil porosity is summarized in Table 4-2. The EPC_0 values were significantly higher ($p<0.001$) when using SSR that were increased to represent the field conditions. The average SSR for core 1 was 1:0.67 (± 0.03), core 2 was 1:0.75 (± 0.1), core 3 was 1:0.74 (± 0.1), and core 4 was 1:0.63 (± 0.1). The relationship between field condition versus 1:20

SSR was explained using a log normal regression shown in Figure 4-5 ($r^2 = 0.76$). Nair et al. (1984) found “inconsistent” results based on their study using two separate SSRs (1:10 versus 1:25) to evaluate its effect on EPC_0 ; their relationship between the two SSRs was linear. Hope and Syers (1976) found that the concentration of P in solution at equilibrium (C_{eq}) was not always exactly equal at varying SSR. They concluded that at higher SSR the greater mass of soil offers more P-sorbing sites if kinetics involved the fast adsorption of P from solution into the solid phase. I found that the deviation in EPC_0 values using the field condition ratios (versus 1:20 SSR) was most dominant at low initial P concentrations. Generally, at the higher initial concentration (typically between 0-22 cm) the increase in EPC_0 using field conditions was 5.8 (± 2.8) compared to 1:20 SSR, and below 22 cm the increase in EPC_0 values was 19.5 (± 9.9) compared to 1:20 SSR. Increasing the SSR to mimic field conditions showed convergence towards the measured pore water concentrations, especially at the 10-12 cm depth. The pore water concentrations below 12 cm were still higher than the new field condition EPC_0 values, and this could be because of a combination of the downward diffusion of high concentration pore water at the surface and the transient hydrology.

Soil P Storage Capacity

Soil P storage capacity (SPSC) was estimated using oxalate-extractable (ox-) P, Fe, and Al for all four cores. I found a good correlation ($r = 0.91$) between ox-P and ox-(Fe+Al) from all four cores (Figure 4-2). My intention was to evaluate the surface and subsurface distribution of ox-DPS in the soil profile, and determine whether the DPS in subsurface samples (irrespective of horizon type) could be related to water soluble P (WSP). The DPS values were highest at the surface horizons (0-2 and 10-12 cm) for the wetland cores 16.6% (± 3.2), and the DPS value in the upland core was 20.2% at the surface (0-2 cm), and as high as 35.2% at 20-22 cm depth. Below 12 cm the DPS value in the wetland was 4.3% (± 2.7), compared to slightly higher DPS

values in the upland 9.6% (± 11.3). The higher DPS values in the upland suggest that the upland soils have higher ox-P content compared to ox-(Fe+Al), and possibly higher P storage capacities. Reddy et al. (1998) had estimated that 60-70% of the P imported to the Okeechobee watershed was stored within the Bh horizon in upland soils. Although these soils could still have up to 75% of their maximum P storage capacity remaining, Capece et al. (2007) suggested that they are already a significant source of non-point P, despite their total storage capacity. The relationship between WSP and DPS from surface and subsurface horizons seems to generate a “change-point” at around 12% (Figure 4-6), corresponding to a PSR of 0.06. Nair et al. (2004) were able to show a change-point of 20% between the oxalate-extractable calculated DPS and WSP from surface and subsurface soil horizons (including upper Bt) from the middle Suwannee River Basin, with relatively good confidence ($r^2 = 0.88$) based on a non-linear fit. DPS values of $>30\%$ in topsoils have been reported as a threat to water quality for Mid-Atlantic Soils, associated with P losses from runoff (Pautler and Sims, 2000). Deviations in P release indices have also been closely linked with the presence of OM, and the soil test method used to evaluate the P indices (Mukherjee et al., 2009).

The soils within the wetland (cores 1, 2, and 3), and upland (core 4) all seem to have significant remaining capacity to serve as a sink for P based on SPSC (Figure 4-7). Excluding the surface horizon, these results along with TP values that are not appreciably elevated suggest that the soils have been only minimally impacted by cattle farming activity. Except for the E horizon (20 cm) within the upland the soils seem to behave as sinks for P. Horizons with $SPSC < 100 \text{ mg kg}^{-1}$ may be susceptible to behaving as sources in the future provided the soils cease to retain additional P, and if continued application of manure persists on these sites. The high SPSC observed at the surface of core 2 and between 70-90 cm in core 4 is a result of the high Fe-Al

concentration observed at those depths. Based on these SPSC values it appears that the high pore water P concentration is not entirely controlled by *in situ* soil conditions, and that ground water hydrology may have a much greater influence on pore water P concentrations than anticipated. A highly fluctuating water table at the wetland site could cause that P and Fe become associated as the water table drops. Specifically, some entrained Fe is oxidized as air enters the profile and some entrained P becomes associated with it. Organic matter in the > 1 m of stratified soil would promote rapid reduction in that zone when the water table rises. The P associated with Fe would be released upon Fe reduction resulting in higher solution P concentrations. This redox-driven P immobilization and release would be cyclic. Unusually high P concentrations in the pore water would be the result of the scavenging of P by Fe in the oxidizing phase of the cycle. The crystallinity of Fe would be constantly perturbed and its rate of oxidation or reduction would be rapid. The Fe would be in its scavenging state when the sample is dried and Fe is oxidized, resulting in low WSP, PSR (positive SPSC), and EPC.

Summary and Conclusions

The P sorption capacity and resulting soil characteristics from this study were well described using the Langmuir model. The highest sorption capacities (S_{\max}) were restricted to the surface (0-2 cm) horizons in both the wetland and upland soil cores, probably because of the high Fe and Al concentration at those depths. In the deeper horizons the increase in S_{\max} may be a result of the accumulation of finer clay content present below 120 cm. There was a strong positive correlation between the oxalate-extractable Fe+Al and S_{\max} ($r = 0.84$) and oxalate-extractable P ($r = 0.91$) from all four cores and horizons. However, the presence of > 4% OM in the soils seem to have a 10% diminishing effect between oxalate-extractable (Fe + Al) and S_{\max} , probably due to the number of available adsorption sites being reduced as a result of metal-complexing with organic acids.

The EPC_0 values from all four cores were highest at the surface horizon, between 0.81-3.28 mg P L⁻¹ in the wetland, and 8.99 mg P L⁻¹ in the upland. Below the surface horizon the EPC_0 value dropped until it reached an asymptotic value below 40 cm. The high EPC_0 values in the surface layer may potentially act as a source of labile P that could be redistributed vertically within the soil profile, or even laterally by the movement of groundwater. The EPC_0 values of the wetland cores were significantly lower than the P concentration in pore water measured at all depth horizons. This may be because under field conditions factors such as transient local hydrology, biotic uptake and release, and complex reactions such as precipitation are just as dominant as adsorption-desorption; making it difficult to assess pore water P dynamics based on EPC_0 values alone. At most, EPC_0 can be used as a good first estimate for the mobilization potential of P under natural conditions. Based on our investigation, changing SSR did increase the on the final EPC_0 values, however they were still lower than those measured in the pore water. This investigation has relevance to several practical aspects of the chemistry of soil P. In particular, the effect of varying SSR in soil-testing procedures for P needs to be explained more rationally. We do not believe that there is a single “best” method to measure P sorption isotherms and estimating EPC_0 values. Nonetheless, it is in the application of the values if used as a tool to assess P loading that scientists need to pay added attention in correlating the results in the future.

Except for the 20-22 cm horizon in core 4, the positive SPSC values would suggest that these soils can safely sequester additional P before the added P becomes an environmental concern. However, elevated concentrations of pore water P at the surface horizons indicate that the soils and surrounding pore water may not be in complete equilibrium, probably because of the transient behavior of groundwater hydrology. It may be possible that prolonged dry-outs cause soil oxidation and subsequent mobilization and export of soil-bound P, in which case the

wetland simply alternates between storage and release during the wet and dry periods of the year. Based on our findings we recommend retaining water in the wetland for prolonged periods by reducing loss from drainage. This could allow for sufficient time for groundwater to kinetically equilibrate with the soils thereby removing some of the P from solution prior to reaching their maximum sorption capacities.

