

PHOSPHORUS SORPTION AND FLUX IN NORTHERN EVERGLADES SOIL
UNDER DRAINED AND FLOODED CONDITIONS

By

JENNIFER A. LEEDS

A THESIS PRESENTED TO THE GRADUATE SCHOOL
OF THE UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF
MASTER OF SCIENCE

UNIVERSITY OF FLORIDA

2006

ACKNOWLEDGMENTS

This research was made possible by the South Florida Water Management District through financial, technical and facility support and conducted as part of the Downstream Monitoring and Research Program in the Everglades Division. I would like to acknowledge District staff that provided assistance in the field and nutrient analysis in the water quality lab. In addition, I would like to thank Dr. Mark Clark, Dr. Jana Newman, Dr. Susan Newman and Dr. Samira Daroub for the invaluable support, guidance and contributions they made to this research and thesis.

TABLE OF CONTENTS

	<u>page</u>
ACKNOWLEDGMENTS	ii
LIST OF TABLES	v
LIST OF FIGURES	vi
ABSTRACT	vii
CHAPTER	
1 PHOSPHORUS MOVEMENT BETWEEN THE SOIL AND OVERLYING WATER COLUMN IN WETLANDS.....	1
Introduction.....	1
Equilibrium Phosphorus Concentration (EPC).....	2
Factors Regulating P-sorption	4
Phosphorus Flux	5
Northern Everglades Field Site.....	7
Need for Research.....	9
2 PHOSPHORUS SORPTION AND DESORPTION CAPACITY	12
Introduction.....	12
Methods	13
Isotherm calculations.....	15
Results.....	16
Discussion.....	24
3 FLUX OF BIOAVAILABLE PHOSPHORUS.....	27
Introduction.....	27
Methods	28
Results.....	32
Discussion.....	46
4 CONCLUSIONS	51
Phosphorus Isotherms	52

P-Sorption Factors	54
P-flux	55
Conclusion	56

APPENDIX

A P-ADSORPTION RESULTS FROM THE LINEAR, FREUNDLICH AND LANGMUIR ISOTHERM EQUATIONS AT EACH SITE AND P-CONCENTRATION.	58
B WATER QUALITY NITROGEN RESULTS FROM INTACT SOIL CORES SAMPLED FROM THE P-FLUX EXPERIMENT.	60
LITERATURE CITED	61
BIOGRAPHICAL SKETCH	65

LIST OF TABLES

<u>Table</u>	<u>page</u>
2-1 List of regression (R^2) coefficients used to determine which isotherm equation, linear, Freundlich or Langmuir, best fit the P-sorption data.	20
2-2. P-sorption parameter results for the linear, Freundlich and Langmuir equations for equilibrium phosphorus concentration (EPC).	20
2-3 RWMA soil nutrient concentrations for each site in the RC transect..	24
2-4 Comparison of oxalate extractable Fe and Al content in soils	24
3-1 Water Quality standard testing methods according to Clescerl et al. 1999 and the South Florida Water Management District water quality procedures.	31
3-2 Fluxing rates of SRP in $\text{mgL}^{-1}/\text{hr}$ for dry soil cores at each transect site.	34
3-3 Percentage of oP and iP fluxing from the soil into the water column over time.....	45
3-4 Algae TP concentration measurements in mg/kg	46

LIST OF FIGURES

<u>Figure</u>	<u>page</u>
1-1 Map showing the location of the Rotenberger Wildlife Management Area.	8
2-1 Linear isotherm result for the RC transect A) RC1 site. B) RC2 site C) RC3 site D) RC4 site.	18
2-2 Freundlich and Langmuir isotherms for the RC transect A) RC1 site. B) RC2 site. C) RC3 site. D) RC4 site.	21
2-3 Oxalate-extractable Al composite samples.	23
2-4 Oxalate-extractable Fe composite samples.	23
3-1 SRP water column concentrations in mg/L at a)RC1 site. b)RC2 site. c)RC3 site. d)RC4 site.	33
3-2 TP water column concentrations in mg/L at a)RC1 site. b)RC2 site. c)RC3 site. d)RC4 site.	35
3-3 TDP water column concentrations in mg/L at a)RC1 site. b)RC2 site. c)RC3 site. d)RC4 site.	37
3-4 NH ₄ water column concentrations in mg/L at a)RC1 site. b)RC2 site. c)RC3 site. d)RC4 site.	38
3-5 SRP water column concentrations measured in mg/L at RC1, RC2, RC3 and RC4.	40
3-6 NH ₄ water column concentrations measured in mg/L at RC1, RC2, RC3 and RC4.	40
3-7 Dissolved organic phosphorus (DOP) water column concentrations in µg/L at a)RC1 site b)RC2 site. c)RC3 site d)RC4 site.	41
3-8 Organic phosphorus (oP) water column concentrations in µg/L at a)RC1 site. b)RC2 site c)RC3 site d)RC4 site.	43
3-9 Particulate phosphorus (PP) water column concentrations in µg/L at a)RC1 site. b)RC2 site c)RC3 site d)RC4 site.	44

Abstract of Thesis Presented to the Graduate School
of the University of Florida in Partial Fulfillment of
the Requirements for the Degree of Master of Science

PHOSPHORUS SORPTION AND FLUX IN NORTHERN EVERGLADES SOIL
UNDER DRAINED AND FLOODED CONDITIONS

By

Jennifer A. Leeds

May 2006

Chair: Mark W. Clark
Major Department: Soil and Water Science

Wetland soils have the potential to function as a phosphorus (P) source or sink depending on antecedent soil conditions, P loading rates, water column P concentrations and characteristics. Hydrology, water quality and soil chemistry are primary factors affecting soil P sorption and desorption. The Rotenberger Wildlife Management Area (RWMA), part of the northern Everglades, has undergone alterations in hydrology resulting in shortened hydroperiods, severe soil oxidation and peat fires. These alterations have subsequently elevated available P concentrations in the soil. In accordance with the Everglades Forever Act (EFA), the South Florida Water Management District began hydropattern restoration in RWMA in July 2001, utilizing discharges from Storm Water Treatment Area 5 (STA-5). As part of the northern Everglades, it is uncertain whether the RWMA soils will act as a source or sink for P. To address this question, P-isotherms were run to determine the equilibrium phosphorus concentration (EPC) of the soil, while soil P-flux differences between drained vs. flooded

soils were assessed using intact soil core microcosms collected from the field. Results show EPC measurements across the marsh ranged from $73.6 \mu\text{gL}^{-1}$ to $94.5 \mu\text{gL}^{-1}$ at three of the four sites, with one site measuring $18.8 \mu\text{gL}^{-1}$. The P-flux in intact soil cores indicated drained soil treatments fluxed significantly higher concentrations of soluble reactive phosphorus (SRP) ($110 \mu\text{gL}^{-1}$) versus continuously flooded soil treatments ($7 \mu\text{gL}^{-1}$). Water column SRP concentrations of intact soil cores peaked between 8 and 24 hours after re-flooding with ambient marsh water then water column concentrations declined to SRP levels measured in flooded soil cores by 380 hours. Flooded soils, at all sites, released low levels of SRP concentration upon re-flooding within one hour and then appeared to reach equilibrium, as concentration levels remained constant. Additionally, results measured concentrations of oxalate-extractable Fe (1039.5 g/m^3) and Al (514.5 g/m^3), normalized based on bulk density (0.21 g/cm^3), and are significantly higher compared to other Everglades soil, which may be regulating P sorption. EPC measurements suggest P water column concentrations less than $90 \mu\text{gL}^{-1}$ will result in P-release from most soils in RWMA. Furthermore, this system continues to experience soil dry out and oxidation for several months (February – June) during the dry season, which can lead to rapid and elevated flux of SRP upon re-flooding, as compared to continuously flooded soils. These results can be incorporated into adaptive management strategies to modify operations of the system to achieve hydropattern restoration targets while slowing the movement of existing soluble soil P further into the Everglades.

CHAPTER 1
PHOSPHORUS MOVEMENT BETWEEN THE SOIL AND OVERLYING WATER
COLUMN IN WETLANDS

Introduction

Wetland soils can function as a source or sink for phosphorus (P) depending on antecedent soil conditions and interstitial porewater P concentration. Phosphorus flux from soils is an important biogeochemical process occurring in all types of wetlands. Because P cycles within the soil and does not have a significant gaseous phase such as nitrogen (N), P within a wetland can be transferred between soil, water column, flora and fauna, although is not easily released outside of the wetland system (White et al. 2000). For this reason, P movement within a wetland is of major concern in systems such as the Florida Everglades that initially developed under low P concentrations then received high P inflows resulting in increased P loading. Over time, continuous loading of P to soils can shift historically oligotrophic (low nutrient) wetlands, to eutrophic (high nutrient) systems (South Florida Water Management District 1992; Newman et al. 1997). In addition to external P loading, P dynamics and bioavailability can change as a result of altered hydrology, biology or chemistry of a site (Reddy et al. 1998). Due to anthropogenic alterations in hydrology, many areas in the Northern Everglades have severely reduced hydro patterns, leading to excessive drying and oxidation of the soil, thereby raising soil P concentrations and promoting soil loss. Determining environmental conditions regulating P-sorption or flux in the soil, is largely dependant upon the P

concentration and composition of P, both the soil and in the water column, influencing the mobilization of soluble P further into the Everglades marsh interior.

Equilibrium Phosphorus Concentration (EPC)

Phosphorus sorption/desorption studies primarily use P-isotherms to define the equilibrium phosphorus concentration (EPC) of the soil and measure the maximum P-sorptive capacity of a soil. Furthermore, determining the water column P concentration where soil P-sorption and desorption are at equilibrium, EPC, aids in determining when a wetland will act as a source or sink for P. This value, relative to source water P concentrations, or known acceptable water column P concentrations, is an important variable in restoration, and in predicting potential wetland impact and recovery times. For example, in a study by Richardson and Vaithiyanathan (1995) in Water Conservation Area 2A (WCA-2A) conducted along a P-gradient, reported EPC at inflow sites were high in elevated soil P concentrations, and significantly greater than interior marsh EPC and soil P. They concluded the inflow sites have the ability to serve as an internal source for P, even if external P loading was reduced, given the current inflow concentration levels. Additionally, Zhou and Li (2001) showed a positive correlation between EPC and soil P saturation in a study in the southern Everglades.

Wetlands, natural or constructed, can be used to treat runoff or wastewater removing nutrients prior to downstream discharge. The P-sorptive capacity of a soil is an important parameter in determining the amount of time, and range of P concentrations, natural wetlands receiving nutrient enriched inflows, or proposed constructed wetlands designed for nutrient removal, will function. In the northern Everglades, and areas north of Lake Okeechobee, reducing enriched runoff from urban and agricultural areas has become a primary focus of the Comprehensive Everglades Restoration Plan (CERP).

Studies by Nair et al. (1998) and Reddy et al. (1998), established that soils containing enriched P concentrations, such as agricultural soils that are targeted to become Storm Water Treatment Areas (STAs), or enriched Everglades soils found in current inflow areas, may not have the ability to retain sufficient amounts of P for sustained periods of time (~ 10 years or more) due to historic P loading. In fact, these soils could become a potential source of P upon receiving low P water inputs. In addition, this research hypothesized physico-chemical properties of the soil such as aluminum (Al), iron (Fe), magnesium (Mg) and calcium (Ca) content, can contribute to regulating the P-sorption capacity of the soil. However, their effectiveness at retaining P was dependant upon soil P concentrations, as well as aerobic or anaerobic soil conditions (Gale et al. 1994). Similar studies conducted outside of the Everglades support these results (Khalid et al. 1977; Sallade and Sims 1997).

In addition to defining EPC, P-isotherms describe the maximum P-sorptive capacity of the soil using the linear, Freundlich and or Langmuir equations (Nair et al. 1998; Pant and Reddy 2001; Zhou and Li 2001). The linear equation is typically applied to low P concentrations, the Freundlich to medium P concentrations and Langmuir to high P concentrations (Zhou and Li 2001). A principal aspect to consider when applying P-isotherms is they are run under laboratory conditions, in which the soil is isolated from other biological factors, such as plants and algae that could affect the sorptive capacity (Gale et al. 1994). Furthermore, the sample processing method for P-isotherms exposes all available soil sorption sites and cannot be directly related to field conditions where a minimal number of sites are exposed. In addition, pore water diffusion rates play a significant role in the exchange of porewater P with the overlying floodwater. Results are

best utilized in conjunction with other soil characteristics specific to field sites such as nutrient content, dominant P-species (organic or inorganic) in the soil and, oxidized or reducing conditions, as well as P-flux experiments.

Factors Regulating P-sorption

In wetland systems, P-sorption and desorption are influenced by many factors. The physico-chemical properties of a soil, coupled with historic P-loading of a system, can significantly affect P-sorption (Gale et al. 1994; Reddy et al. 1998). Soil chemistry, specifically Fe and Al content, can have a substantial influence on P-sorption as well (Sallade and Sims 1997; Zhou et al. 1997). Additionally, Reddy et al. (1998) found Total Organic Carbon (TOC) significantly reduced P-sorption by forming complexes with Fe and Al. In a report by Richardson (1985) on the P retention capacity of various freshwater wetlands, results suggested the sorption potential of a wetland may be regulated by the extractable Al content of the soil. The Fe and Al concentrations in the soil can sorb P, forming poorly crystalline and amorphous oxide and hydroxide forms (Khalid et al. 1977; Pant and Reddy 2001; Pant et al. 2001). Under aerobic conditions, ferrous iron in the soil oxidizes to form ferric iron, a precipitate which is insoluble, although can increase P-sorption sites (Gale et al. 1994). In systems with high concentrations of Ca in the soil, such as in WCA-2A (Reddy et al. 1991; Richardson and Vaithyanathan 1995) and Everglades National Park (ENP) (Zhou and Li 2001), P-sorption is typically regulated by calcium carbonate (CaCO_3) (Raven and Hossner 1993). Soil chemistry, organic matter, oxidation, as well as the concentration of available cations such as Ca, Mg, Fe and Al, can influence P binding to form inorganic, bioavailable P-species. Phosphorus species such as Ca/Mg-P and Al/Fe-P, which are inorganic P forms,

are regulated by acidic and alkaline soils, as well as aerobic and anaerobic soil conditions influencing P solubility (Pant et al. 2002).

Phosphorus Flux

Phosphorus flux is typically used to describe the process of soluble P moving from the soil to the overlying water column, under conditions where water column P concentrations are less than soil porewater P concentrations (Reddy et al. 1996). Phosphorus flux studies incorporating intact soil cores have been conducted in the Everglades, on surrounding agricultural lands north of the Everglades near Lake Okeechobee, and in eutrophic lakes in Central Florida, as well as in wetlands and lakes in other parts of the country (Reddy et al. 1996; Fisher and Reddy 2001; Pant and Reddy 2003).

External P loading can have a considerable affect on the level of P concentrations fluxing from the soil to the overlying water column. For example, a P flux study in WCA-2A by Fisher and Reddy (2001) using intact soil cores was performed along a P gradient, extending from water inflow structures to approximately 10 km into the marsh interior. Their results indicated soil P flux was greater near inflow points and decreased linearly with distance into the marsh interior, and is directly correlated to the soil P concentration gradient. In addition, agricultural lands which later may be used as constructed wetlands or storm water treatment areas, have the potential to be a nutrient source depending on antecedent P loading of the soil. An initial high P concentration flux can occur when agricultural lands are first flooded. Depending on soil EPC and water column P (Pant and Reddy, 2003), if the EPC of the soil is elevated, the soil could act as a continuous source of P, until an equilibrium is achieved with the overlying water column.

Two types of soil conditions exist in wetlands, aerobic (drained) and anaerobic (flooded), with varying degrees in between depending on hydroperiod. In studies by Pant et al. (2002) and Malecki et al. (2004), P fluxed in significantly higher amounts in re-flooded, aerobic soils than in continuously flooded, anaerobic soils. One reason for these differences in P release is the different form of soil P found under aerobic and anaerobic conditions. Under aerobic conditions, where soils become oxidized, inorganic P species usually form based on existing soil chemistry such as the Fe, Al, Ca or Mg content. In systems with high Fe content, oxidized forms of Fe can adsorb P forming ferric phosphate. Alternatively, in anaerobic conditions where the soil is not oxidized, P-species primarily remain in their reduced, predominately organic state. Typically, organic bound P is an immobilized form and not immediately available for uptake by plants or algae. Therefore, for organic P to become bioavailable, it must first undergo mineralization, which breaks down into non-bioavailable dissolved organic compounds and bioavailable inorganic P. However, anaerobic conditions slow the mineralization process of organic compounds thereby preserving P that is bound to organic particles.