Table 4-1. A summary of the Langmuir sorption parameters based on batch incubation experiment, and oxalate extractable data for P, Fe and Al. BDL=below detection limit

Core 1 (wetland)										
Depth (cm)	WSP (mg kg ⁻¹)	ox-P (mmol kg ⁻¹)	ox-Fe (mmol kg ⁻¹)	ox-Al (mmol kg ⁻¹)	S _{max} (mg kg ⁻¹)	k (L mg ⁻¹)	K _d (L kg ⁻¹)	EPC ₀ (mg L ⁻¹)	DPS (%)	PSR
0-2	8.19	1.2	2.0	7.7	57	12.6	2.6	3.280	25.3	0.127
10-12	10.98	3.2	3.9	26.9	172	1.7	7.4	0.970	20.8	0.104
20-22	0.70	1.8	2.5	40.5	172	8.2	19.4	0.040	8.3	0.041
30-32	0.32	1.5	2.3	40.0	172	11.6	19.0	0.013	7.1	0.036
40-42	0.13	0.9	1.9	30.1	145	9.8	18.6	0.004	5.5	0.028
50-52	0.08	0.3	2.3	21.8	114	5.8	19.3	0.004	2.8	0.014
60-62	0.11	0.1	2.8	17.4	99	4.6	18.3	0.002	1.4	0.007
70-72	0.12	0.02	2.7	12.1	81	2.3	19.2	0.004	0.3	0.002
80-82	0.05	BDL	4.0	13.0	91	3.9	18.5	0.001		
90-92	0.12	BDL	6.6	9.8	93	5.1	19.2	0.051		
100-102	0.05	BDL	10.7	12.6	132	7.6	20.1	0.005		
110-112	0.10	BDL	17.3	16.9	167	15.0	19.0	0.002		
120-122	0.05	BDL	17.4	13.9	170	8.4	19.7	0.002		
130-132	0.08	BDL	18.5	15.4	172	7.3	19.9	0.004		
138-140	0.02	BDL	12.4	13.5	143	8.6	19.4	0.000		

Core 2 (wetland)										
Depth (cm)	WSP (mg kg ⁻¹)	ox-P (mmol kg ⁻¹)	ox-Fe (mmol kg ⁻¹)	ox-Al (mmol kg ⁻¹)	S _{max} (mg kg ⁻¹)	k (L mg ⁻¹)	K _d (L kg ⁻¹)	EPC ₀ (mg L ⁻¹)	DPS (%)	PSR
0-2	13.56	13.6	42.5	128.0	588	3.4	14.3	0.810	15.9	0.080
10-12	6.04	1.0	2.5	13.9	74	1.5	4.3	0.640	12.8	0.064
20-22	0.99	2.0	3.6	38.5	172	5.3	16.9	0.054	9.5	0.047
30-32	0.17	1.1	2.3	36.5	159	9.0	18.8	0.006	5.8	0.029
40-42	0.11	1.4	2.7	47.2	185	10.8	18.5	0.003	5.5	0.028
50-52	0.04	0.6	1.6	26.8	115	6.7	19.2	0.002	4.5	0.022
60-62	0.06	0.6	2.1	30.3	137	7.3	19.7	0.003	3.8	0.019
70-72	0.06	0.4	3.3	27.8	127	3.9	18.5	0.000	2.4	0.012
80-82	0.06	0.2	4.9	30.3	127	6.1	19.1	0.002	1.0	0.005
90-92	0.03	BDL	11.6	19.7	132	8.4	20.0	0.002		
100-102	0.08	BDL	1.1	3.9	44	2.5	17.0	0.003		
110-112	0.02	BDL	0.8	4.1	46	2.3	20.0	0.001		
120-122	0.02	BDL	10.8	11.4	125	5.3	19.7	0.001		
130-132	0.01	BDL	16.9	12.7	149	16.7	20.1	0.001		
142-144	0.05	BDL	15.7	10.3	154	13.0	19.9	0.002		

Core 3 (wetland)										
Depth (cm)	WSP (mg kg ⁻¹)	ox-P (mmol kg ⁻¹)	ox-Fe (mmol kg ⁻¹)	ox-Al (mmol kg ⁻¹)	S _{max} (mg kg ⁻¹)	k (L mg ⁻¹)	K _d (L kg ⁻¹)	EPC ₀ (mg L ⁻¹)	DPS (%)	PSR
0-2	11.48	5.4	19.4	53.7	250	2.2	8.3	1.200	14.7	0.074
10-12	2.80	0.9	2.4	14.3	63	2.0	9.4	0.310	10.2	0.051
20-22	0.36	1.4	2.8	32.2	147	7.5	18.3	0.015	8.2	0.041
30-32	0.07	1.5	2.7	45.2	189	13.3	19.4	0.003	6.2	0.031
40-42	0.08	1.1	2.0	37.7	159	12.6	19.3	0.003	5.8	0.029
50-52	0.06	1.0	3.8	46.9	175	14.3	19.2	0.002	4.0	0.020
60-62	0.05	0.5	4.0	30.6	137	8.1	19.0	0.001	3.0	0.015
70-72	0.04	0.1	3.1	17.0	90	5.8	18.6	0.001	1.1	0.005
80-82	0.05	0.1	5.7	10.5	70	4.8	18.8	0.000	0.9	0.004
90-92	0.03	BDL	7.6	12.3	92	21.8	20.0	0.002		
100-102	0.03	BDL	7.9	10.9	89	5.9	18.7	0.001		
110-112	0.04	BDL	8.1	11.3	81	3.6	19.4	0.000		
120-122	0.02	BDL	16.1	15.6	105	3.5	19.6	0.001		
128-130	0.02	BDL	13.6	11.7	98	5.6	18.7	0.001		

Core 4 (upland)										
Depth (cm)	WSP (mg kg ⁻¹)	ox-P (mmol kg ⁻¹)	ox-Fe (mmol kg ⁻¹)	ox-Al (mmol kg ⁻¹)	S _{max} (mg kg ⁻¹)	k (L mg ⁻¹)	K _d (L kg ⁻¹)	EPC ₀ (mg L ⁻¹)	DPS (%)	PSR
0-2	74.40	6.8	40.1	27.3	263	0.5	6.8	8.990	20.2	0.101
10-12	1.82	0.5	6.8	4.5	40	2.4	8.1	0.250	9.4	0.047
20-22	3.02	1.8	4.1	6.2	71	10.1	10.7	0.420	35.2	0.176
30-32	0.88	0.9	3.7	3.4	42	10.4	7.1	0.070	26.4	0.132
40-42	0.16	3.3	44.4	14.3	196	25.5	18.4	0.004	11.3	0.056
50-52	0.03	BDL	30.8	17.1	135	6.7	20.4	0.001		
60-62	0.03	BDL	35.9	20.0	159	10.5	19.6	0.001		
70-72	0.03	BDL	76.1	16.6	145	9.8	19.7	0.001		
80-82	0.04	0.1	101.9	12.0	116	4.7	20.1	0.002	0.2	0.001
90-92	0.03	BDL	12.0	11.0	78	6.1	20.5	0.002		
100-102	0.03	0.04	5.0	11.7	82	10.1	20.6	0.001	0.4	0.002
110-112	0.02	0.1	4.8	11.9	86	7.8	19.5	0.001	1.7	0.009
120-122	0.02	0.2	4.8	11.1	86	3.6	20.0	0.001	2.2	0.011
130-132	0.03	0.3	4.7	11.2	93	15.4	20.4	0.001	4.1	0.021
140-142	0.02	0.5	5.2	12.9	109	9.2	20.4	0.002	5.7	0.028
150-152	0.04	1.0	6.1	17.1	143	23.3	20.1	0.002	9.0	0.045
158-160	0.05	1.2	6.3	18.9	152	22.0	19.2	0.002	9.5	0.048

Table 4-2. A comparison between (i) effect of soil:solution ratio on EPC₀ for soil samples from all four cores. (ii) field condition EPC₀ values with pore water concentrations for cores 1, 2, and 3

Core 1				
Depth (cm)	EPC ₀ (mg L ⁻¹)		Increase in EPC ₀	Pore water (mg L ⁻¹)
	soil/soln ratio (1:20)	soil/soln ratio (field condition)		
0-2	3.28	6.4 (1:0.71)	× 2	
10-12	0.97	5.1 (1:0.66)	× 5	3.92 (±2.1)
20-22	0.040	0.22 (1:0.73)	× 6	2.65 (±1.8)
30-32	0.013	0.19 (1:0.72)	× 15	2.47 (±1.3)
40-42	0.004	0.088 (1:0.71)	× 22	0.99 (±0.5)
50-52	0.004	0.058 (1:0.67)	× 17	0.34 (±0.2)
60-62	0.002	0.082 (1:0.66)	× 37	0.82 (±0.4)
70-72	0.004	0.078 (1:0.70)	× 21	0.64 (±0.4)
80-82	0.001	0.037 (1:0.67)	× 34	0.72 (±0.4)
90-92	0.051	0.085 (1:0.66)	× 2	1.24 (±0.7)
100-102	0.005	0.033 (1:0.64)	× 7	
110-112	0.002	0.071 (1:0.65)	× 39	2.71 (±1.3)
120-122	0.002	0.034 (1:0.64)	× 21	
130-132	0.004	0.052 (1:0.63)	× 14	
138-140	0.001	0.015 (1:0.62)	× 15	

Core 2				
Depth (cm)	EPC ₀ (mg L ⁻¹)		Increase in EPC ₀	Pore water (mg L ⁻¹)
	soil/soln ratio (1:20)	soil/soln ratio (field condition)		
0-2	0.81	4.9 (1:0.91)	× 6	
10-12	0.64	4.0 (1:1.05)	× 6	3.36 (±1.4)
20-22	0.054	0.33 (1:0.84)	× 6	1.22 (±0.6)
30-32	0.006	0.11 (1:0.80)	× 18	0.67 (±0.3)
40-42	0.003	0.072 (1:0.83)	× 21	0.40 (±0.2)
50-52	0.002	0.021 (1:0.78)	× 12	0.65 (±0.4)
60-62	0.003	0.040 (1:0.76)	× 14	0.19 (±0.1)
70-72	0.001	0.036 (1:0.73)	× 36	0.17 (±0.1)
80-82	0.002	0.040 (1:0.71)	× 21	0.08 (±0.1)
90-92	0.002	0.021 (1:0.69)	× 12	0.06 (±0.1)
100-102	0.003	0.053 (1:0.66)	× 19	
110-112	0.001	0.022 (1:0.65)	× 18	0.04 (±0.03)
120-122	0.001	0.007 (1:0.64)	× 7	
130-132	0.001	0.013 (1:0.64)	× 19	
142-144	0.002	0.03 (1:0.63)	× 15	

Core 3				
Depth (cm)	EPC ₀ (mg L ⁻¹)		Increase in EPC ₀	Pore water (mg L ⁻¹)
	soil/soln ratio (1:20)	soil/soln ratio (field condition)		
0-2	1.2	5.2 (1:0.92)	× 4	
10-12	0.31	1.9 (1:0.68)	× 6	2.23 (±0.4)
20-22	0.015	0.24 (1:0.83)	× 13	1.53 (±0.3)
30-32	0.003	0.043 (1:0.84)	× 14	0.90 (±0.4)
40-42	0.003	0.053 (1:0.80)	× 21	0.60 (±0.2)
50-52	0.002	0.035 (1:0.77)	× 18	0.59 (±0.2)
60-62	0.001	0.036 (1:0.74)	× 53	0.74 (±0.1)
70-72	0.001	0.032 (1:0.72)	× 36	0.37 (±0.04)
80-82	0.001	0.032 (1:0.71)	× 32	0.30 (±0.1)
90-92	0.002	0.025 (1:0.72)	× 11	0.44 (±0.04)
100-102	0.001	0.021 (1:0.66)	× 36	
110-112	0.001	0.026 (1:0.65)	× 26	0.37 (±0.01)
120-122	0.001	0.016 (1:0.65)	× 15	
128-130	0.001	0.022 (1:0.63)	× 32	

Core 4				
Depth (cm)	EPC ₀ (mg L ⁻¹)		Increase in EPC ₀	
	soil/soln ratio (1:20)	soil/soln ratio (field condition)		
0-2	8.9	9.96 (1:0.87)	× 1	
10-12	0.25	1.73 (1:0.74)	× 7	
20-22	0.42	2.92 (1:0.68)	× 7	
30-32	0.070	0.38 (1:0.71)	× 5	
40-42	0.004	0.11 (1:0.65)	× 25	
50-52	0.001	0.02 (1:0.58)	× 14	
60-62	0.001	0.023 (1:0.60)	× 16	
70-72	0.001	0.024 (1:0.59)	× 18	
80-82	0.002	0.026 (1:0.58)	× 14	
90-92	0.002	0.024 (1:0.58)	× 16	
100-102	0.001	0.011 (1:0.60)	× 9	
110-112	0.001	0.012 (1:0.59)	× 15	
120-122	0.001	0.017 (1:0.60)	× 17	
130-132	0.001	0.018 (1:0.60)	× 15	
140-142	0.002	0.018 (1:0.59)	× 8	
150-152	0.002	0.026 (1:0.59)	× 14	
158-160	0.002	0.042 (1:0.58)	× 18	