The type of P, inorganic or organic, has significant ecological implications. There are three forms of P present in both the soil and water column, dissolved inorganic P (DIP) also known as soluble reactive phosphorus (SRP), dissolved organic P (DOP) and particulate organic P (POP). Soluble reactive phosphorus is readily available for uptake, whereas DOP and POP must be mineralized to an inorganic form prior to becoming bioavailable. The P species, and their relative concentrations in the water column, as well as drained or flooded soil conditions, dictate which species will flux (Eckert et al. 1997; Novak et al. 2004). These relative concentrations and composition in soil and

water, affect the soluble P front at the landscape scale, having significant implications within the Everglades ecosystem. The importance of which, is soluble P (DIP) is bioavailable, a major factor in driving the system to transition at inflow points from an oligotrophic to eutrophic marsh.

Northern Everglades Field Site

The Rotenberger Wildlife Management Area (RWMA), part of the Northern Florida Everglades, is a 29,120 acre marsh located west of the Miami Canal and north of Water Conservation Area 3A (Figure 1-1). Once part of the historic sawgrass plains receiving continuous overland flow from Lake Okeechobee (McVoy, personal communication), the RWMA became a degraded wetland, cutoff from continuous water inflow, resulting in shortened hydroperiods and extended marsh draw downs. The continuous cycle of short hydroperiods, allowed the soil to undergo severe dry out and oxidation, elevating P levels, which led to soil subsidence (Newman et al 1998). Consequently, perpetually dry soils, and low (<65%) soil moisture content (Wade et al. 1980) often resulted in typical wildfire becoming muck fires. Muck fires can combust organic matter within the soil, thus significantly altering soil chemistry, increasing P-levels and volatilizing N (Newman et al. 1998; Smith et al. 2001). Loss of soil organic matter can change P soil storage pools from organic to inorganic forms (Leeds et al. in progress). The combination of slow, biologically mediated oxidation of organic matter and rapid thermally mediated oxidation of organic matter through muck fires has significantly increased soil P levels, which now average 640 mg/kg. This change in P concentration has resulted in a shift in marsh trophic state from oligotrophic to a eutrophic system. DeBusk et al. (1994) suggested that Everglades soil P concentrations greater than 500 mg/kg are considered enriched. The RWMA soils may contain a lower

organic matter content, due to the history of muck fires, and a higher mineral content, although may still be classified as an enriched system as evidenced by soil TP content and vegetation composition, as a result of severely altered hydrology.

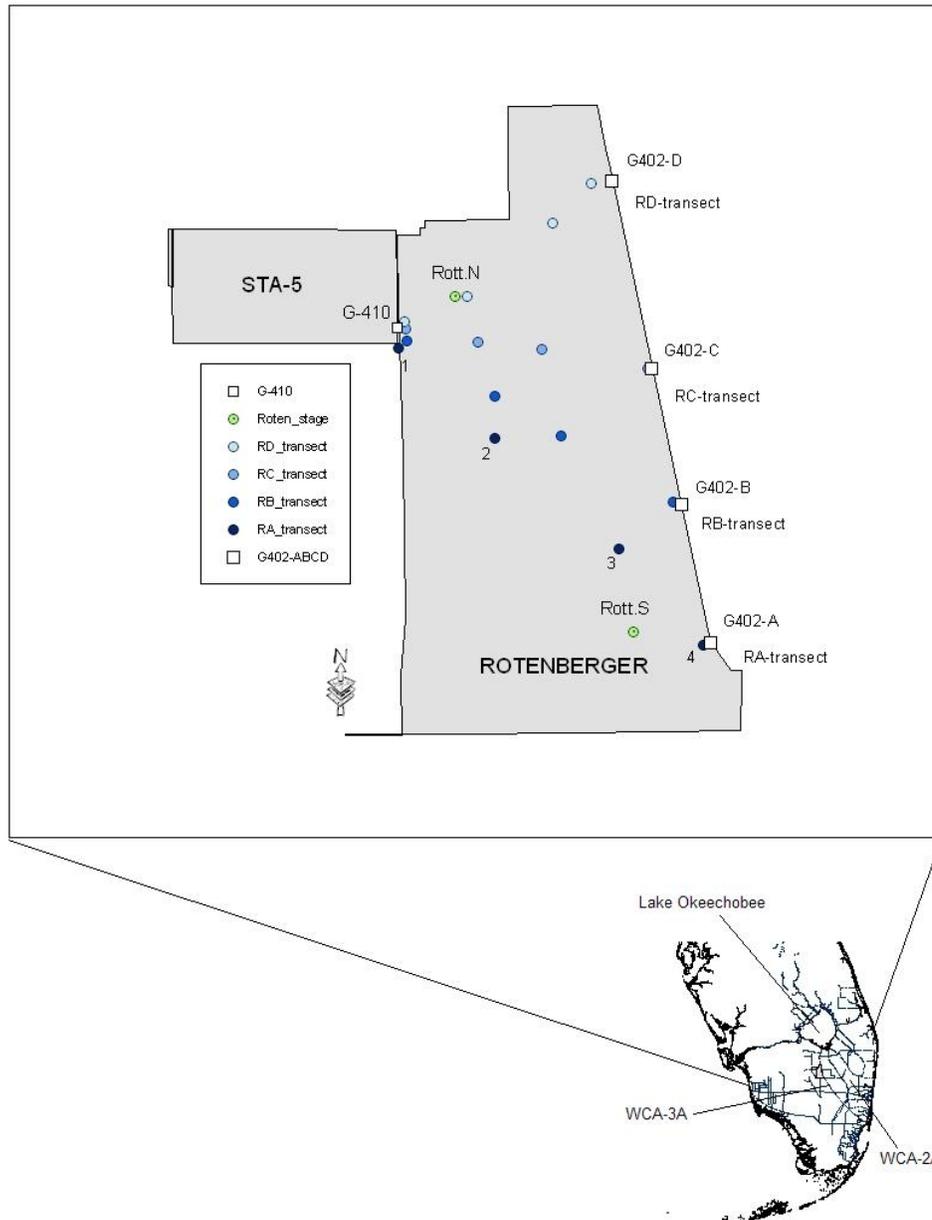


Figure 1-1. Map showing the location of the Rotenberger Wildlife Management Area (RWMA) north of Water Conservation Area 3A (WCA-3A) and south of Lake Okeechobee with inflow point (G-410) from Storm Water Treatment Area 5 (STA-5), the study transect RC and relative outflow point (G402-C).

Need for Research

The Everglades Forever Act (EFA) recognized the RWMA as part of the historic northern Everglades requiring hydropattern restoration. To achieve this, the South Florida Water Management District (SFWMD) began constructing Storm Water Treatment Areas (STAs) to improve hydrology and water quality, from urban and agricultural runoff, prior to discharge into downstream areas of the Everglades. In July 2001, STA-5 began discharging into RWMA. However, due to years of P enrichment and hydrologic alterations, it is unknown if soils in the RWMA will serve as a P source or sink, relative to STA-5 floodwater concentrations. Since STA-5 began discharging, water column TP concentrations have averaged $50 - 70 \mu\text{gL}^{-1}$, with spikes in concentration entering the marsh as high as $130 \mu\text{gL}^{-1}$. Because the RWMA is not considered part of the Everglades Protection Area (EPA), inflow TP concentrations are not required to meet the $10 \mu\text{gL}^{-1}$ P-limit criteria set by the Florida Department of Environmental Protection. However, as dictated by the EFA permit for STA-5, discharges are required to be at $50 \mu\text{gL}^{-1}$ or below, a annual average. Determining the ability of the soil to adsorb P, as well as defining the EPC of the soil, will aid in predicting P-flux and the affect of STA-5 floodwater on RWMA marsh recovery.

Existing soil nutrient data shows fairly uniform TP concentrations throughout the RWMA marsh, as well as with depth, therefore it is hypothesized EPC values and P-fluxing concentrations would be spatially homogeneous. However, spatial differences in EPC and P flux across the RWMA needs to be verified to clarify differences between sites and variances in soil P concentrations that may occur from inflow to outflow. Moreover, determining the type of P-species flowing into and out of the marsh, in addition to fluxing out of the soil, is critical information for management of the system.

For example, inorganic P is readily available to plants and microorganisms where as dissolved organic P is not directly available for uptake resulting in less effect on plants within the marsh, but a higher probability of transport downstream. Also, the type of P available in the soil will influence what P species is available to flux (Novak et al. 2004). Finally, the potential of the soil to sorb P, over time, will assist in marsh recovery calculations and establish concentration levels, at which P will be a significant source.

As water flows from the RWMA into the central Everglades, high outflow P concentrations have the potential to impact P-loading limits at main pumping structures, specifically the S-8 structure located on the Miami Canal. This structure pumps water into northern WCA-3A, part of the EPA, affecting marsh areas further downstream. Currently, the RWMA soils still experience excessive, dry season soil drying and oxidation despite receiving STA discharges. Therefore, in its current state and operations, and based on soil nutrient data previously collected, the RWMA soils can potentially act as a source of P to downstream areas. The purpose of this study is to determine if the RWMA soils will act as a P source or sink to downstream areas as well as ascertain the potential of the soil to sorb additional P flowing in from STA-5.

By establishing the amount of P flux under dry vs. flooded soil conditions, in addition to the amount of P which can be sorbed by the soils, changes to system operations can be evaluated. For instance, if significantly more P fluxes from dry soils than flooded soils, retaining water within the system, by altering inflow and or outflow operations, may suppress significant P-fluxing and allow for biological interactions. Through this adaptive management approach, results from P-flux and P-isotherm experiments will be utilized to evaluate modifications of hydrologic operations to provide

conditions that meet restoration goals. In addition, the P flux research will provide data for the SFWMD recovery model, used in predicting ecological responses of impacted areas of the Everglades to STA effluent, as outlined by the Long Term Plan (LTP) and directed by the EFA.

CHAPTER 2 PHOSPHORUS SORPTION AND DESORPTION CAPACITY

Introduction

Soil in many parts of the Everglades, has become P enriched due to years of over drainage and oxidation, or as a result of high P inflows from urban and agricultural runoff. The ability of these soils to retain P and not become an internal source is an important factor in Everglades restoration. The water column P concentration level at which no P-sorption/desorption occurs is defined as the equilibrium phosphorus concentration (EPC) (Richardson and Vaithyanathan 1995; Nair et al. 1998; Pant et al. 2001). Ascertaining the EPC of the soil can be accomplished through the use of P-isotherms run under laboratory conditions from samples collected at desired field locations. To define the maximum P-sorptive capacity of the soil, isotherms are performed utilizing various solution P concentrations, based on site specific soil P data. Results can be used to determine whether a soil will flux P into the overlying water column based on P concentrations of inflow water.

Phosphorus retention in the soil is affected by several factors such as historic P loading, existing P levels of the soil and incoming water column P concentration levels. In addition, several biological factors, algae and macrophytes, uptake P from the water column and soil, respectively (Bostrom et al 1988; Gale et al 1994). The ability of the soil to release sorbed P or retain P, is dependent upon antecedent soil conditions, soil chemistry and, P adsorption capacity of the soil (Zhou and Li 2001), all of which directly effects ecosystem restoration. For example, if water column P levels from inflows are reduced below EPC levels, P will desorb from soil and flux into the water column.

Soil chemistry primarily affects the solubility of P and influences P-sorption. In studies by Khalid et al. (1977), Richardson (1985) and Sallade and Sims (1997), aluminum (Al) and iron (Fe) content in the soil significantly affected P solubility. Furthermore, oxidation of the soil, promoted by prolonged marsh draw downs, affects the types of Fe (ferrous to ferric) available to bond with P. Under oxidative conditions, soils containing high Fe content can regulate P-sorption (Reddy et al. 1998). These inorganic crystalline forms of Fe-P can become soluble upon flooding versus organic forms, thereby releasing inorganic bioavailable P (Patrick and Khalid 1974; Pant et al. 2002). Specifically, high Al/Fe content in the soil can affect inorganic phosphorus (iP) species formation. High concentrations of Al and Fe oxides will bond with P forming inorganic Fe-P and Al-P bound compounds (Sallade and Sims 1997).

Generally wetland soils assimilate iP in greater concentrations than organic P (oP) (Pant and Reddy 2001) and depending on soil chemistry, hydrology and biological factors, can store iP more readily than oP. In addition, P storage pools in the soil can affect P-sorption and solubility, based on predominately inorganic or organic forms. Ascertaining P species (bioavailable) retained or released from the soil is ecologically important to wetlands with respect to eutrophication. Depending on P-species in the water column, antecedent soil conditions and oxidation, oP or iP can be released.

The objectives of this study were to 1) establish the EPC of the soil spatially from inflow point across the marsh to outflow and 2) measure the maximum P-sorptive capacity of the soil when exposed to low P and high P treatments.

Methods

Phosphorus isotherms were run on composite soil samples, collected from the RWMA along an existing representative transect (RC) of soil, vegetation and hydrologic conditions,

located in the northern portion of the marsh, to determine the EPC of the soil and maximum P adsorptive capacity of the soil. The 0-2 cm depth was collected being the most reactive soil layer with the overlying water column, based on current soil nutrient data, containing the highest P concentration. Three replicates of the top 0-2 cm layer of soil were combined into one composite sample per site, representing each of the four sites (RC-1, RC-2, RC-3, RC-4). The RC transect runs from west to east, the direction of water flow, with RC-1 located near the western side (inflow) of the RWMA adjacent to the inflow structure (G-410 pump), and RC-4 located near the eastern side (outflow), adjacent to the outflow structure (G-402 C, a gated box culvert).

Each sample was collected using a 2 cm deep, 10.16 cm diameter wide coring ring. Prior to field sampling all plant material was removed. Samples were then placed in plastic bags, stored in a cooler on ice and transported back to the lab. All soil was spread out in a thin layer on individual trays and air dried at room temperature (25.5° C), for approximately five weeks. Prior to drying the soil, all plant material and small stones were removed. Then, the soil trays were covered with screen to prevent contamination and, as seedlings emerged from the soil, they were removed. Once dry, the soil was ground, passed through two sieve sizes (2 mm and 0.88 mm), then ground and sieved again. Any remaining material which could not pass through the sieves was discarded.

Initially six P concentrations plus a control (0 - control, 10, 30, 50, 100, 500 and 1000 μgL^{-1}) were used to produce P-isotherm curves for each site, to determine the EPC and the potential maximum P-sorptive capacity of the soil. Therefore, each site consisted of seven treatments, with three replicates per treatment, for a total of 84 initial samples along the RC transect. Three grams of soil were weighed and placed into 50 ml centrifuge tubes then

spiked with 50 mM KCL solution. Each spike contained one of the seven P concentrations prepared from 1000 ppm standard stock solution, derived from dissolving 1.0985 g of potassium dihydrogen phosphate (KH_2PO_4) into 100 ml of D.I. water, contained in a 250 mL class A volumetric flask, then diluting with D.I. to the mark and mixing. Two sub-stock solutions, 5 mgL^{-1} and 50 mgL^{-1} , were prepared from an original 1000 mgL^{-1} solution to spike each of the seven treatment concentrations. The KCL-P solution treatments were prepared by measuring out 1.863 g of KCL dissolved into 200 ml of D.I. water within a 500 ml class A volumetric flask, spiked with the appropriate P sub-stock solution, then filled to the mark with D.I. and mixed, yielding a total of 500 ml each of 0 (control no P additions), 10, 30, 50, 100, 500 and $1000 \text{ }\mu\text{gL}^{-1}$ P-treatment solutions. Centrifuge tubes were then placed on a shaker table set at 180 rpm for 24 hours, to ensure complete mixing of soil and solution. After shaking, tubes were centrifuged for 15 minutes at $22 \text{ }^\circ\text{C}$ at 4000 rpm, and approximately 5 – 8 ml of the supernatant was extracted using a transfer pipette. The supernatant was then filtered through a $0.45 \text{ }\mu\text{m}$ filter. Each sample was measured for soluble reactive phosphorus (SRP) by the SFWMD Water Quality lab using standard methods (SM4500PF, Clescerl et al 1999) and SFWMD methods (SFWMD 3080.1 Rev. 2.2).

Ground soils used for P isotherms were sub-sampled and submitted to DB Environmental Labs, Rockledge, Florida for analysis of oxalate extractable Iron (Fe) and Aluminum (Al) analysis using standard methods EPA 236.1 and EPA 202.1, respectively.

Isotherm calculations

Phosphorus sorption data was calculated and fit using the linear, Freundlich and Langmuir isotherm equations (Reddy et al. 1998; Zhou and Li 2001). The linear equation was used to fit low P concentration results, while the Freundlich equation fit low to medium

P concentrations, and the Langmuir equation is applied to high P concentrations (Zhou et al. 1997).