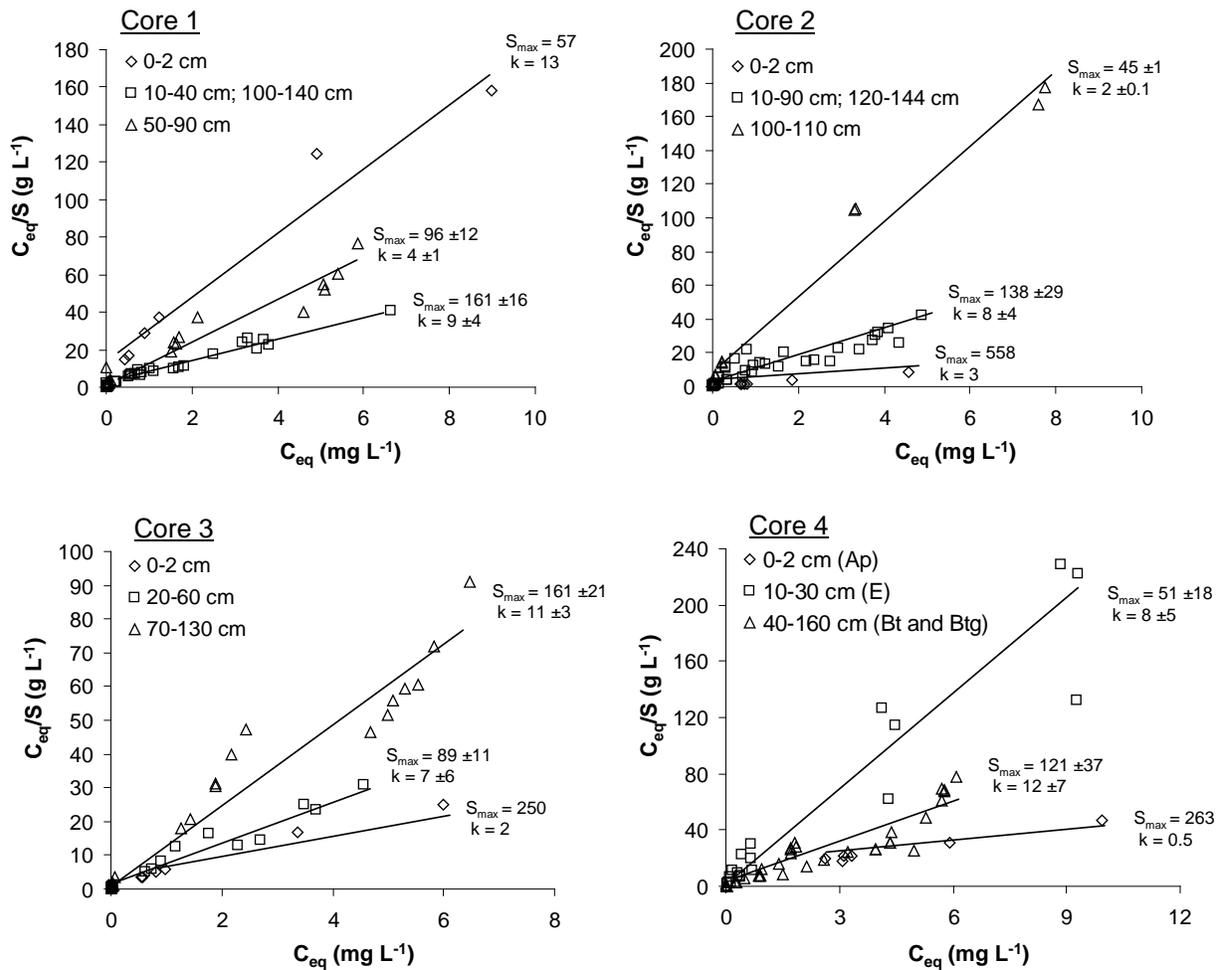


Figure 4-1. Langmuir plots for P sorption of all four cores. The P sorption maxima, S_{max} (mg kg^{-1}) and bonding energy constant, k (L mg^{-1}) are shown next to the regression derived for different soil horizons. Overall $R^2 \geq 0.88$.

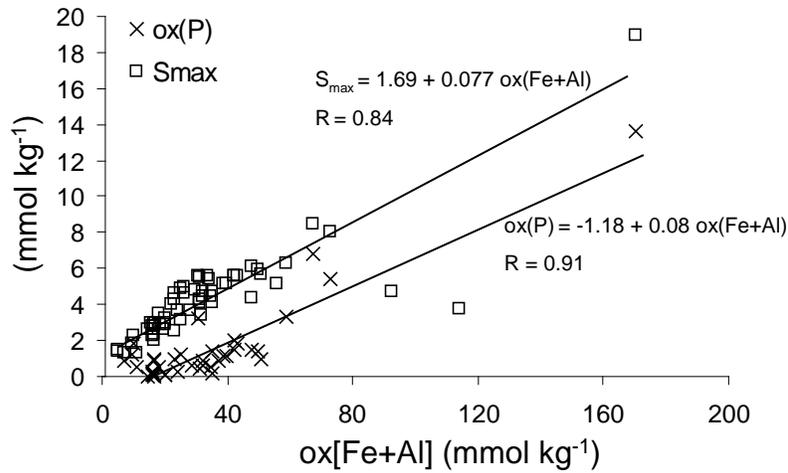


Figure 4-2. Relationship between (i) oxalate-extractable P (n=39) versus oxalate-extractable (Fe+Al), and (ii) P sorption maxima (S_{max}) versus oxalate-extractable (Fe+Al) for all four cores and depth horizons (n=61).

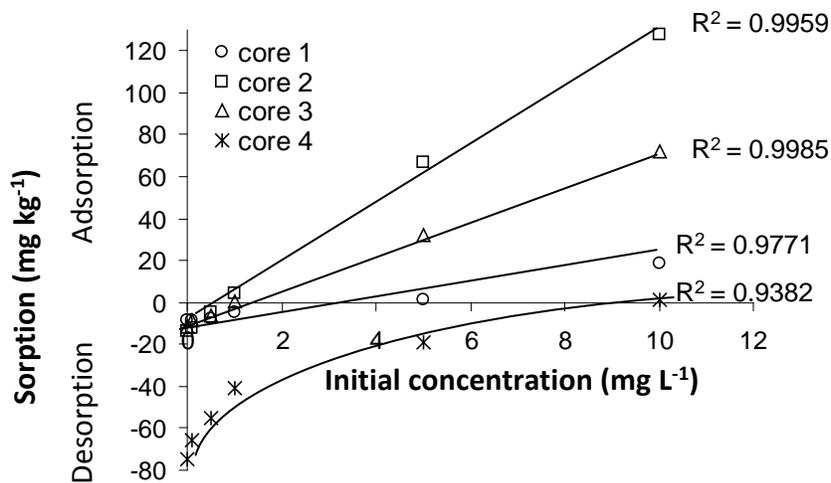


Figure 4-3. Surface horizon (0-2 cm) EPC_0 values for cores 1, 2, 3, and 4 calculated using a six point isotherm as a function of SRP adsorption and desorption. X- axis corresponds to initial P concentration ($mg L^{-1}$). Regression based on linear fit using all six points for cores 1, 2, 3, and a non-linear fit for core 4.

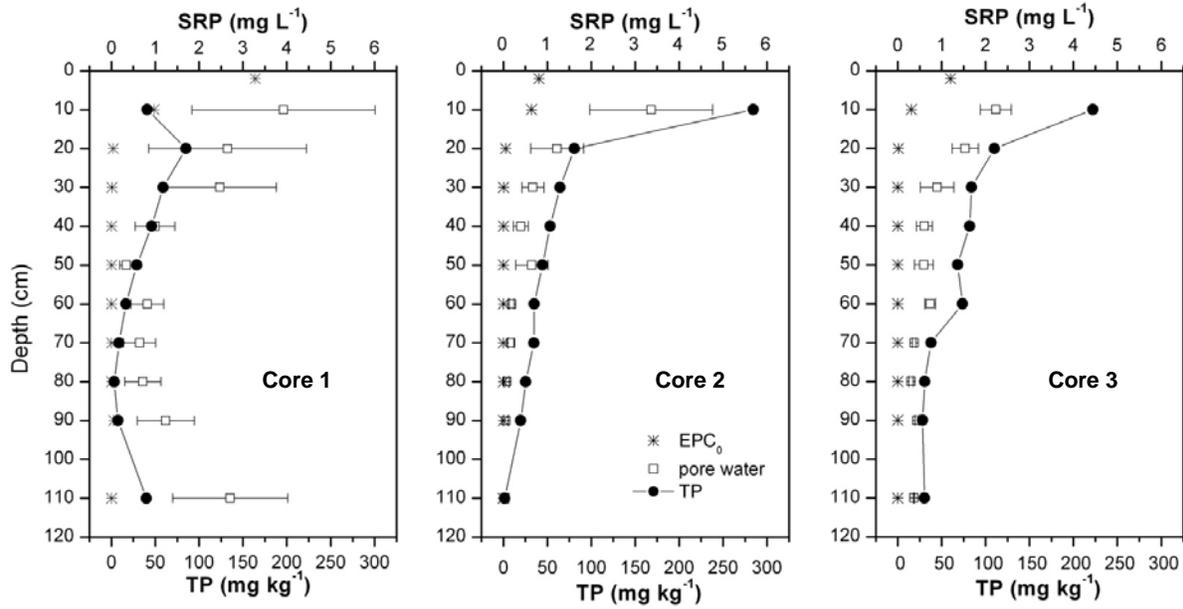


Figure 4-4. Depth distribution of EPC_0 values (mg SRP L^{-1}) compared with seasonally variable pore water concentrations (mg SRP L^{-1}), and soil total P from wetland cores 1, 2 and 3. $EPC_0 = 8 \times 10^{-4} e^{(x)}$ ($x = 1.65 \times \text{pore water}$) ($r^2 = 0.64$) based on all four soil cores.