Linear isotherm: $S = KC - S_0$

S = the amount of P sorbed in the solid phase, $\mu\text{g g}^{-1}$

K = P-sorption coefficient

C = P concentration in solution after 24-h equilibration μgL^{-1}

S_0 = constant, amount of originally adsorbed P

In addition, the equilibrium phosphorus concentration (EPC), which is defined as the concentration of P in a solution when neither sorption or desorption is occurring, is equal to C when $S = 0$ (Pant et al. 2002). Therefore the EPC was calculated from regression statistics data as the intercept (point at which a line intersects the y-x-axis) divided by the x-variable.

Freundlich isotherm: $S = K_f C^n$

K_f = constant

$n < 1$

S as above

Langmuir isotherm: $C/S = 1/(bS_{\max}) + C/S_{\max}$

S_{\max} = P sorption maximum $\mu\text{g g}^{-1}$

b = a constant related to bonding energy

C/S = as defined earlier

Results

All three isotherm equations (linear, Freundlich and Langmuir) were applied to the initial P-sorption results measured from each site. For each site, P-sorption data remained linear (Figure. 2-1 a-d), with no inflection point indicating the P-concentration in which the maximum P sorptive capacity of the soil was reached. Therefore, the linear isotherm

equation best describes the low P-concentrations of all sites, supported by high regression (R^2) coefficients (Table 2-1). Additionally, EPC of the soil for each site was calculated and results reported in Table 2-2. Sites RC1 (inflow) and RC4 (outflow) had similar EPC measurements of 94.5 and 93.2 μgL^{-1} respectively. The RC3 site, which is in the marsh interior, was lower at 73.6 μgL^{-1} , though not significantly. Conversely, the RC2 site was significantly lower ($P = 0.05$) than all other sites measuring 18.8 μgL^{-1} .

To ascertain the potential maximum P-sorptive capacity of the RWMA soils, additional P-isotherms of 2000, 5000 and 10,000 μgL^{-1} were run and the data added to the initial results. The Freundlich and Langmuir equations were then applied to determine the best fit according to R^2 values (Table 2-1). While both equations fit well, according to R^2 values, the Freundlich equation is a better fit for the higher P-concentrations (Figure 2-2 a-d). P-sorption parameters measured from each treatment concentration at each site are reported in Table 2-2. The isotherm inflection points indicate the P-concentration at which the soil is reaching its maximum sorptive capacity. Because inflection points (line begins to curve) on each graph for each site is not well defined, estimates of the P-sorptive capacity of the soil is approximated as: RC1 ~ 40-60 ug g^{-1} , RC2 ~ 40-60 ug g^{-1} , RC3 ~ 40-60 ug g^{-1} , RC4 ~ 40-60 ug g^{-1} .

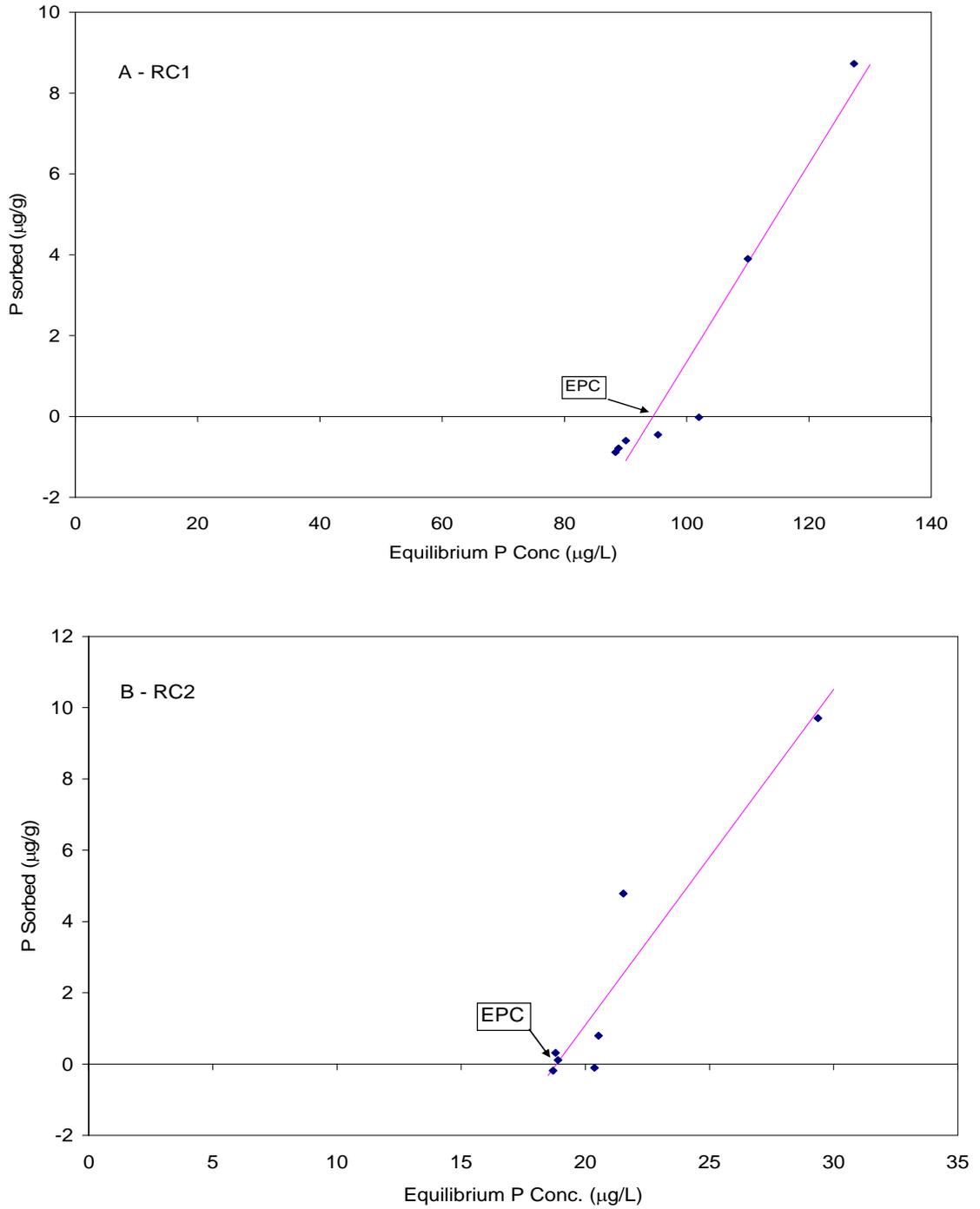


Figure 2-1 Linear isotherm result for the RC transect depicting the equilibrium phosphorus concentration (EPC) on the x-axis and the amount of P-sorbed on the y-axis. The line is the best fit for all values which shows EPC is actually a range of values. A) RC1 site. B) RC2 site C) RC3 site D) RC4 site.

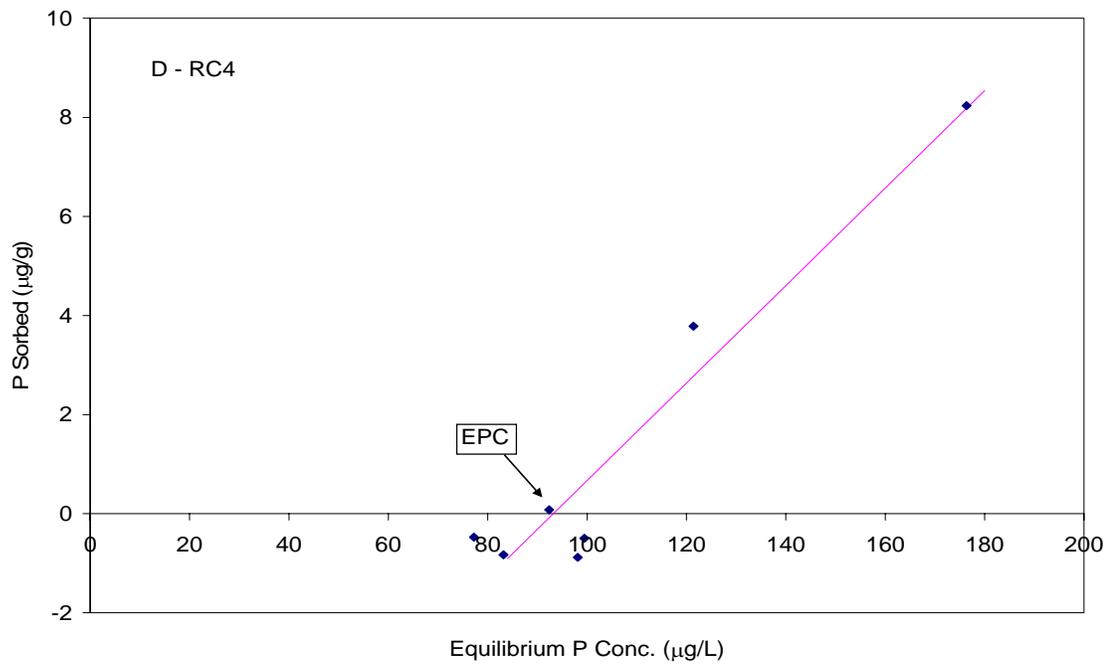
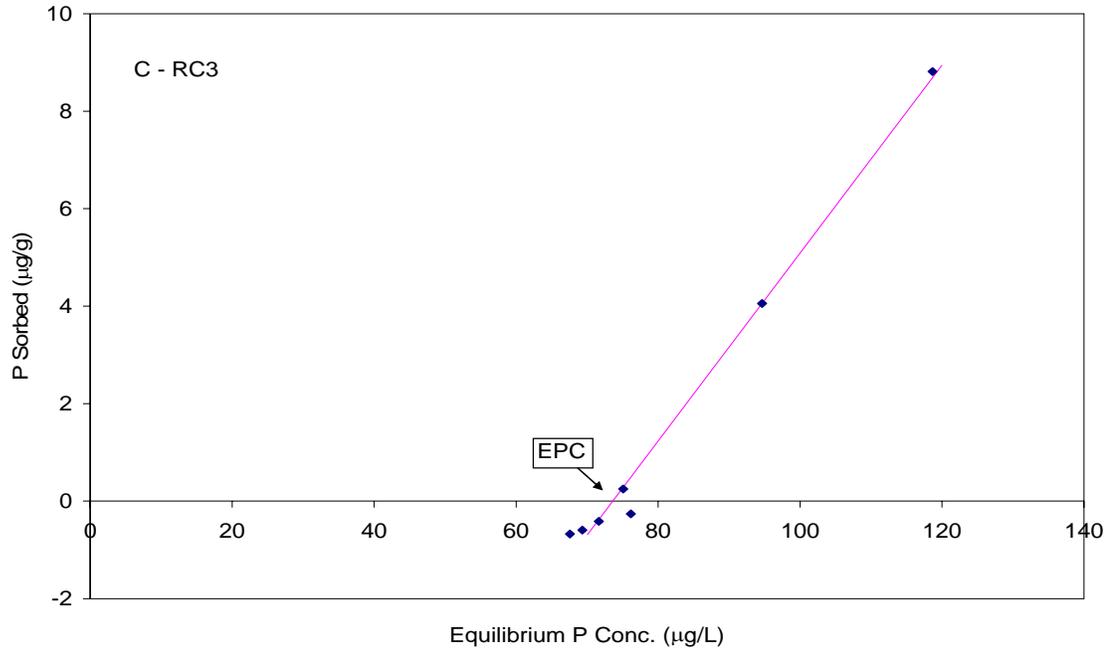


Figure 2-1. Continued.

Current soil nutrient concentrations for each site are reported in Table 2-3. All P-isotherm P-concentration measurement data used to calculate each isotherm equation and associated plot

Table 2-1. List of regression (R²) coefficients used to determine which isotherm equation, linear, Freundlich or Langmuir, best fit the P-sorption data.

	Linear,R²	Freundlich,R²	Langmuir,R²
RC1	0.930	0.990	0.880
RC2	0.900	0.980	0.830
RC3	0.980	0.990	0.980
RC4	0.920	0.980	0.840

Table 2-2. P-sorption parameter results for the linear, Freundlich and Langmuir equations for equilibrium phosphorus concentration (EPC), K_f- a constant in the Freundlich equation, Cⁿ – measure of P concentration in solution after 24 hours, S_{max} – the P sorption maximum and b – a constant in the Langmuir equation.

	Linear	Freundlich		Langmuir	
	EPC, μgL^{-1}	K _f	C ⁿ	S _{max} $\mu\text{g g}^{-1}$	b
RC1	94.5	0.469	0.858	397.7	0.0007
RC2	18.8	1.49	0.853	268.4	0.0041
RC3	73.6	0.506	0.78	206.4	0.0009
RC4	93.2	0.201	0.848	189.5	0.0006

concentration measurement data used to calculate each isotherm equation and associated plot data is listed in Appendix 2-1.

Results of oxalate-extractable Al (Figure 2-3) and oxalate-extractable Fe (Figure 2-4) were variable with no apparent spatial trends, therefore results are combined. The isotherm soils were composite samples collected from the field and not replicates. Due to the single measurement per site, statistical differences between sites could not be established, and are used to characterize soil chemistry. Concentrations of Fe and Al were high compared to other Everglades marsh areas. The average Fe content for the RC transect in RWMA is 4950 ± 275 mg/kg compared to Fe content in WCA2A at 344 ± 37 mg/kg (SFWMD, Everglades Threshold data) and Loxahatchee National Wildlife Refuge (LNWR) of 339 ± 57 mg/kg (SFWMD, Everglades Threshold data). Average Al content is 2450 ± 515 mg/kg for the RC transect in RWMA, 248 ± 13 mg/kg in WCA2A (SFWMD, Everglades Threshold data) and

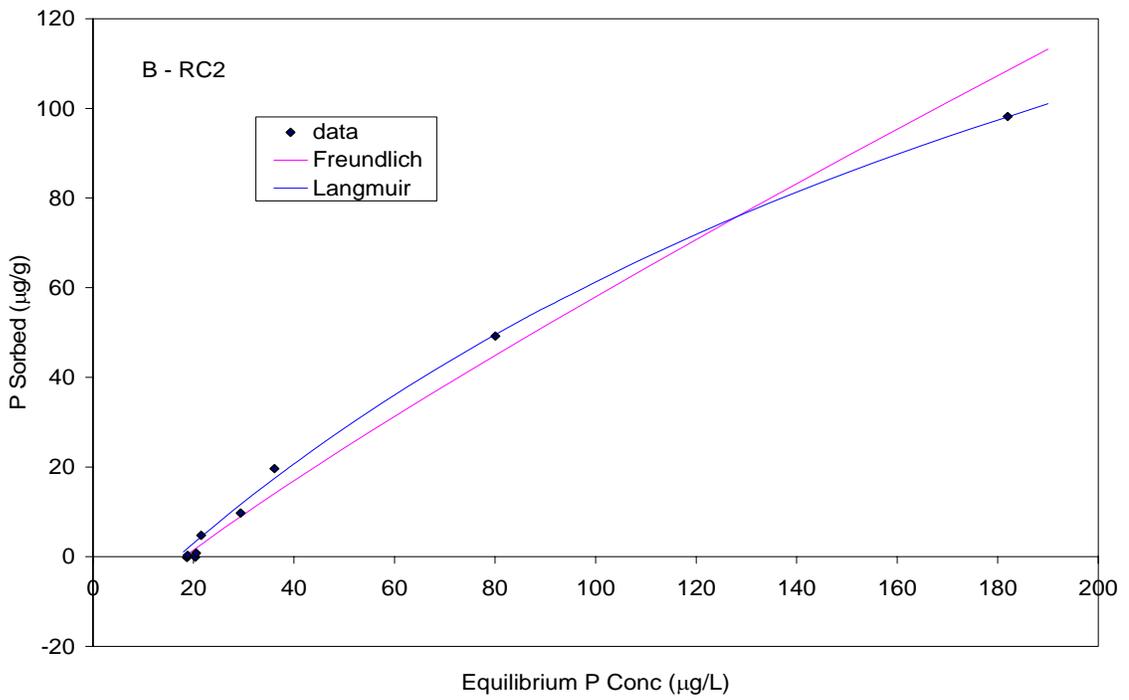
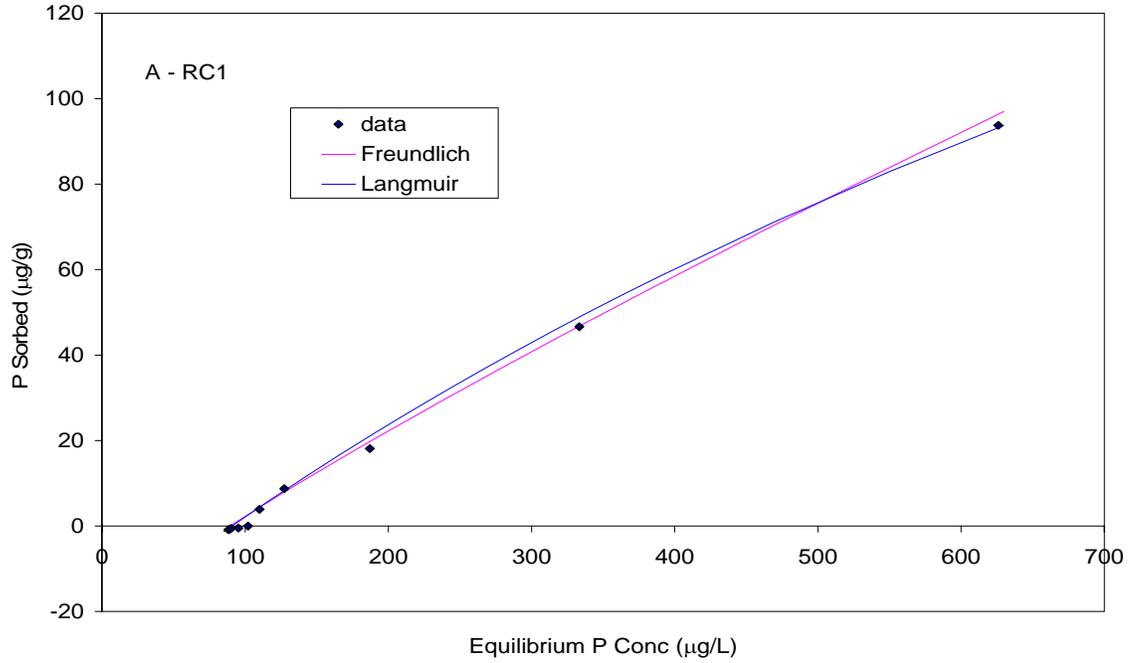


Figure 2-2 Freundlich and Langmuir isotherms for the RC transect depicting which equation best describes the P-sorption maximum. A) RC1 site. B) RC2 site. C) RC3 site. D) RC4 site.

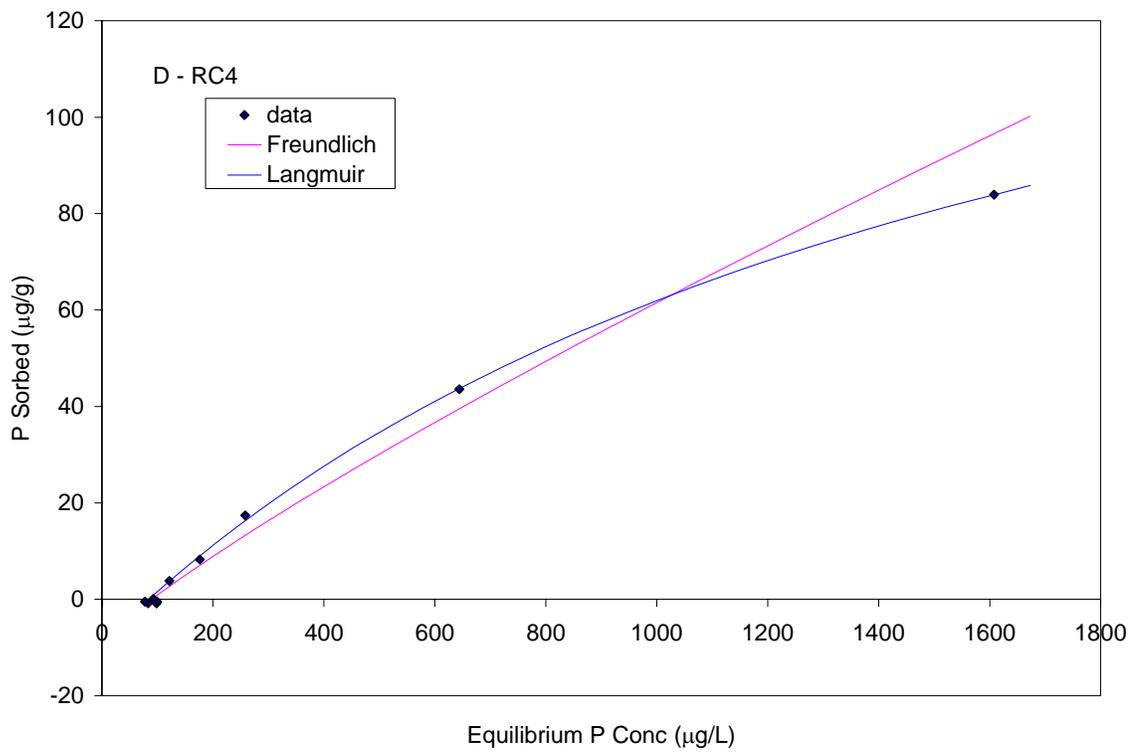
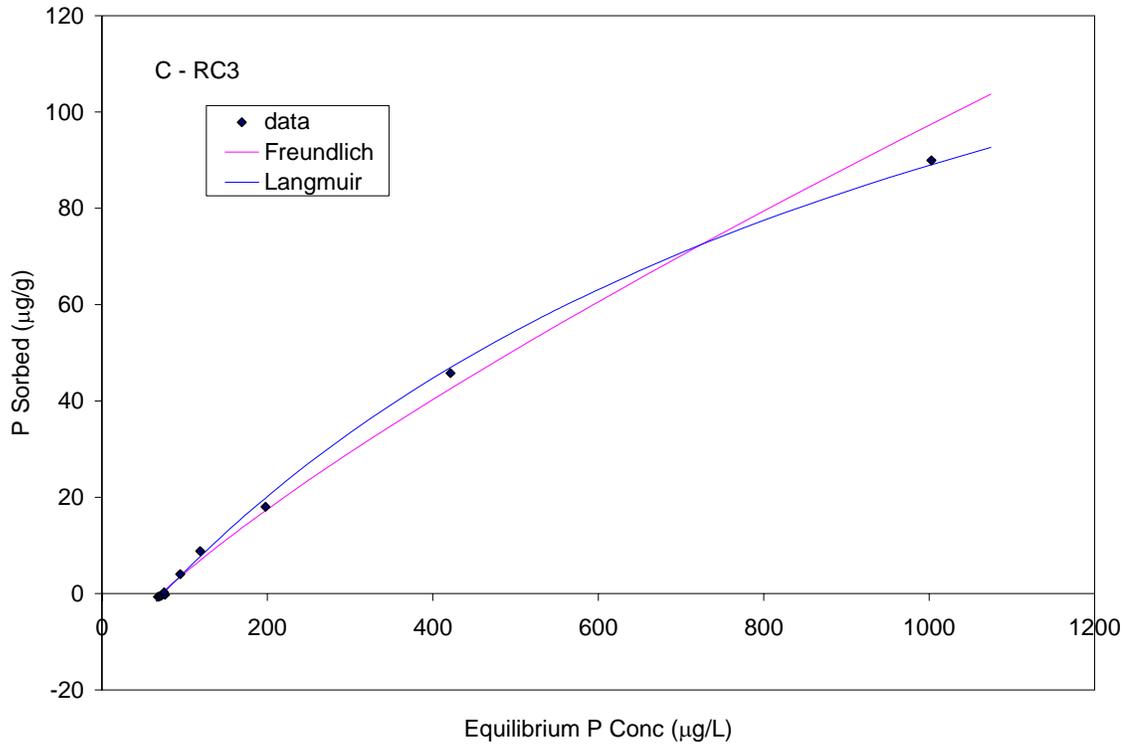


Figure 2-2. Continued.

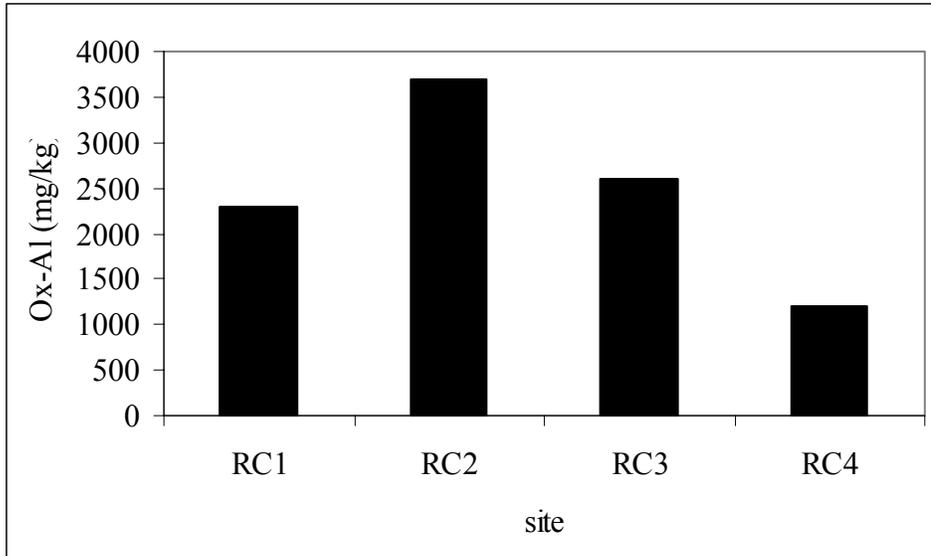


Figure 2-3. Oxalate-extractable Al composite samples collected at the sites along the RC transect and therefore are not replicates so error bars are not shown.

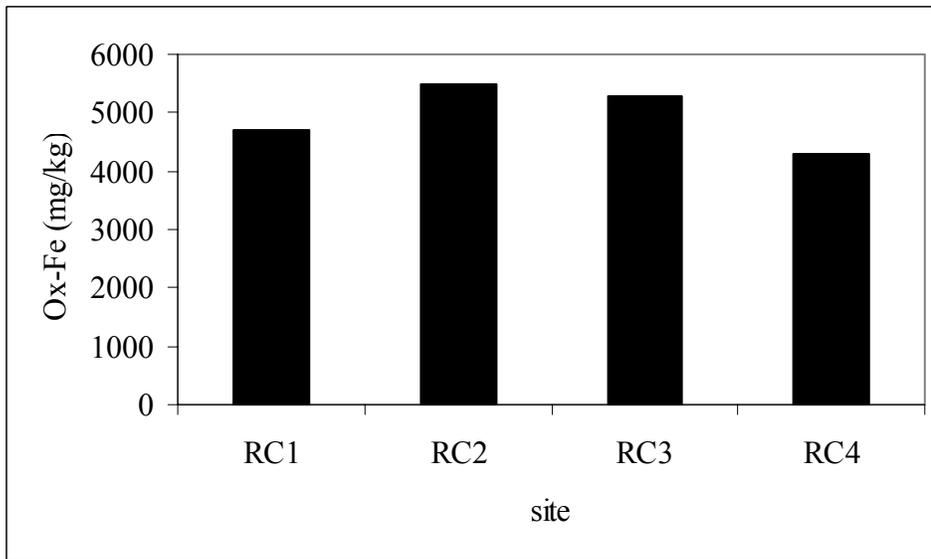


Figure 2-4. Oxalate-extractable Fe composite samples collected at sites along the RC transect and therefore are not replicates so error bars are not shown.

In LNWR, 353 ± 51 mg/kg (SFWMD, Everglades Threshold data). For comparison purposes, the results were corrected for bulk density and compared to soil from LNWR and WCA-2A (Table 2-4).

Table 2-3. RWMA soil nutrient concentrations for each site in the RC transect. Data collected by the SFWMD, Downstream Monitoring and Research Program.

	TP, mg/kg	TN, mg/kg	TC, mg/kg	Bulk Density	% Ash
RC1	741 ± 53	34066 ± 2140	465333 ± 9135	0.16 ± 0.015	16.46 ± 2.22
RC2	740 ± 79	33000 ± 643	454333 ± 2333	0.16 ± 0.012	17.1 ± 0.58
RC3	547 ± 44	33300 ± 1007	449666 ± 5696	0.20 ± 0.015	20.96 ± 0.86
RC4	694 ± 18	32000 ± 557	468666 ± 1764	0.17 ± 0.003	14.63 ± 0.26

Table 2-4. Comparison of oxalate extractable Fe and Al content in soils, corrected for bulk density, from the RWMA, LNWR and WCA-2A. Data reported for LNWR and WCA-2A from the SFWMD, Everglades Threshold Program.

	Bulk density, g/cm³	Ox-Fe, g/m³	Ox-Al, g/m³
RWMA	0.21	1039.5	514.5
LNWR	0.06	20.34	21.18
WCA-2A	0.068	23.39	16.86

Discussion

The inflow (RC1) and outflow (RC4) sites had similar EPC values, as did the RC3 site, while the RC2 site was significantly lower from the other three sites. Topographic elevations indicate the RWMA resembles a saucer, with the western and eastern edges of the marsh higher in elevation than the interior, suggesting the two outer sites (RC1, RC4) are drier and oxidize for longer periods of time than the interior sites (RC2, RC3). While soil TP data (~640 mg/kg) of the top 2 cm of soil is consistent throughout the RWMA (SFWMD, Downstream Monitoring and Research Program), hydrology may have a significant influence on soil conditions with increased oxidation (Leeds et al. in progress).

Although the difference in EPC value at RC2 was unexpected, this site as well as the RC3 site, is slightly lower in elevation equating to a longer hydroperiod. Additionally, the RC2 site is closer to the STA-5 inflow point from than the other interior site, RC-3, and maybe be affecting by increased water levels due to exposure to inflows. Therefore, the soils do not dry out and oxidize as frequently, suppressing the formation of soluble P. The EPC

results of all transect sites reveals the heterogeneity of the soil composition. One hypothesis for these results is, while the RC-2 site has a greater ability to sorb P, sites closer to the inflow receiving water lower in P concentration than the soil, will flux P into the water column. The fluxed soluble P is transported downstream to lower EPC sites, where P-sorption will occur, thereby increasing the soil P concentrations. Over time the localized P-flux and sorption cycle may eventually reach equilibrium. However, ecological impacts could be significant if equalization is due to, high P inflows and continued oxidation and reduced hydroperiods.

In comparing the RWMA P-isotherm data to other Everglades areas, EPC is correlated with P-enrichment of the soil (Richardson and Vayithianyan 1995; Zhou et al. 1997). In WCA-2A, Richardson and Vayithianyan (1995), using both the linear and Langmuir models, showed a linear decrease in EPC, from enriched to un-enriched soil EPC values along an existing P gradient. Additionally, they had reported higher EPC values at inflow, which contains an approximate soil TP concentration of 1500 mg/kg (SFWMD, Everglades Marsh Ecology Program) versus the RWMA TP soil concentrations at 640 mg/kg. Alternatively, they predicted maximum P-sorptive capacity to be ~ 700 mg/kg, where as I estimated the RWMA maximum P-sorptive capacity closer to 40 - 60 mg/kg, based on the amount of P sorbed at $80 \mu\text{g/L}^{-1}$. In WCA2A and other areas of the Everglades, P-sorption is controlled by calcium (Ca) and may have a higher sorption potential than Fe as it is not influenced by redox. Furthermore, the difference between these two studies could be the higher TP soil enrichment in WCA-2A which, increases P-sorption, or could be due to a difference in available cations in the soil. When RWMA isotherm results are compared to un-enriched ($\leq 650 \text{ mg/kg}$) southern Everglades soil (Zhou and Li, 2001) where EPC values

(0.002 – 0.010 μgml^{-1}), maximum P-sorptive capacity ranges from 1780 – 2575 $\mu\text{g g}^{-1}$ and soil TP concentrations are low, the RWMA soil had a much lower maximum P-sorptive capacity, 40 – 60 $\mu\text{g g}^{-1}$.

When corrected for bulk density, the Fe and Al content in the RWMA soil is high compared to other Everglades marsh areas regardless of TP content. While both Fe and Al concentrations are elevated, the Fe content is higher than Al concentrations, suggesting Fe could be the primary regulator of P sorption and Al a secondary regulator (Zhou et al 1997; Pant et al. 2002), as there are more available cations for P to bind to. Similar studies by Reddy et al. 1998 and Nair et al. 1998, reported P retention was strongly correlated to Fe and Al content present in the soil. Furthermore, Khalid 1977, stated under reduced conditions, Fe and Al were primary factors in P retention in flooded soils, and anaerobic conditions will increase P solubility (Gale et al. 1994).