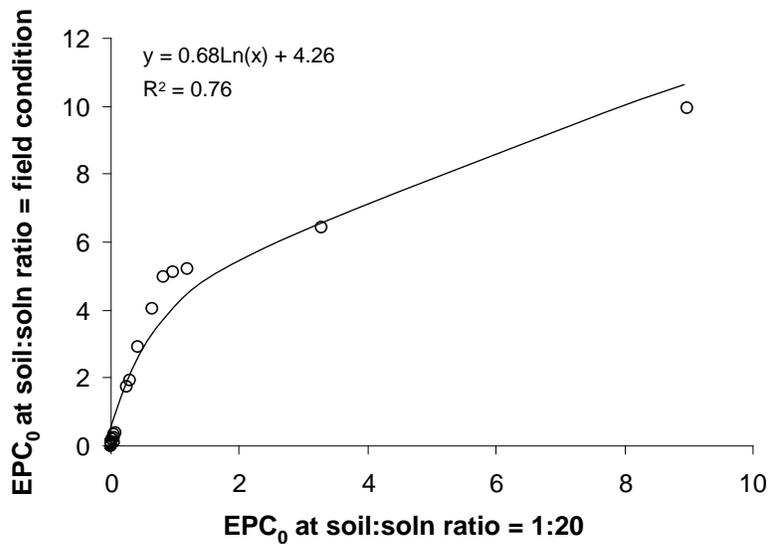


Figure 4-5. Relationship between EPC_0 (mg L^{-1}) at field condition versus those measured using 1:20 soil:solution ratio for all four soil cores ($n=61$).

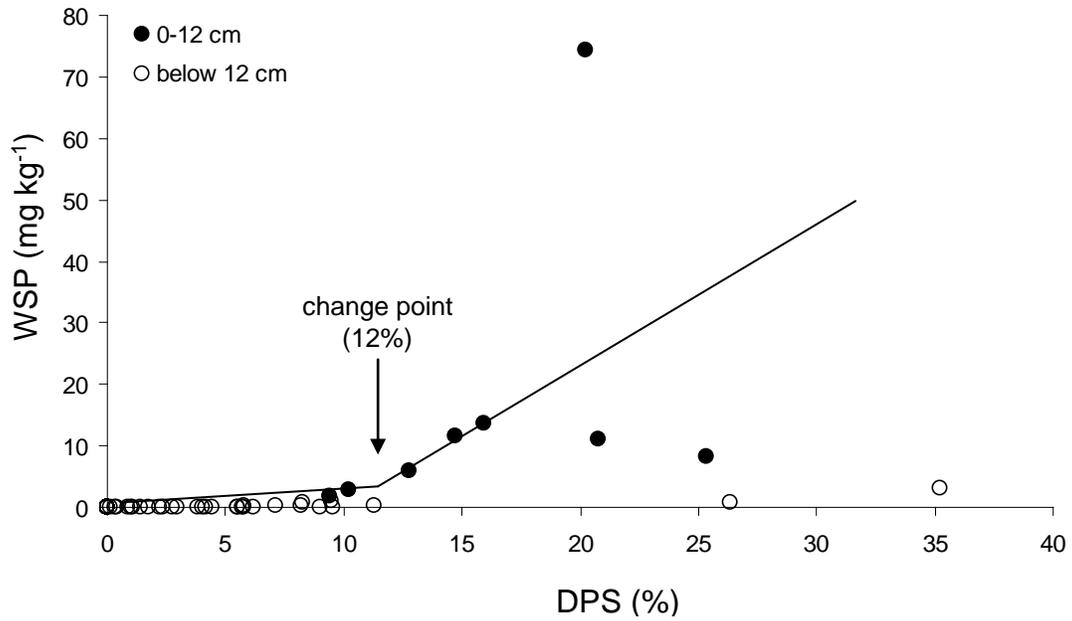


Figure 4-6. Relationship between the water soluble P (WSP) and the degree of P saturation (DPS) calculated using an oxalate extraction from surface and subsurface horizons of all four cores.

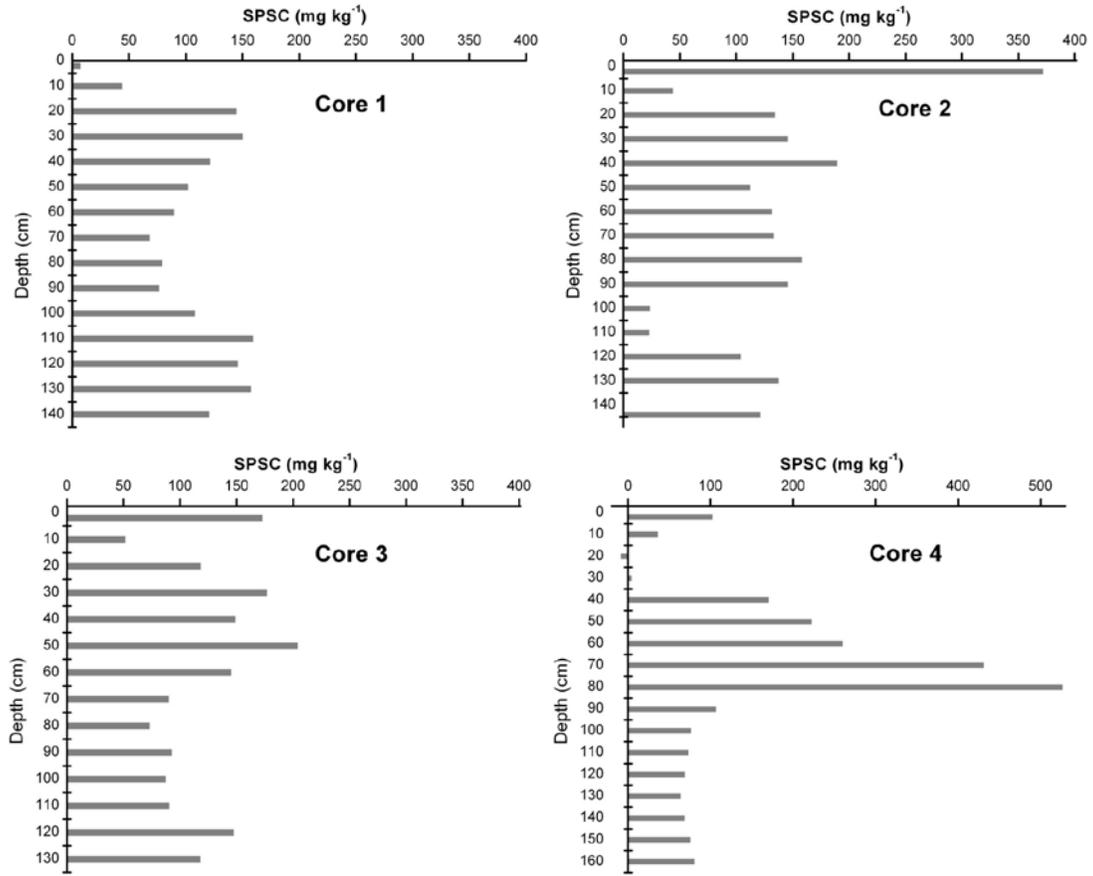


Figure 4-7. Soil P storage capacity for all four cores, calculated using the PSR values and oxalate extractable Fe, Al concentrations in the soil.