Therefore, soils that are highly enriched, such as in WCA-2A, are not able to sorb as much P from the water column, possibly because they have reached a P-saturation point. These soils have the potential to act as an internal source of P, if inflow water to the marsh is low (below EPC). In marsh areas similar to the RWMA, where EPC is variable and max P-sorptive capacity is less than highly enriched areas, the potential exists to contain soluble P, partially due to the availability of Fe and Al cations without negatively affecting marsh areas downstream. In addition, soil chemistry conditions, in particular the high Fe and Al content, which may be regulating P adsorption, are influenced in the RWMA by hydrology. Restoring or adjusting the hydrology to prevent conditions conducive to oxidation and muck fires is a critical component to RWMA restoration.

CHAPTER 3 FLUX OF BIOAVAILABLE PHOSPHORUS

Introduction

Wetland soils that have undergone nutrient enrichment can become internal sources of Phosphorus (P) and Nitrogen (N) thus affecting restoration goals. Additionally, hydrologic conditions can exhibit a significant affect on the flux rate of these nutrients when hydroperiods are severely altered (shortened), resulting in elevated water column concentrations (Olila et al. 1997; Pant and Reddy 2001). Furthermore, the inorganic or bioavailable P and N species present, plays a major role in contributing to the eutrophication of a wetland (Moore et al. 1991). Flux of P and N is dependant upon antecedent soil conditions as well as, the various P storage pools in the soil, and P concentrations in the overlying water column. Nitrogen can be lost to the system through volatilization (Reddy et al. 1996), whereas P accumulates in the soil, often resulting in a long-term mass increase in total P. If long-term P immobilization processes are altered, or if antecedent soil conditions are anthropogenically enriched, marsh areas that once provided a P sink can become a source of P, especially when receiving inflow containing low P concentrations. The internal loading potential of these enriched or hydrologically altered soils can perpetuate eutrophication and prolong marsh recovery efforts (Pant and Reddy 2003).

The Florida Everglades has undergone anthropogenic alterations to hydrology and water quality for over 50 years. Changes in hydrology have extensively reduced hydroperiods, particularly in areas of the marsh cutoff from continuous water inflows,

resulting in extended periods of dry out. Urban and agricultural runoff containing high P concentrations have artificially elevated soil P concentrations in downstream areas of the Everglades. When soil dries out for prolonged periods, moisture level is reduced, resulting in aerobic conditions and increased rates of organic matter decomposition. In addition, when soil moisture content reaches 65% (on a mass basis) and less, organic soil becomes susceptible to burning (Wade et al. 1980). During organic soil burning (muck or peat fires), P soil storage pools can shift from predominately organic to inorganic forms (Smith et al. 2001; Newman et al. 2001), becoming available to flux out of the soil upon re-flooding.

The RWMA has been cutoff from overland flow for over 50 years, which drastically altered the hydrology in this system. As a result, hydroperiods were reduced to an average of three months and, during the remaining nine months, drained soil conditions predominated. Prolonged marsh draw downs severely oxidized the soil, leading to subsidence and muck fires. As a consequence of this altered hydrologic cycle, soil P concentrations became elevated (Newman et al. 1998).

In July 2001, the SFWMD began utilizing STA-5 discharges to increase the hydroperiod in RWMA, in accordance with hydropattern restoration as directed by the Everglades Forever Act (EFA). The effect of re-flooding of these drained soils on P-fluxing, and the movement of soluble P to downstream areas, was unknown. Therefore, the objectives of this study were 1) determine the difference in P and N flux in dry versus continuously flooded soils and 2) quantify differences in flux spatially.

Methods

Soil P concentrations, bulk density measurements and vegetation compositions, do not vary significantly across the RWMA, therefore one representative transect (RC) was

chosen for the intact soil core P-flux study to characterize the soils throughout the marsh. Four sites (RC-1, RC-2, RC-3 and RC-4) compose one transect running west to east with the first, western most site RC-1, located adjacent to the inflow structure (G-410 pump) and the eastern most site, RC-4, located adjacent to the outflow structure (G-402C gated box culvert). The study was conducted during the dry season (December to May) for the Everglades, hence air temperatures and day/night hours were identical to the required environmental conditions. To alleviate the problem of soil within the intact soil core tube pulling away from the side wall during drying and artificially increasing the surface area in which the water column interacts, initial drying and flooding treatments were performed in five gallon soil bucket cores. A standard five gallon bucket with the bottom removed was used as an initial soil coring device. Two five gallon soil bucket cores were collected from each site for dry and flooded treatments. Prior to inserting the bucket into the soil, all vegetation was cleared then, a knife was used to sever all roots, minimizing soil compaction. Cores were taken to a depth of 0–20/30 cm, then transferred to a treatment bucket, by sliding the intact core out of the bottom of the soil core bucket and into a treatment bucket. All soil cores were transferred to a SFWMD research facility located in West Palm Beach, FL and placed in enclosures to prevent incoming rain. Prior to treatment, any remaining vegetation or algae was removed. One soil treatment bucket from each site was continuously flooded with ambient marsh water, and maintained at an approximate flooding depth of 5 cm, while the other experienced 45 days of dry down. Seedlings were removed as they emerged during the treatment period.

During a pilot coring study it was concluded that three, 10 cm diameter soil cores could be collected from each bucket core. Therefore, at day 45 which is an average

duration of draw down for this area of the Everglades, three replicates for each treatment, dry and continuously flooded, were cored for a total of six intact soil cores per site and an experiment total of 24 soil cores. The plastic coring tubes were placed on the soil surface and any remaining root material was severed with a knife to minimize soil compaction. The intact soil cores were removed, capped on the bottom and sealed to contain the core and treatment. The coring tubes were then randomly placed on a table, within an open enclosure containing a clear plastic roof to prevent rainwater from entering, but allowing for full sunlight. Air temperature conditions at the time (February/March) of the study ranged from daytime highs of 18.3° – 25.5° C, and nighttime lows of 7.2° – 18.3° C. Ambient marsh water, collected from the RWMA marsh interior, was used to flood each soil core tube from the top down in an effort to simulate the flooding processes in the field, to a depth of 30 cm. No additional water was added to the tubes after the initial flooding. Finally, all coring tubes were wrapped in aluminum foil to retard algal growth with the top of each core left uncovered.

Water quality samples were extracted from each soil core tube with a syringe inserted into the water column, and filtered as specified by lab analyte requirements, with a 0.45 µm filter, then placed on ice prior to submittal to the SFWMD Water Quality Lab. Samples were analyzed for total phosphorus (TP), total dissolved phosphorus (TDP), soluble reactive phosphorus (SRP), total Kjeldahl nitrogen (TKN), total dissolved Kjeldahl nitrogen (TDKN), nitrate/nitrite (NO_x) and ammonium (NH₄) at time zero, day 7 and day 21 according to standard (Clescerl et al. 1999) and SFWMD methods (Table 3-1). In addition SRP and NH₄ were analyzed at 1hour, 4hrs, 8hrs, 18hrs, 24hrs and days 2, 4 and 14.

Table 3-1. Water Quality standard testing methods according to Clescerl et al. 1999 and the South Florida Water Management District water quality procedures.

Water Quality Parameter	Standard Methods, Clescerl et al. 1999	SFWMD, water quality procedures
SRP,(Orthophosphate, OPO ₄)	SM4500 PF	SFWMD 3080.1, Rev. 2.2
Total Phosphate, TP	SM4500 PF	SFWMD 3100.1, Rev. 3.0
Total Dissolved Phosphate, TDP	SM4500 PF	SFWMD 3100.1, Rev. 3.0
Ammonium, NH ₄	SM4500 NH ₃ H	SFWMD 3060.4, Rev. 1.0
Nitrate/Nitrite, NO _x	SM4500 NO ₃ F	SFWMD 3060.4, Rev. 1.0
Total Kjeldahl Nitrogen, TKN	EPA 351.2	SFWMD 3070.1, Rev. 2.0
Total Dissolved Kjeldahl Nitrogen, TDKN	EPA 351.2	SFWMD 3070.1, Rev. 2.0

From the water quality results, the different forms of phosphorus P species present in the water was calculated, then compared with field water quality data for similar concentration percentages and P availability for algae and plants. The dissolved organic phosphorus (DOP) concentration that fluxed into the overlying water column was calculated by subtracting OPO₄ from TDP. In addition, the organic phosphorus (oP) concentration present in the water column was calculated by subtracting SRP from TP. Finally water column particulate phosphorus (PP) was calculated as TDP subtracted from TP.

Algal growth occurred in the dry soil core tubes after approximately 168 hours as a floating mat, which gradually became thicker until conclusion of the experiment, at which time the majority of the mat sank to the soil surface. The remaining floating mat was skimmed off the top of the water, the soil core dropped out of the bottom of the tube, and the remaining algae attached to the tube wall, scraped and added to the sample. No soil was included in the algae samples, which were sent to DB Environmental Labs, Rockledge, Florida for TP analysis.

Water quality data from the intact soil cores was analyzed using SAS Jump™ version 5, SAS Institute Inc., Cary NC. A two-way, repeated measures ANOVA was run, to determine significant differences for each analyte, temporally and spatially and treatment, drained and flooded. A significance level of (α) 0.05 was used for all analyses. Fluxing rates were calculated based on steepest curve at time 1, 4 and 8 hours.

Results

Drained versus continuously flooded soils were compared for significant differences in flux for all water quality parameters, at each site along the RC transect. The dry soils exhibited higher flux concentrations across all sites and analytes compared to flooded soils. In dry soil, SRP flux was significantly higher ($P < 0.05$) than flooded soils at all sites (Figure 3-1 a,b,c,d). At the RC1 (inflow) and RC4 (outflow) sites, dry soil SRP concentrations were greater than the internal marsh sites RC2 and RC3. Additionally, time 0 results of dry and flooded soils were similar until the one hour time mark, at which point concentrations between the two treatments were significantly different until the 168 to 212 hour time mark. The exception is RC3 which peaked at four hours, then water column P concentrations declined at the eight hour time mark to initial P concentration levels at time 0 which, is also similar to flooded water column P concentrations. Final concentrations measured at time 380 for the RC1 dry soils were significantly lower ($P = 0.03$) than the beginning time 0 concentrations. Fluxing rates, based on steepest curve, were greatest at the RC4 and RC1 sites respectively, than RC2

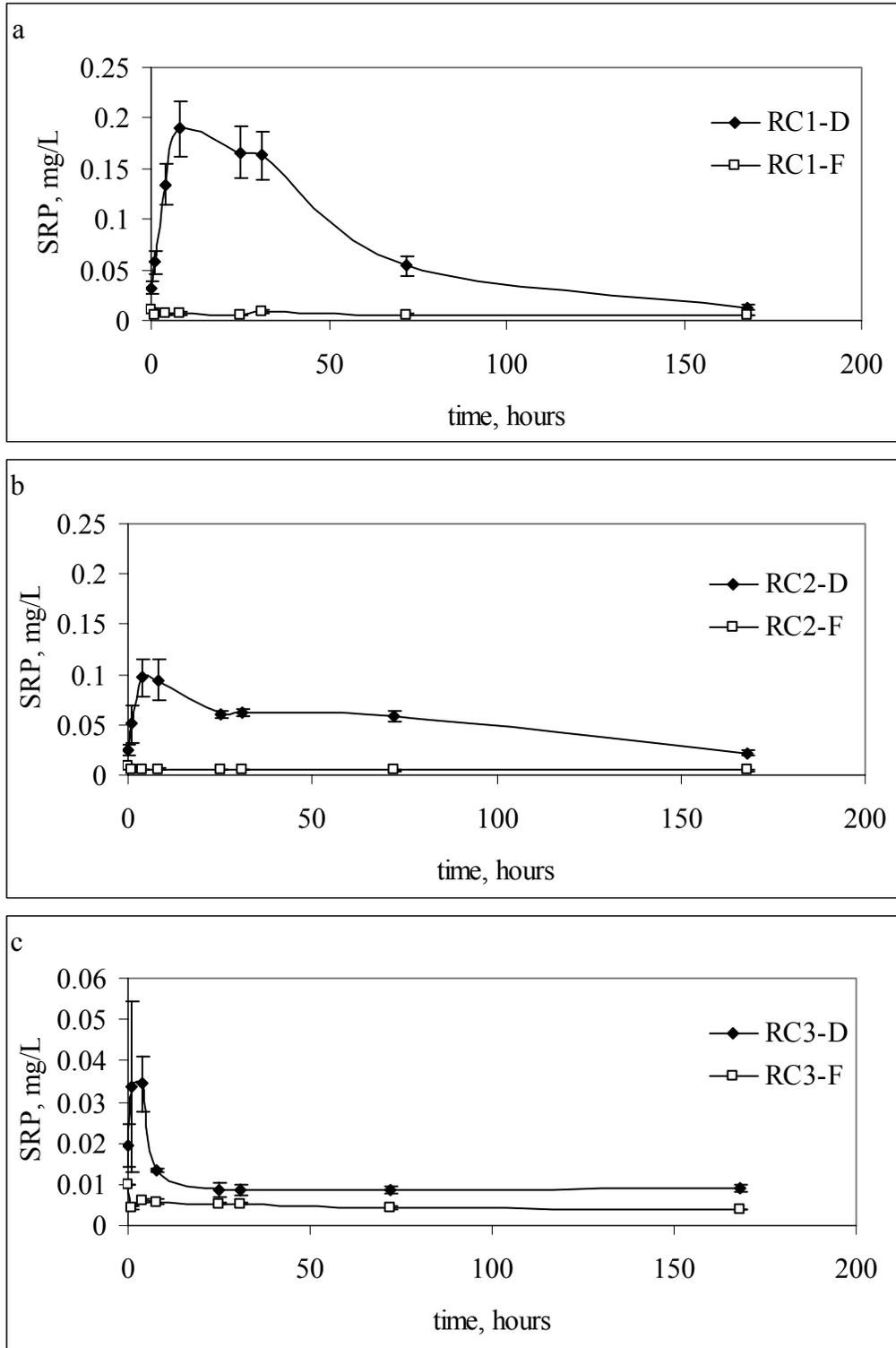


Figure 3-1 SRP water column concentrations in mg/L measured in dry vs. flooded soil core tube treatments at a)RC1 site. b)RC2 site. c)RC3 site. d)RC4 site. All scales are the same with the exception of (c) the RC3 site, which was re-scaled to display the slope of the initial flux.

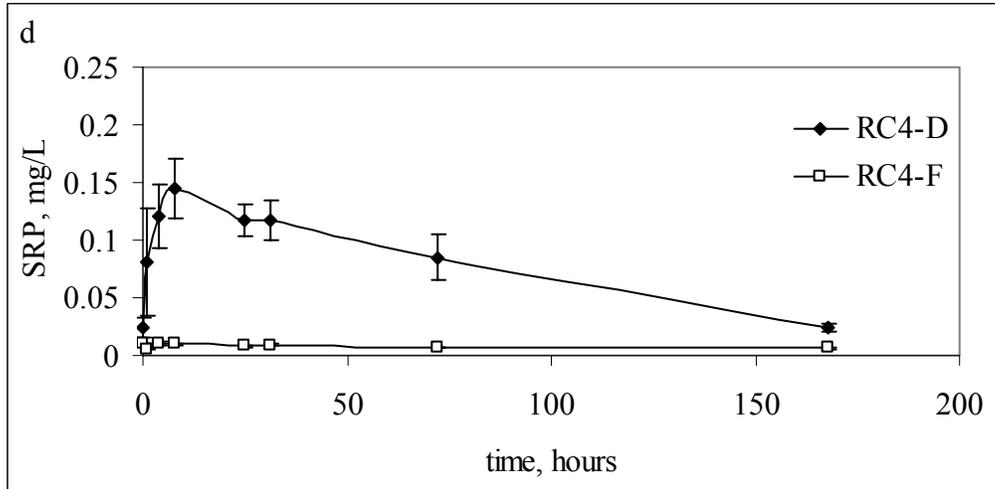


Figure 3-1. Continued.

and RC3 (Table 3-2). Flooded RC1 soils exhibited no significant changes in SRP concentrations measured in the water column throughout the experiment. Total phosphorus (TP) measurements for dry and flooded soils at time 0 were not significantly different, however final concentrations at time 380 hours were significantly different for all sites (Figure 3-2 a,b,c,d). Total phosphorus trends for concentrations were different between dry and flooded soil cores, as dry soil TP concentrations increased with time and flooded TP concentrations decreased with time. Total dissolved phosphorus (TDP) exhibited a similar trend at all sites for both dry and flooded soils, with the highest concentration measurements at time 168 hours then decreasing in concentration levels at time 380 to time 0 concentration levels (Figure 3-3 a,b,c,d).

Table 3-2. Fluxing rates of SRP in $\text{mgL}^{-1}/\text{hr}$ for dry soil cores at each transect site based on steepest curve for time 1, 4 and 8 hours.

time, hours	RC1-D, $\text{mgL}^{-1}/\text{hr}$	RC2-D, $\text{mgL}^{-1}/\text{hr}$	RC3-D, $\text{mgL}^{-1}/\text{hr}$	RC4-D, $\text{mgL}^{-1}/\text{hr}$
1	0.090	0.076	0.053	0.106
4	0.056	0.043	0.022	0.057
8	0.052	0.033	0.013	0.046

For all sites Ammonium (NH_4) fluxed out of the dry soil treatments at significantly greater concentrations ($P < 0.05$) than the continuously flooded soil from the 4-8 hour time to 168 and 212 hour measurements (Figure 3-4 a,b,c,d). Additionally, final concentrations measured at time 380 returned to similar concentrations measured at time 0. All flooded soils released a small amount NH_4 into the water column within the first eight hours then concentrations appeared to reach equilibrium between the soil and overlying water NH_4 concentrations at the final time of 380 hours. The RC1 inflow site dry soil treatment NH_4 concentrations were significantly less ($P < 0.05$) than the RC2,

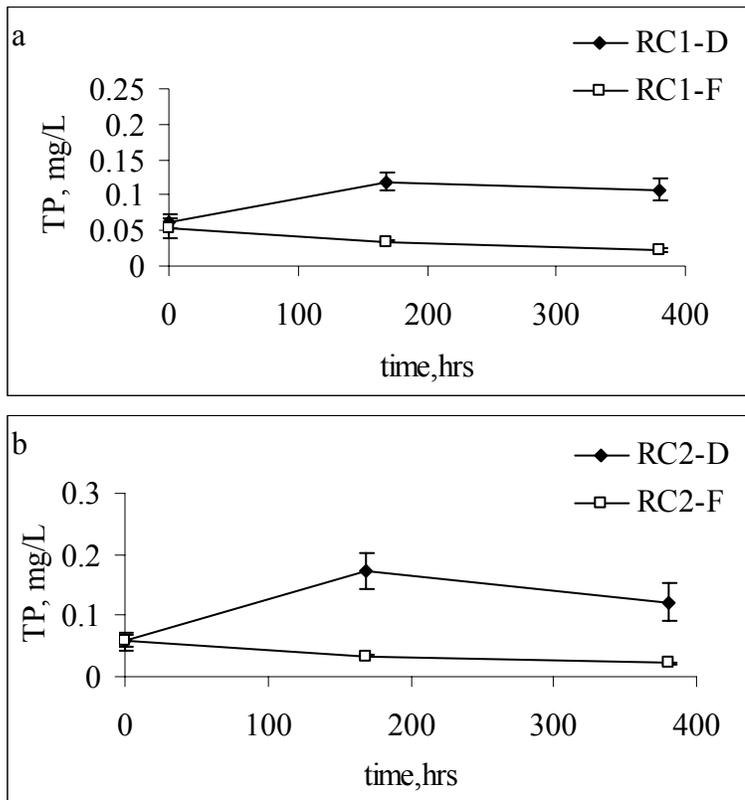


Figure 3-2 TP water column concentrations in mg/L measured in dry vs. flooded soil core tube treatments at a)RC1 site. b)RC2 site. c)RC3 site. d)RC4 site.

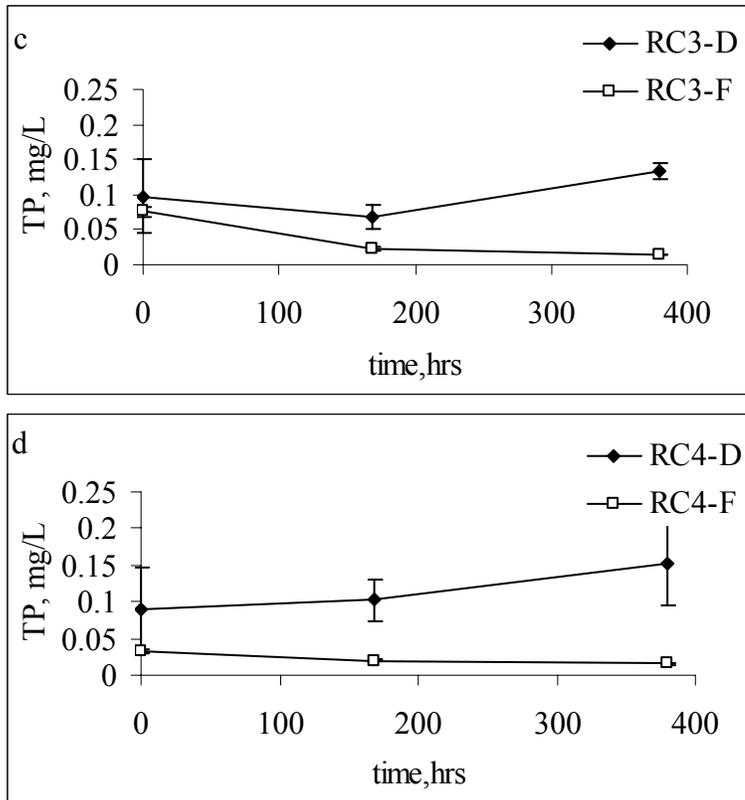


Figure 3-2. Continued.

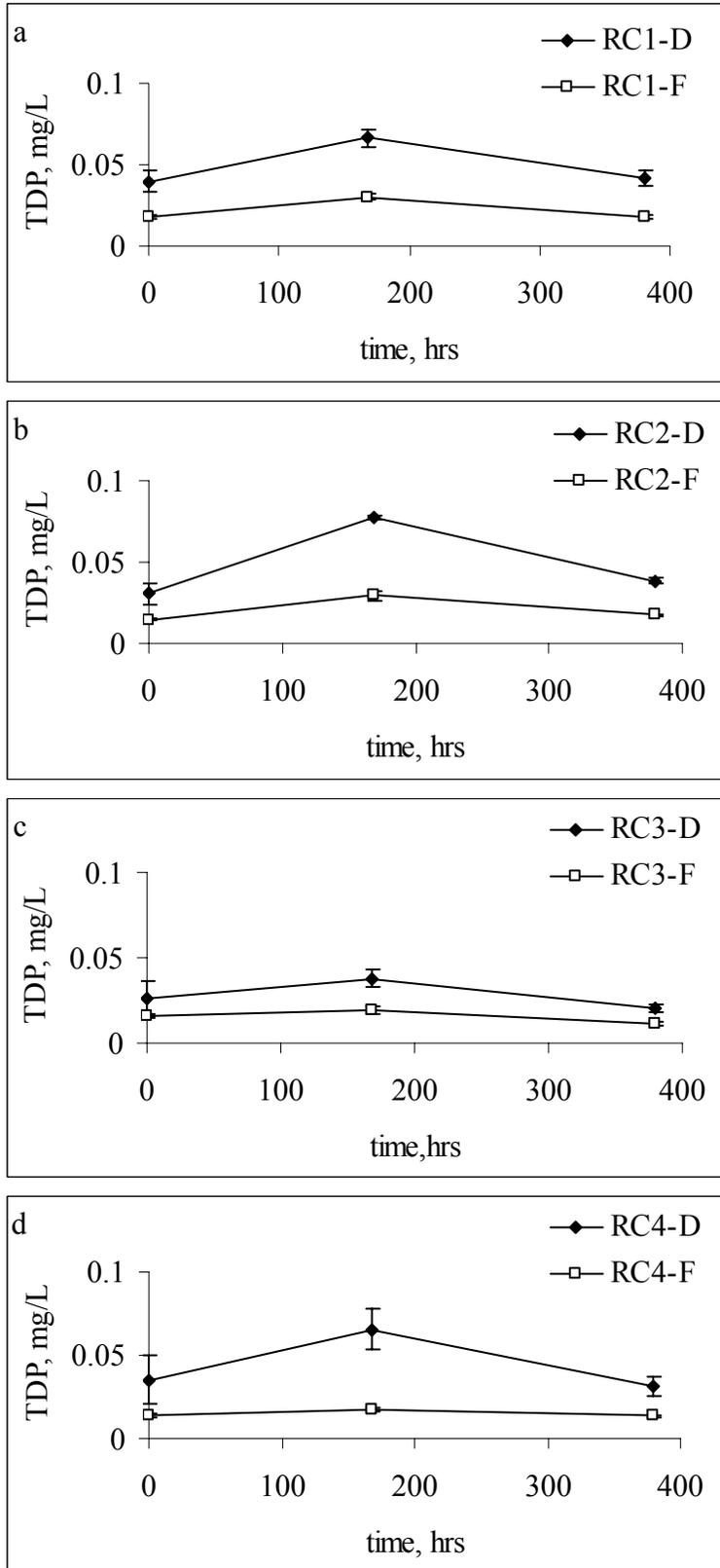


Figure 3-3. TDP water column concentrations in mg/L measured in dry vs. flooded soil core tube treatments at a)RC1 site. b)RC2 site. c)RC3 site. d)RC4 site.

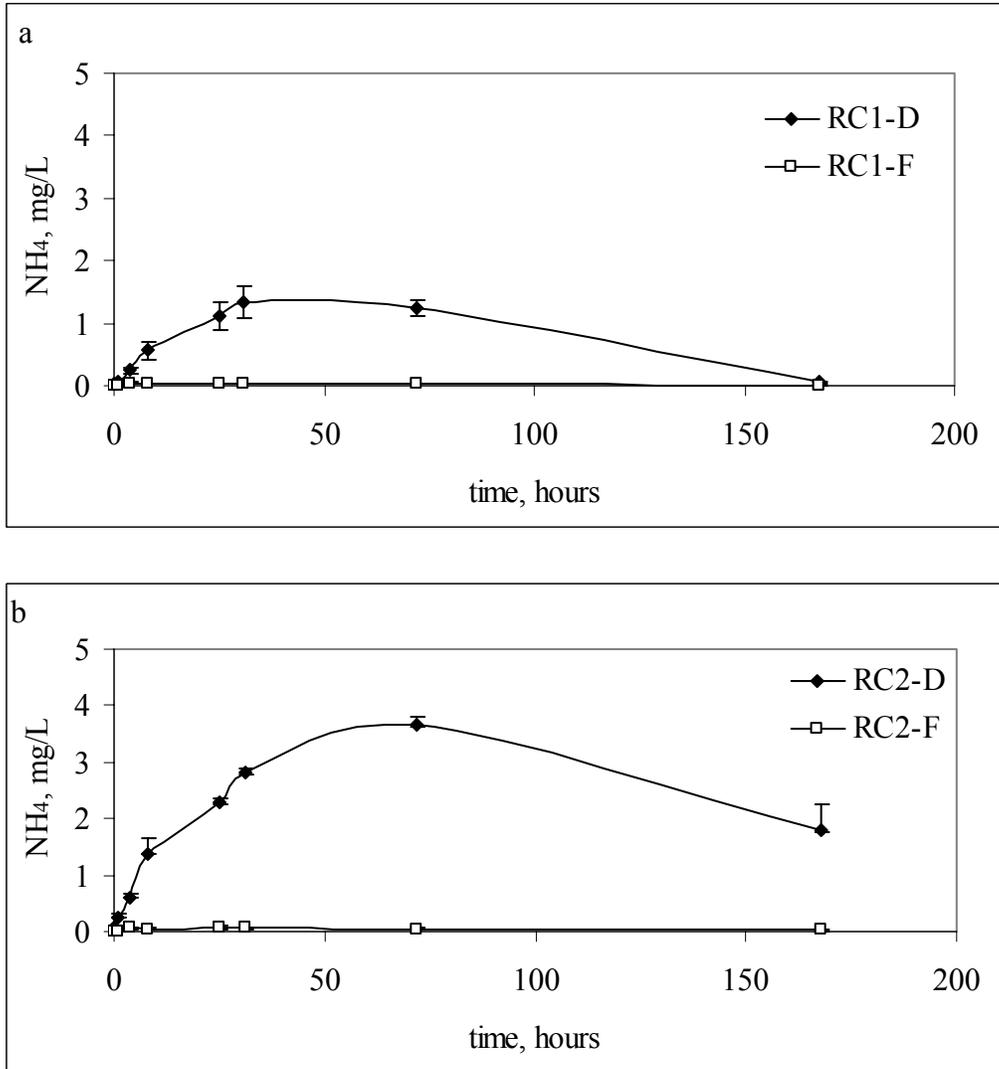


Figure 3-4 NH_4 water column concentrations in mg/L measured in dry vs. flooded soil core tube treatments at a)RC1 site. b)RC2 site. c)RC3 site. d)RC4 site.

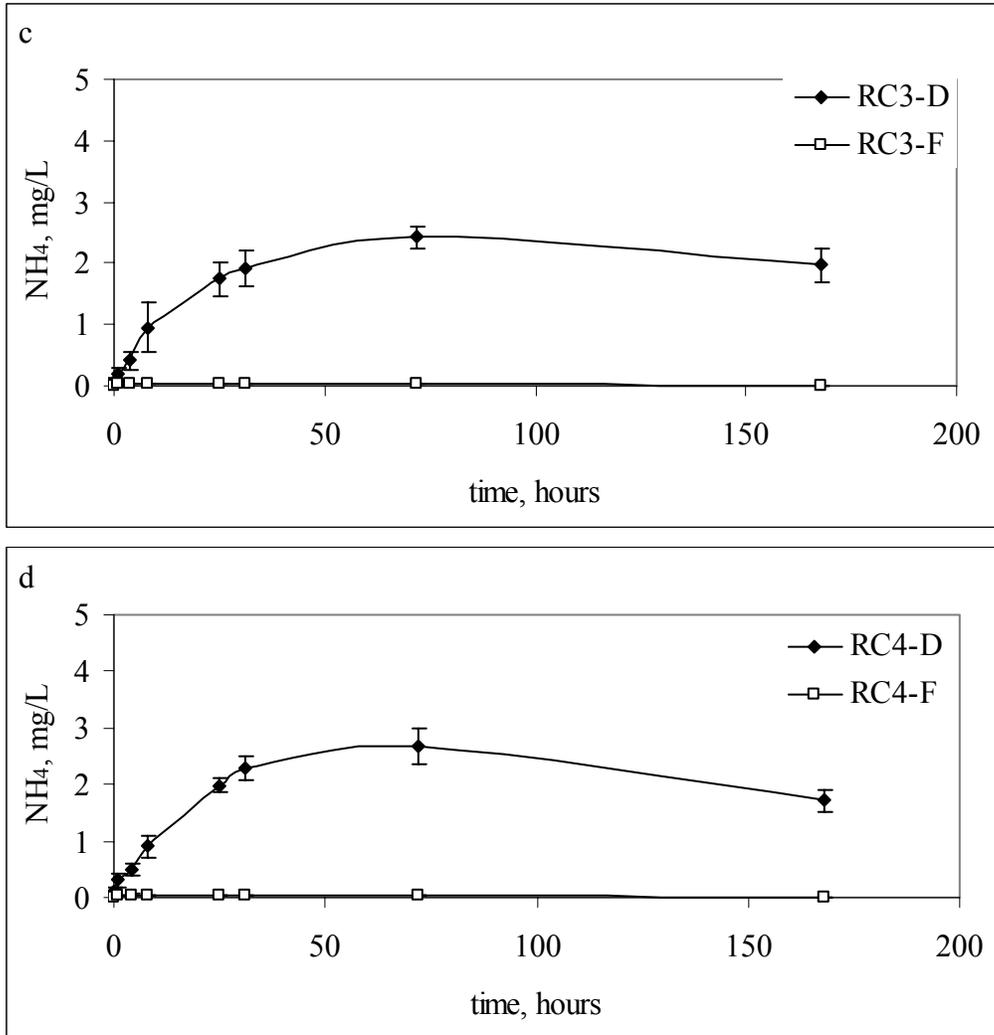


Figure 3-4. Continued.

RC3 and RC4 sites. The additional nitrogen parameters measured in the water quality samples, Total Kjeldahl Nitrogen (TKN), Total Dissolved Kjeldahl Nitrogen (TDKN) and Nitrite/Nitrate (NO_x) results are listed in Appendix 3-1.

Finally, for each parameter and soil treatment, results of all drained treatments and flooded treatments were compared between sites, within the transect, for significant differences in concentration. Significantly higher concentrations of SRP ($P < 0.05$) occurred during peak flux (time 1 hr to time 8 hr) in the drained soils between RC1 and RC4 (inflow and outflow sites respectively) versus RC2 and RC3 (interior transect sites)

(Figure 3-5). However, there were no significant differences between sites in dry or flooded soils, for TP or TDP and SRP. Conversely, results in dry soils for NH_4 , at the RC1 site had significantly ($P < 0.05$) lower concentrations ($P < 0.05$) compared to RC2, 3 and 4 (Figure 3-6). However, there were no significant differences between sites in either dry or flooded soils for TKN, TDKN and NO_x as well as NH_4 for flooded soil.