CHAPTER 5 PRACTICAL IMPLICATIONS AND RECOMMENDATIONS

Soil Erosion and Stratification

The soils encountered within the Okeechobee Basin wetland and upland were generally sandy, consisting of high P and OM content at the surface that gradually decreased with depth. What was very striking about the wetland soils was the presence of un-disturbed stratification observed in all three wetland soil profiles, which seemed unusual at first; however, I believe that continued soil erosion and subsequent deposition of the upland soils by wind and cattle activity may have resulted in the formation of these features. Typically, during the dry season surface soils are susceptible to being exposed to wind erosion thereby being displaced and redistributed. During numerous field visits I have observed large areas of both wetland and upland soils that have been exposed as a result of erosion. Overgrazing by cattle in a particular area has also been known to cause erosion, by reducing the vegetation cover and exposing the topsoil. Organic matter along with both inorganic and particularly organic P is displaced as a result of soil erosion. Most farm management plans for P assume that if erosion is controlled, so are P losses. One way to address this issue is through soil conservation measures, such as crop rotations, or by making sure that there is a good vegetation cover year round. Knowing the crop nutrient limit of the soils, and proper manure management plans can help to retain vegetation through out the year, thereby reducing soil erosion. Stratification within soil profiles may not allow for a B horizon to form, as new material is being constantly deposited over the existing soil profile. All three wetland cores (1, 2 and 3) were lacking the presence of a well-formed Bh or Bt horizons seen in the upland core. This could have implications for P sequestration, as Bh horizons have a high capacity to retain P. One strategy for wetland restoration would be to increase the wetland

hydroperiod. This could potentially help reduce the erosion of soil by wind, and would also allow for denser vegetation cover if soil moisture were higher than present.

Scaling-up to Basin-wide P Loads Based on Using Local Flux Measurements

The total P fluxes (diffusive and advective) calculated in Chapter 3 were used to scale-up to estimate basin-wide P loads associated with isolated wetlands within the Lake Okeechobee drainage basin. These estimates could be useful to predict the amount of P load reduction to Lake Okeechobee that would occur if wetland restoration work can increase P retention in soils and reduce P fluxes exiting the wetland via overland modes. To estimate the amount of P associated with isolated wetlands that could potentially be stopped (controlled) from reaching Lake Okeechobee I used P fluxes numbers from this study and extrapolated them to the four priority basins of the Lake Okeechobee watershed. These priority basins (S-65E, S-65D, S-154, and S-191) have consistently produced the highest levels of P concentrations of all the tributary basins to Lake Okeechobee (Flaig and Reddy, 1995). These four basins are dominated by beef and dairy operations and account for 12% of the land area of the Okeechobee basin, yet contribute 35% of the P to the Lake (Dunne et al., 2006). In 1999, the Lake Okeechobee Action Plan was put in place to address the issue of reducing high P loads to the Lake. Between 1997 and 2001, estimated P loads to the Lake from 25 contributing basins was ~ 303 tons yr^{-1} (Hiscock et al., 2003). In 2004, SFWMD reported the total P load entering the Lake to be ~ 543 tons yr^{-1} . It is estimated that if the four priority basins met their target loads, then P loading to Lake Okeechobee could be reduced by over 100 tons yr^{-1} .

Basin-wide P Loads from Isolated Wetlands

The four priority basins cover an estimated area of 3340 km^2 within the Okeechobee drainage basin, of which isolated wetlands represent about 7%, totaling 234 km^2 (McKee, 2005). Assuming the average size of a wetland to be about 0.011 km^2 (size of Wetland 1 on Larsen

Ranch), I estimate there are some 21,273 such isolated wetlands scattered within the four priority basins. Bevc (2007) had also estimated a comparable number (22,400) of isolated wetlands within the priority basins. By using the average of the total mass load of P entering and leaving the wetland (from Chapter 3) multiplied by the number of wetlands in the basins I estimated a basin-wide effect of loading associated with diffusion and advection into the wetland, and ground water out of the wetland (Table 5-1). To estimate P loads associated with ditch flows, I assumed that only about 45% of the total isolated wetlands in the priority basin are ditched (McKee, 2005; Dunne et al., 2007b). On a basin-wide extent, the total P load out of wetlands via advective and diffusive fluxes accounts for 131 ton yr⁻¹. This does not mean that all 131 tons reach the Lake. By restoring the wetlands it should be possible to reduce this load, depending on the efficiency of the restored wetlands to retain P. The total amount of P load exiting the wetlands is a lot higher, 250 ton yr⁻¹. The estimated amount of P exiting these wetlands via ditch flow is 24 ton yr⁻¹. Damming the ditches to provide for greater hydroperiods could (i) reduce the P load associated with fluctuating water tables, and (ii) substantially reduce the export via ditches. This would however increase P loading into the ground, assuming that P inputs to the wetland remain the same. However, based on the soil P storage capacities the wetland soils still have substantial capacity to retain P. Perkins (2007) had estimated between 0.2 and 9.6 metric tonnes per year of P load entering Lake Okeechobee from isolated wetlands with the watershed. His estimates were significantly smaller compared to other basin-scale estimates of 415 tonnes yr⁻¹ (Boggess et al., 1995) and 582 tonnes yr⁻¹ (SFWMD, 2001). In his defense, he acknowledges that not all historically drained isolated wetlands function hydrologically similarly within the landscape, or have had similar historic and current land use practices (fertilizer, cattle stocking, etc.). His estimates of basin-scale load are only pertinent to the fraction of runoff passing through

depressional wetlands and out ditches. It does not incorporate P load related to regional drainage from ditch networks, land use contribution of dissimilar nature (dairies and other relatively high-intensity operations), and P load from tributary and in-stream internal loads.

Literature estimates of P reduction due to water detention in wetlands range between 4-80% (Zhang et al., 2006). With such a wide range in reduction, it is obvious that more research is necessary to confirm the effectiveness of water detention in isolated wetlands to reduce P loads. However, the estimated 100 ton yr⁻¹ load reduction from the four priority basins discussed in the Lake Okeechobee Action Plan of 1999 may not be achievable by water detention alone, and other possible strategies need to be considered. Perkins (2007) showed that P treatment in these wetlands was comparable to that using the landscape-scale pseudo-2d modeling approach. He concluded that under current managed wetland hydrology, the utility of these wetlands to retain P does not fully result in P load reduction to Lake Okeechobee, but with measures to increase retention time in the wetlands; higher treatment potential might be expected. The duration of P treatment under a modified hydraulic regime, such as blocking the export of P loading via ditches, is not known and would require a more in-depth look at the mechanisms and limits of the P cycle.

Basin-wide P Loads from Ditches

It has been proposed that drainage ditches behave similarly to isolated wetlands and can serve as either a source or sink for P (Dunne et al., 2007b). Ditches can serve as temporary P sinks; as overland flow transports with it both organic and inorganic forms of P. If the water in these ditches can be retained then the ditches could function as sinks, provided the soils underlying these ditches have not been impacted with high concentrations of P.

Bevc (2007) estimated the range of P load associated with drainage ditches and canals within the four priority basins to be between 31 and 362 ton yr⁻¹. The high degree of variability

was associated with the range in P fluxes associated with ditch soils. There was also some discrepancy with regard to the total areal cover of ditches occupied within the basins. Comparing the P loads associated with isolated wetlands with drainage ditches, it is evident that best management practices should be applied to the ditches in the same manner in which they target isolated wetlands. Perkins (2007) had estimated that groundwater outflow comprised approximately 35% of the total hydraulic outflow from the study wetlands, and that the principal component responsible for the majority of P export was ditch flow, which yielded between 7.6 and 43.7 % (wetland-averaged) of the total TP outflow. This finding was critical in the development of a conceptual model of the P dynamics in these wetlands because the treatment effectiveness was a function of not only what comes out the ditch as surface water export, but also the load to groundwater that will ultimately reach the lake.

Kinetic Control of Dissolved P in Aquatic Systems

An understanding of the chemical parameters required to regulate P uptake and release in natural aquatic systems requires a detailed assessment of the controls on the bioavailability of P. These efforts are hampered by the difficulty of distinguishing between inert and bio-reactive P. The ultimate source of dissolved phosphate is the weathering of continental rocks, where it may exist in a variety of insoluble minerals at a concentration of about 0.1% (Froelich, 1988). In lentic aquatic systems such as lakes, wetlands, and ponds, it is generally assumed that some of these minerals are in equilibrium with water, thus controlling the concentrations of dissolved P. Seldom, however, is equilibrium proved by laboratory manipulations, demonstrating the solubility control of the reactive solid phase phosphates in natural systems, except in a few cases (Emerson and Widmer, 1978; Golterman, 1995), due to lack of sufficient P concentrations in the solid phase. Presently, a large potential reservoir of available reactive P to natural aquatic systems is from anthropogenic sources like fertilizers and manure, due to the growing demands

on the food-crop and live-stock industries. The environmental and economic consequences of P in soils resulting from anthropogenic sources have prompted a significant long-term effort to understand soil-solution phosphate reactions.

In solution, phosphate reacts quickly with a wide variety of surfaces, being taken up by and released from particles through a complex series of sorption reactions. In the field of soil sciences and agricultural research, phosphate sorption has been known to occur both fast and slow, with reactions being reversible or irreversible depending on the sorption (or buffering) capacity of the solid phase, and the residence time in contact with the solution (Barrow, 1983; Froelich, 1988). The simplest plausible model capable of explaining the wide variety and complexity of observed behavior of phosphate soil-solution reactions involves the uptake and release of dissolved phosphate via a two-step process (Barrow, 1983; Mansell, et al., 1995; Chen, et al., 1996): rapid surface adsorption or desorption of phosphate onto or off of reactive surfaces, followed by a slow penetration or release by solid state diffusion of this surface phosphate into or out of the interior of the particles. The initial fast reaction has time scales of minutes to hours, and the second slow reaction has time scales of days to months, or even years (Barrow, 1983). The fast reaction can account for 50-90% of the total P response, and the log-log plots of P sorbed vs. time can often be fit to one or more equilibrium models such as Langmuir or Freundlich. Studies related to impacted soils involving short-term effect of P (Graetz and Nair, 1995; Reddy et al., 1998; Pant et al., 2002, 2003) typically ignore the consequences of two-step kinetics, and plot P sorption after 24 h to be near “equilibrium”. These plots, often referred to as adsorption isotherms, are taken to represent the loci of points of a series of equilibrium conditions between solid (soil sample) and solution. Each point on these diagrams is termed an equilibrium phosphate (phosphorus) concentration (EPC) (as shown in Figure 4-3 in Chapter 4).

True equilibrium is seldom attained on laboratory time scales except for conditions chosen to entirely mimic those of natural systems (Sharpley et al., 1981; Froelich, 1988). The phosphate retention characteristics of the soils are determined based on the adsorption isotherms.

The literature is full of incomplete interpretations of data on P sorption because of the synergistic effect of kinetics on the other variables associated with P sorption experiments. Rao et al. (1980) may have been the first group to point out that the procedures used to determine the P adsorption over the years had varied widely, making the comparison of isotherm coefficients from different research difficult, if not impossible. Phosphate adsorption has been shown to vary with soil:solution ratios (SSR), as shown in this study and by others (Hope and Syers, 1976; Barrow and Shaw 1979; Nair et al., 1984), ionic strength (Ryden et al., 1977); and cation species of the supporting electrolyte (Helyar et al., 1976; Barrow et al., 1980., Nair et al., 1984). Even though adsorption is rapid, varying the equilibration period between 0.5 to 7 d has also resulted in differences in adsorption capacities (Rao et al., 1980). In addition, Nair et al., (1984) offered other possible variables that could affect equilibration, such as condition and duration of sample storage prior to experiment, range of initial P concentrations used in the experiment, geometry of mixing (volume of soil suspension to headspace volume in equilibration vessel), rate (low, medium, high) and type of shaking device (reciprocal vs. end-over-end). In order to eliminate some of the inconsistencies associated with P adsorption procedures, Nair et al. (1984) proposed a “standard” P adsorption protocol for soils and sediment based on the ability of multiple laboratories to produce consistent results over a wide range of soil samples. Their procedure included:

- a. Weight of soil/sediment– 0.5 to 1.0 g
- b. Soil:Solution ratio– 1:25
- c. Extraction time– 24 h

- d. Electrolyte– 0.01M CaCl₂
- e. Initial dissolved inorganic P concentrations– 0, 6.45, 16.13, 32.26, 161.3, 323 μmol P L⁻¹ as KH₂PO₄ or NaH₂PO₄
- f. Temperature– 24 to 26 °C
- g. Microbial inhibition– 20 g L⁻¹ chloroform
- h. Equilibration vessel– 50 ml to provide at least 50% head space
- i. Shaking– end-over-end shaker
- j. Separation– filter through 0.45 μm (0.2 μm for clays)
- k. Analysis– any procedure for determination of orthophosphate, manual or automatic, capable of detecting >750 μmol P
- l. Replication– duplicate equilibrations, and single analysis of orthophosphate in solution

Nair et al. (1984) concluded that P sorption was generally lower (up to 40%) with K⁺ as the supporting electrolyte cation compared with Ca₂⁺, consistent with the finding of Barrow et al. (1980) and Heylar et al. (1976). The effect was most pronounced at the higher initial P concentration. They also found that changes in SSR had an effect on EPC₀ values, and even though this effect was generally smaller than the effect of the supporting electrolyte, they concluded that it was large enough to warrant standardizing both factors in the procedure.

Role of pH, Soil and Solution Composition in Evaluating P Mobilization

pH: The dominant P species in solution of natural environments in the pH range of 4.8-6.0 is the H₂PO₄⁻ ion (White and Taylor, 1977). Koski-Vahala and Hartikainen (2001) showed that the effect of pH on the mobilization of P was dependent on the concentration of suspended solids in the system. Their objective was to evaluate the role of pH at different concentrations of suspended solids in solution, so as to assess the risk of P loading due to resuspended sediments. They found that at solid concentrations between 17 to 170 mg L⁻¹, P release increased sharply below pH 5 and above pH 7. At a high concentration level of 1700 mg L⁻¹ no effect was

observed at pH ranging from 3 to 8.5, and no significantly enhanced P mobilization was found until above pH 9. As the concentration of suspended solids diminished, the acid-induced increase in the P release (pH < 5) was more distinct than the base-induced release (pH > 7). While the effect of pH on P mobility were not evaluated in this study, its effect on suspended solids can have practical implications for this study because wetland soils located on dairy and beef farming facilities are constantly being re-suspended due to cattle activity. Already there have been best management practice programs in place which requires the implementation of fencing ponds, troughs, or tanks used for cattle watering, as well as the setting of stocking rates for individual pastures based on P loading characteristics of the site. It may be feasible in the future to limit (if not completely eliminate) the access of cows to open water wetlands.