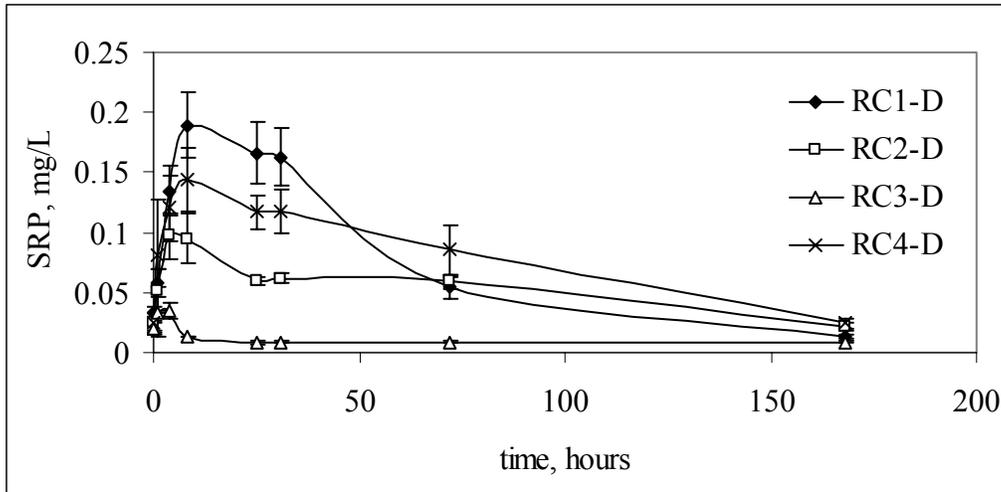


Figure 3-5. SRP water column concentrations measured in mg/L in drained soil core treatments all sites RC1, RC2, RC3 and RC4. The RC1 and RC4 sites fluxed at higher rates and greater concentrations of SRP than the interior marsh sites, RC2 and RC3.

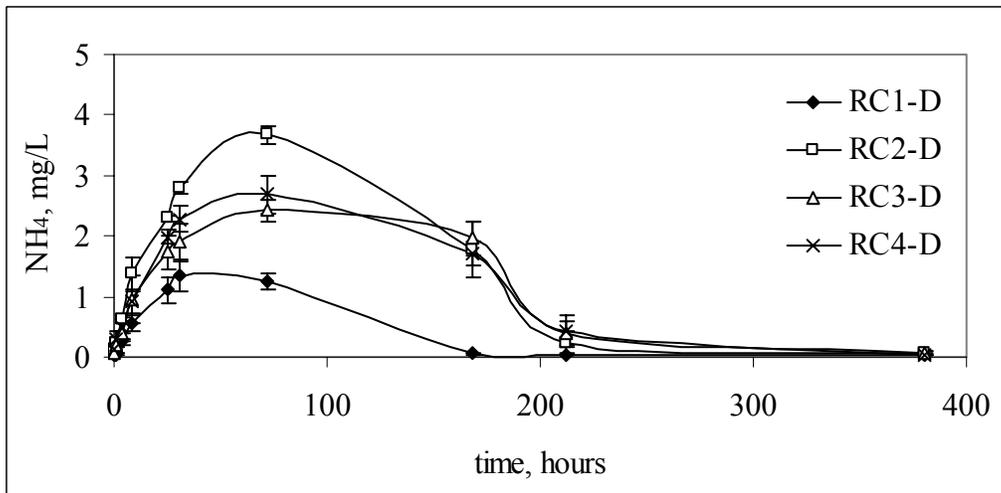


Figure 3-6. NH_4 water column concentrations measured in mg/L in drained soil core treatments all sites RC1, RC2, RC3 and RC4.

Dissolved organic phosphorus, which fluxed from the soil into the overlying water column, exhibited a similar increase in concentration with time in the flooded soils (Figure 3-7 a,b,c,d). Flooded soil water column DOP measured at the RC1 site was significantly ($P=0.05$) higher than the dry soil treatment. Drained soil DOP concentrations in the water column remained constant throughout the experiment. Alternatively, water column oP (Figure 3-8) and PP (Figure 3-9) concentrations within drained soil significantly ($P=0.05$) increased over time, while flooded soil water column oP and PP concentrations steadily decreased over time. When calculating percentages of oP and iP fluxing concentrations from the soil to the water column spatially and temporally (Table 3-3), two separate patterns emerge. At time 0, in both dry and flooded soil cores, the percentage of oP fluxing from the soil measured in the water column samples was greater than iP. Over the course of the study this trend remained, becoming significant ($P = 0.05$) at time 168 and 380 hours, with a majority of the P measured in the

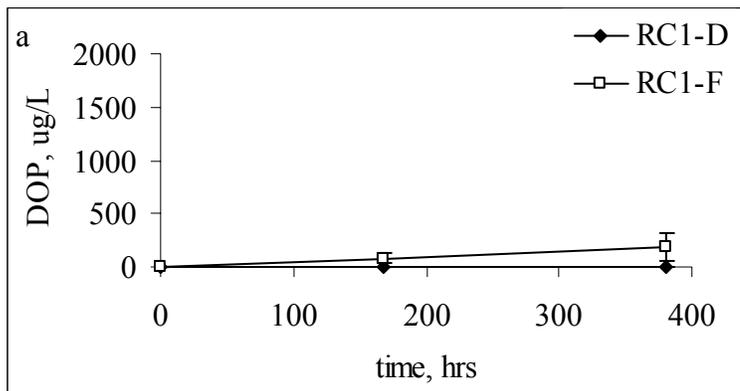


Figure 3-7 Dissolved organic phosphorus (DOP) water column concentrations in $\mu\text{g/L}$, calculated in dry vs. flooded soil core treatments for a)RC1 site b)RC2 site. c)RC3 site d)RC4 site.

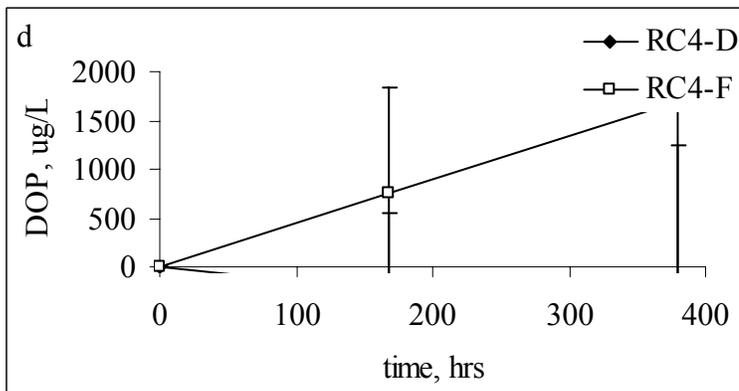
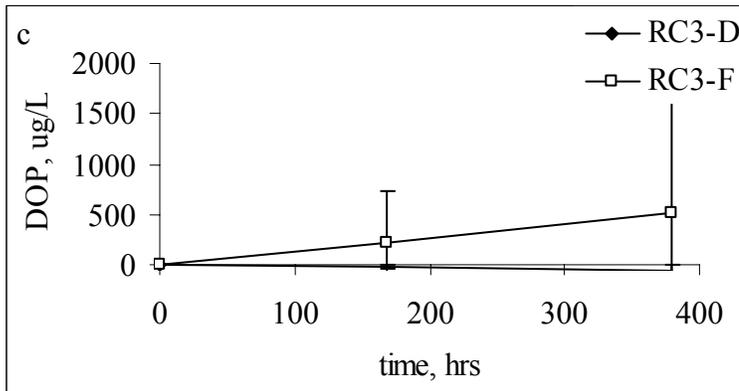
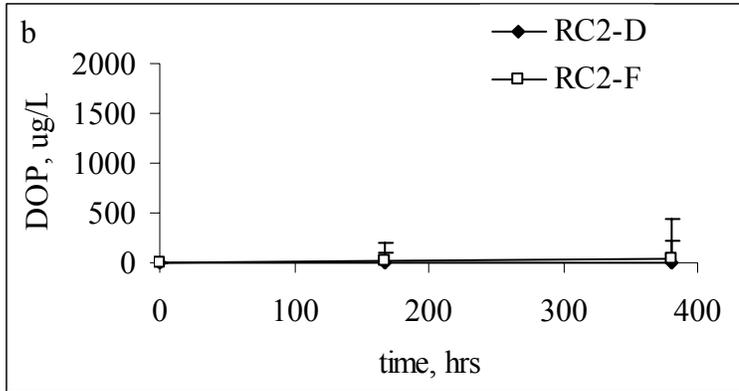


Figure 3-7. Continued.

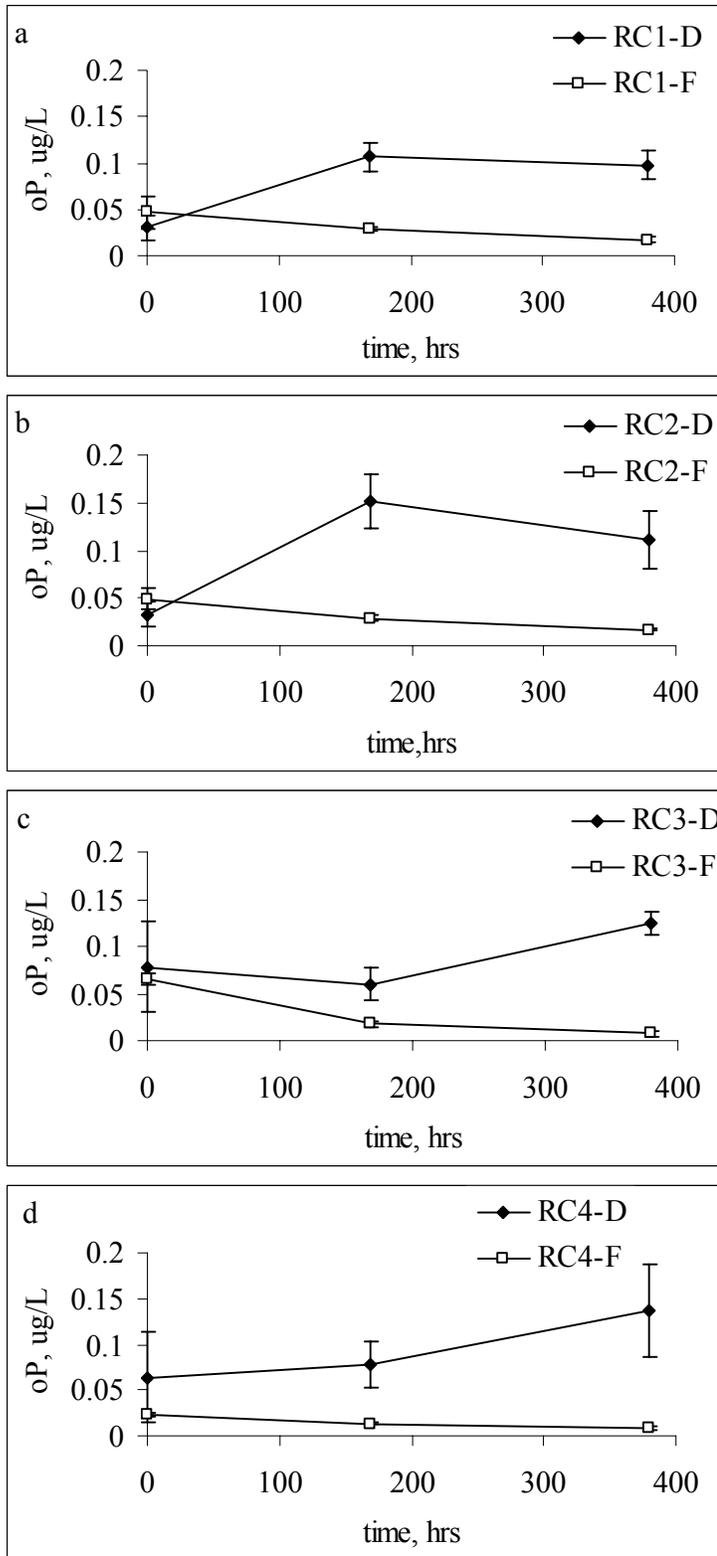


Figure 3-8 Organic phosphorus (oP) water column concentrations in $\mu\text{g/L}$, calculated in dry vs. flooded soil core treatments for a)RC1 site. b)RC2 site. c)RC3 site d)RC4site.

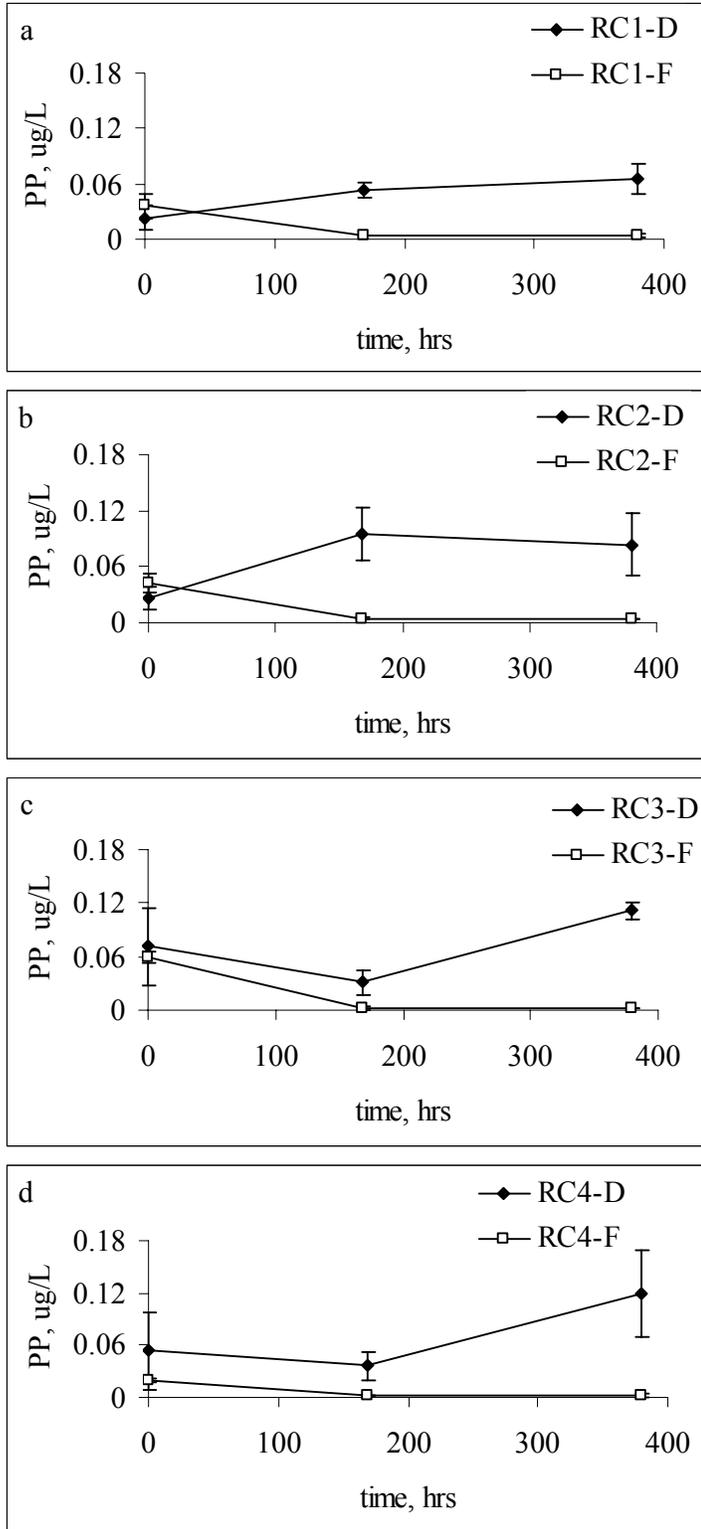


Figure 3-9 Particulate phosphorus (PP) water column concentrations in $\mu\text{g/L}$, calculated in dry vs. flooded soil core treatments for a) RC1 site. b) RC2 site. c) RC3 site d) RC4 site.

water column as organic. Inorganic P percentages decreased over time in dry soil cores and either remained the same in flooded cores or increased, though not significantly.

Algae began growing in the drained soil treatment core tubes at time 168 (~1 week) and continued through out the remainder of the experiment, while no algae was present in the continuously flooded treatment core tubes. The algae samples that were sent off for TP analysis, exhibited sufficient variability among replicates and between cores, so results were not significantly different (Table 3-4), and therefore were combined into one average concentration. The average algal TP tissue concentration from the soil core tubes (1183 ± 195 mg/kg) were compared to average algal TP tissue concentrations reported at RWMA field sites (999 ± 100 mg/kg), representing an average of samples collected prior to and after STA-5 discharges. The differences in TP concentrations from the field sites versus the soil cores were not significant.