Soil composition: The initial P adsorption process is dependent on charge balance and surface area, and can occur on a variety of natural particle surfaces. The second slow diffusion step is very dependent on the composition of the solid phase (Froelich, 1988). Soils containing Fe and Al hydroxides, or surfaces coated with these phases, display a much higher “slow” sorption capacity due to the reaction of phosphate with the oxides. The effect of time and concentration on P sorption by Fe and Al hydroxide surfaces has been well documented (Barrow 1983; Bolan et al., 1985). Soils in which P adsorption is mainly associated with Fe-oxides are especially likely to show slow uptake into particles, particularly with the poorly crystallized oxides. Further, the capacity of these oxides to sorb P decreases with their “age” and apparent crystallinity (McLaughlin et al. 1981). There is a recognizable relationship between “extractable” Fe and Al hydroxides and the P sorption capacity, as shown in this study, and in many previous studies (Richardson, 1985; Reddy et al., 1998a; Pant et al., 2002). These metal oxides have show high P sorption capacity over short experimental time scales, however over longer time periods

they may lose some of the P if the redox condition within the system is altered (Baldwin et al., 2000; Watts, 2000; Klotz and Linn, 2001). This could potentially affect the resulting EPC values depending on the redox condition (potential) of the soil when sampled. I therefore highly recommend measuring the redox potential of the soil at the time of sampling.

Solution composition: The effect of ionic strength in the solution phase on P mobilization has received only sporadic attention (Nair et al., 1984; Koski-Vahala and Hartikainen, 2001). In general, sorption increases as the ionic strength of the solution increases (Nair et al., 1984). However, this may not be the case in the presence of anions such as SO_4^{2-} , F^- , OH^- that compete with phosphate (or H_2PO_4^-) ions for surface sorption sites, reducing the amount of P sorbed during the fast reaction, and consequently affecting the rate and mass of phosphate taken up or released during the slow reaction. In order to minimize artifacts associated with solution composition, experiments are generally performed using a buffering electrolyte such as 0.01M CaCl_2 or KCl. Some experiments have also relied on using natural water from the site itself to overcome the effect of solution composition. The EPC values calculated using site-specific waters are represented as EPC_w , and do not necessarily equal to EPC_0 . For example, Dunne et al. (2006) calculated EPC_w for the Larson wetland soils using water from the Kissimmee River as the buffering solution. Their EPC_w values were lower (nearly 64%) than those estimated using 0.01M KCl solution from this study. I therefore recommend using either CaCl_2 or KCl solution as long as there is consistency while comparing data.

Strategy to Reduce P Loads

Plans to restore isolated wetlands within the watershed have been proposed as a viable option to store water, increase wetland hydroperiod, and sequester P. One way to do this is to build a control structure at the head of the ditch or simply damming it. This dissertation and other related studies (Dunne et al., 2006; and Perkins, 2007), indicate believe that P loads exiting the

wetlands via the ditches could be reduced by damming ditches that drain water out of wetlands. This plan was put in place in April 2009, where the ditch connected to wetland 1 was dammed to reduce (if not completely prevent) loss of water from the wetland, thereby increasing the wetland hydroperiod (Figure 5-1). Sampling work and experiments in the future will be conducted so as to evaluate the effectiveness of damming the wetland to mitigate P loss. Results will be compared with wetland 2, whose undammed ditch will serve as a control for comparison.

Table 5-1. Basin-wide estimate of P load from isolated wetlands associated with diffusion, advection, ditch flow, and ground water

	Wetland wide load (kg yr ⁻¹)	Basin wide load (ton yr ⁻¹)
	Into the wetland	
Diffusion	5.2	111
Advection	0.93	20
	Out of the wetland	
Ditch flow	2.5	24
Ground water	10.6	226

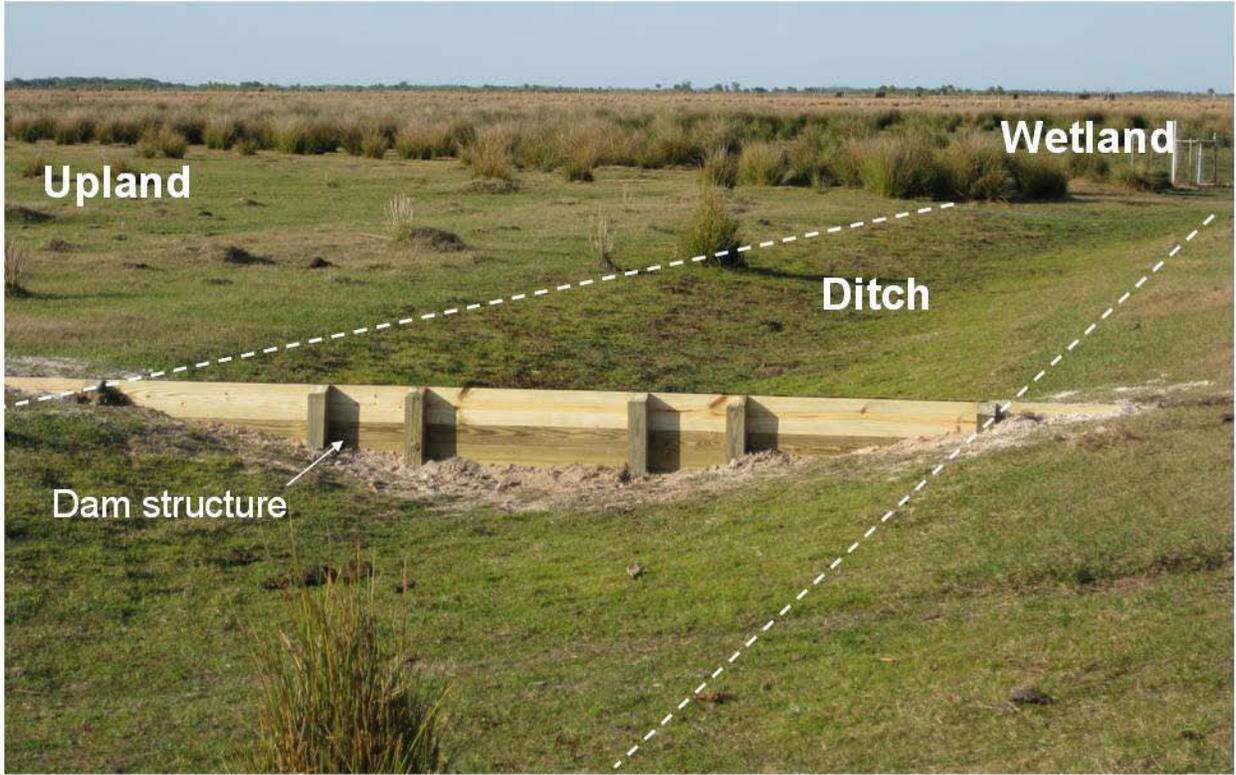


Figure 5-1. Dam structure constructed to reduce the amount of water exiting wetland 1 via ditch flow.

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BIOGRAPHICAL SKETCH

Dr. Jehangir H. Bhadha started his education in 1980 when he joined St. Peter's High School, Bombay, India. He studied there for twelve years, from kindergarten to tenth grade. In 1992 he joined St. Xavier's College, a part of the University of Bombay, and completed the Junior College (high school equivalent) level in 1994. He then went on to the Degree College in St. Xavier's where he graduated in May 1997 having earned a Bachelor of Science (Honors) degree majoring in geology, and a minor in gemology. In 1997 he began his master's degree program from St. Xavier's College and graduated in June 1999 with a Master of Science (Distinction) degree, majoring in geology. In Fall 2000 he joined the Department of Geological Sciences at the University of Florida (Go Gators!). He graduated in Spring 2003 with a Master of Science degree, major in geology and a minor in environmental engineering sciences. Apart from this he also received a certificate in hydrologic sciences as part of the Hydrologic Sciences Academic Cluster from the University of Florida. In Spring 2005 he joined the Soil and Water Science Department at U.F. in pursuit of a doctorate degree; and successfully graduated in Summer 2009.