Table 3-3. Percentage of oP and iP fluxing from the soil into the water column over time

Time 0 hours								
	RC1-D	RC1-F	RC2-D	RC2-F	RC3-D	RC3-F	RC4-D	RC4-F
%oP	48.13	79.63	56.98	85.06	80.14	86.73	72.18	70.00
%iP	51.87	20.37	43.02	14.94	19.86	13.27	27.82	30.00
Time 168 hours								
	RC1-D	RC1-F	RC2-D	RC2-F	RC3-D	RC3-F	RC4-D	RC4-F
%oP	89.11	85.44	87.48	85.29	86.96	81.54	76.22	67.80
%iP	10.89	14.56	12.52	14.71	13.04	18.46	23.78	32.20
Time 380 hours								
	RC1-D	RC1-F	RC2-D	RC2-F	RC3-D	RC3-F	RC4-D	RC4-F
%oP	90.12	76.47	90.71	75.76	93.22	54.76	90.51	60.00
%iP	9.88	23.53	9.29	24.24	6.78	45.24	9.49	40.00

Table 3-4. Algae TP concentration measurements in mg/kg collected from drained soil core tubes at the conclusion of the study.

Site	TP, mg/kg
RC1	1116.3 ± 157.8
RC2	1230 ± 101.4
RC3	1015.6 ± 207.3
RC4	1370 ± 316.6

Discussion

In the RWMA two primary soil conditions exist, drained and flooded. Although hydropattern restoration has been implemented (July 2001), hydroperiods had not been of sufficient length to prevent the soil from drying in the outer and northern portions of the marsh, therefore extended dry soil conditions continued to exist at the end of the wet season, and throughout the dry season. Soil oxidation continued to occur during these dry times, altering the soil chemistry.

As soil oxidizes, the Fe-P forms are soluble upon re-flooding (Pant et al. 2002) especially when high Fe concentrations are present (Gunnars and Blomqvist 1997) in the soil such as the RWMA soils. Additionally, upon re-flooding, iP species (SRP) will flux from the soil to the overlying water column. Those species of P that are now soluble, and bioavailable, can be transported further downstream to areas of the marsh containing lower soil P, resulting in sorption, thereby moving the soluble P front further downstream into previously un-impacted areas. While Al-P is not soluble upon re-flooding, the high concentrations of Al ions are available to bind with P.

Results from the RWMA intact soil core experiment suggest that, drained soil conditions significantly increase the flux of SRP, TP and TDP to the water column compared to continuously flooded soils. Total phosphorus of drained soils, both inorganic and organic forms, began at time 0 with similar concentration levels. Despite

some transect sites having different flux patterns, each drained soil core had significantly increased P concentrations at the final sample time compared to the flooded soil. In fact, the flooded soils appeared to release very little phosphorus into the water column and quickly reaching an equilibrium.

For all sites, the drained soil cores, with the exception of the RC3 site which is subject to slightly longer hydroperiods, fluxed significant concentrations of bioavailable P (SRP) into the water column. In the initial hour of the study, the RC1 and RC4 sites had higher flux rates compared to the RC2 and RC3 sites, suggesting the soils may experience longer drying and oxidation, as the sites are located near the edge of the marsh based on the difference in elevation reported on the RWMA 2005 topographic survey and measured water depths at each site. However, by the final sample event, drained soil water P concentrations were similar to those measured in the flooded soils. One explanation for the decrease in bioavailable P concentrations in the drained treatment soil cores could be from the algal growth, which began approximately one week after re-flooding. By the conclusion of the study, all drained soil cores contained substantial amounts of filamentous green algae. However, there was no algal growth in the continuously flooded soil cores. Algae uptakes P directly from the water column, which appeared to influence the SRP concentrations measured in the water quality samples, after peaking at day 8 when the algae first appeared. Analysis of the P concentration of the algae tissue samples were representative of P concentrations measured at the RC transect sites and indicative of high nutrient soils. Under field conditions, soluble P fluxing from the soil into the water column may be taken up by the algae, prior to low P soil areas adsorbing the P into the soil. Similar results by Newman et al. 2004, reported a

rapid uptake of P by periphyton prior to soil adsorption. At the conclusion of the P flux study, SRP levels in dry soil cores were similar to flooded soils.

Calculations of the iP and oP percentages that fluxed showed a greater percentage of oP fluxed out of the soil throughout the study. However, when comparing drained vs. flooded percentages over time, flooded oP is initially higher then decreases over time, with increasing percentages of iP measured in the water column. The opposite trend was observed in the dry soil treatments, in which initial iP percentages measured in the water column were higher then decreased over time, until oP percentages were significantly greater at the conclusion of the study. P-fractionation data in the 0-2 cm layer collected by the SFWMD Downstream Monitoring and Research Program shows an equal amount of P in the soil is stored as organic P and inorganic P (Leeds et al. in progress). However in drained soils, such as those present in the drained soil core treatment, there may be a certain amount of mineralization occurring. A majority of the P is stored in the soil in inorganic forms, possibly explaining the large flux in SRP as more forms of iP are available to flux. In addition, water entering the RWMA from STA-5 is approximately 44 % oP and 56 % iP (SFWMD, Downstream Monitoring and Research Program Water Quality data). This P fractionation characteristic of inflow water may be providing an iP source to bond with the potentially available Fe and Al content in the soil although, this was not specifically addressed by this study. Results by Eckert et al. (1997) and Novak et al. (2004) reported the soil in these studies that were high in iP (Fe-P and Al-P), will flux high concentrations of iP species when water column P is less than soil porewater P.

Spatially, P flux in the intact soil cores in both the drained and flooded treatments was fairly uniform in concentration across the transect, with the exception of the RC3

site, which is located in the interior of the marsh. The RC3 site experiences a longer hydroperiod, possibly due to its location near the center of the marsh, and lower elevation, (RWMA Topographic elevation survey 2004, SFWMD) relative to the other transect sites. According to previous fires mapped by the FFWCC and SFWMD, the RC3 site has not experienced the frequent muck fires compared to other transect sites, therefore soil conditions may have been more stable, relative to sites experiencing shorter hydroperiods and more frequent fire disturbance. However, soil TP concentrations are similar to the other transect sites, suggesting hydrology may be the driving factor in soil conditions.

Nitrogen flux trends were similar to P flux results. Total Kjeldahl Nitrogen and TDKN concentrations were significantly higher in water samples collected at the final time in drained soils compared to flooded soil, which maintained a relatively constant concentration. Furthermore, bioavailable N in the form of NH_4 , showed significantly greater initial flux in dry soils, although by the end of the study, water column concentrations were similar to the flooded water samples. The RC1 site, near the inflow point, fluxed the lowest concentration of NH_4 relative to other sites across the transect. This is maybe due to the vegetation composition of the site taking up the available N, where sawgrass and cattail in this area are very tall and dense when compared to sites with lower soil nutrient concentrations (Miao and Sklar 1998). Moreover, this site has experienced a higher frequency of muck fires, resulting in an increased volatilization of NH_4 in the soil (Smith and Newman 2001). Also, RC1 under goes longer periods of oxidation, due to the slight increase in elevation (RWMA Topographic elevation survey

2004, SFWMD) when compared to the other sites, allowing the soil to dry for longer periods of time.

Intact soil cores are routinely used to quantify approximate P fluxing in the field without conducting in situ measurements which may not be feasible due to transportation, sampling and budget constraints. Though the soil cores contain a small surface area, no continuous water flow or plants, they give a good indication of the potential flux rate occurring in the field at the soil water column interface. In addition, sampling can be conducted at predetermined time intervals, capturing initial flux upon re-flooding of the soil versus the logistics of timing re-flooding in the field. Furthermore, flux data can be incorporated in calculating marsh recovery and determining the affects altered hydrology has on the potential of soluble P movement further into the marsh interior.

CHAPTER 4 CONCLUSIONS

The Rotenberger Wildlife Management Area, part of the northern Everglades, can be monitored for phosphorus (P) inflow and outflow concentrations, as well as controlled hydrologically at inflow point, by a point source discharge pump, and outflow through weir structures. Therefore, determining the potential of P to flux from the soil to the overlying water column, thus moving P further downstream in the RWMA and Everglades system, is a critical factor in determining the operations of the system. For example, results from the P-isotherm experiment suggest water column P concentrations below $90 \mu\text{gL}^{-1}$ may cause P to flux out of the soil. In addition, the intact soil core study indicates antecedent drained soil conditions upon re-flooding, will potentially flux significantly greater concentrations of P to the water column, versus soil that is continuously flooded. Based on this, I recommend adjusting hydrologic operations of the outflow structures, to retain water in the system upon re-flooding. This provides conditions to increase the hydroperiod, thus reducing the potential for over draining and oxidation of the soil and suppress the flux of soluble, inorganic P into the water column. Furthermore, maintenance of flooded soils allows for significantly lower concentrations of inorganic P flux based on calculated iP and oP percentages in the drained and flooded water column samples, thereby reducing the potential for RWMA soils to be a source of soluble P to downstream Everglades marshes.

Phosphorus Isotherms

The P-isotherms, conducted on RWMA soil, displayed some spatial variability in EPC and P-sorption, not evident in soil TP concentrations. RWMA soils ability to sorb P is much less when compared to the max P sorption of soil along the P-gradient in WCA-2A (Richardson and Vaythianyan 1995) despite using similar methods analytical methods. In addition, the systems are different with respect to historic P-loading. WCA-2A became enriched due to high P inflows instead of altered hydrology, oxidation, and muck fires, which were responsible for elevating P concentrations in RWMA soils. This difference may explain the isolated transect site in this study, where EPC results were lower than other transect sites. For example, the high nutrient inflows in WCA-2A were fairly uniform versus RWMA where geographic location of muck fires and topographic variability of soils that dry and oxidize are primary factors. Consequently, P-sorption is uniquely dependant upon soil characteristics representative of each system, as well as historic P-loading. Several studies support this conclusion (Reddy et al. 1998; Nair et al. 1998; Pant et al 2002) suggesting Fe and Al are primary regulators of P-retention when elevated concentrations are measured. In the RWMA, Fe and Al concentrations are high compared to other Northern Everglades marshes such as, the Loxahatchee National Wildlife Refuge and Water Conservation Area 2A, and may be regulating P-retention in RWMA, although this was not specifically addressed in this study. Similar P-retention regulation, related to Ca levels, has been documented in WCA-2A soil (Richardson and Vaythianyan 1995) and from soil located in Everglades National Park (Zhou and Li 2001) suggesting soil chemistry composition should be included in determining the soils ability for P-sorption.

Phosphorus isotherms are applied to define soil characteristics of constructed wetlands and in proposed constructed wetlands sites, to determine the soils suitability to remove P. Two questions typically addressed are 1) will the soil act as a source or sink? and 2) how much P can be retained and for how long? Furthermore, P-retention can be influenced by the biological component present, as vegetation and the algal community will uptake P from the soil and water column respectively. Studies by Gale et al. (1994), Nair et al. (1998) and Reddy et al. (1998) used P-isotherms to address these questions, concluding the EPC of the soil can predict water column concentrations in which soil will uptake or flux P. An example of utilizing such data in the management of a system is in the RWMA. Water inflow and outflow to the marsh is regulated by pumping structures (inflow) and gated weirs (outflow). Therefore, upon determination that inflow TP may cause a significant flux of P, resulting in impacts to downstream areas, outflow water can be retained by adjusting the stage schedule controlling the outflow structures. The data collected during this study from the P-isotherms and P-fluxing experiments can aid in answering these questions.

There are limitations to using isotherm results and their applicability to field conditions. P-isotherms are run under controlled laboratory conditions, eliminating much of the inherent variability present in field conditions that would affect P-sorption or flux i.e., the influence of the microbial and algal community, plants and changes in soil conditions (aerobic and anaerobic). The soil used in the RWMA isotherm study was dried, representing aerobic conditions only, in addition to being shaken for 24 hours thus exposing all available bonding sites. Under field conditions, P would only interact with the exposed soil layer and the zone of porewater diffusion. A study by Schlichting and

Leinweber (2002) on the effect of drying soil, prior to a sequential P fractionation scheme compared to fresh, moist soil, reported a significant variability between the two pre-treatment methods on the P fractionation results. Additionally, the linear, Langmuir and Freundlich equations were initially developed for use with mineral soils rather than organic soils, which may explain some of the discrepancy between the EPC and P-sorption results. Consequently, isotherm data should be incorporated with other soil data (nutrient concentrations and soil chemistry) to predict P-sorption or flux when characterizing the wetland.

P-Sorption Factors

Iron (Fe) and Aluminum (Al) content in RWMA soils, when corrected for bulk density and compared to other systems in the northern Everglades, Loxahatchee National Wildlife Refuge and Water Conservation Area 2, are significantly higher, and may be a significant factor regulating P-sorption in this system. Additionally, the RWMA has experienced severely altered hydrology resulting in draw downs leading to soil oxidation. Iron in the soil, when oxidized, forms iron oxide which is available for sorption reactions with P in the soil. More importantly, Fe-P, a soluble inorganic P, upon re-flooding of the soil is released into the water column and may be available for uptake. Although Ca can also regulate P-sorption, as was determined in WCA-2A and in Everglades National Park, both marsh areas contain higher concentrations of Ca versus Fe and Al.

In support of the role of Fe and Al in P sorption, results from Gale et al. (1994), Nair et al. (1998) and Reddy et al. (1998) in soil studies outside of the Everglades, concluded increased concentrations of Al and Fe are directly correlated with P-sorption. Moreover, each found soils with elevated concentrations of Fe will oxidize upon soil drying conditions, then upon re-flooding, form soluble forms of P. Similar results were

reported in two studies conducted (Khalid et al. 1977; Pant et al. 2001) in marshes outside of Florida. Additionally, the RWMA has experienced severe and widespread muck fires that may have been a factor in concentrating Fe in the soil. At the conclusion of the intact soil core study, Fe stains were present on the sides of the cores, and during soil cores collection in the field, oxidized rhizospheres were present. While Al is available to bond with P, Fe has the greater potential to interact with P.

P-flux

As evidenced by the results in the intact soil cores, marsh hydrology can have a significant influence on the P-flux rate. The concentration and duration of P fluxing out of impacted soils, despite receiving low P water, creates conditions conducive to maintaining a eutrophic system until equilibrium is reached. Results from this study showed bioavailable P (SRP) fluxed in significantly higher concentrations in dry soil versus flooded soils, at each site throughout the transect. Therefore maintaining flooded soils, through retention, would be desirable to minimize large fluxes of inorganic P concentrations into the water column.

The hydrology in RWMA prior to receiving STA-5 discharges was severely altered, allowing for extensive soil oxidation, soil loss and muck fires due to low soil moisture content, all of which contributed to elevated soil P-concentrations. On a smaller scale within the marsh, the outer edges are higher in elevation by approximately 15 cm compared to the marsh interior. The differences in elevation allow water to pool in the interior and dry out for longer periods of time on the edges. The differential in soil drying is reflected in the P-flux results at the RC1 and RC4 sites that are adjacent to the outer edges. In dry soil treatments, the outer edge marsh sites (RC1, RC4) fluxed significantly higher concentrations of SRP when compared to sites located closer to the

interior (RC2, RC3). Alternatively, when all sites are continuously flooded, SRP measurements showed an initial, small concentration increase, and then reached equilibrium for the remainder of the experiment.

Percentages of iP and oP in the water column of drained and flooded soil cores flux upon initial re-flooding were varied. In the drained soil cores over time, iP percentages decreased while oP percentages increased until the conclusion of the study. However, in flooded soil cores, iP percentages and oP percentages remained relatively constant over time with insignificant increases and decreases in composition. Organic P percentages did not significantly change between dry and flooded treatment cores over time, but when oP and iP percentages are compared for each treatment at all sites, the measured water column TP contains a greater percentage of oP. One explanation for the difference in iP versus oP percentages in the water column over time in the drained soil treatment cores would be the algal uptake of iP, which did not occur in the flooded soil core treatments. The same scenario is likely occurring in the natural system after drained and oxidized soils are re-flooded. There is an initial flux of iP into the water column that is assimilated by algal blooms. However the oP is not taken up and therefore over time, a greater percentage of the water column TP is organic. While many studies have addressed the affects of iP to the system ecologically, little is known how oP will impact the marsh.

Conclusion

While P may be fluxing out of the soil near inflow sites, it is potentially undergoing sorption in sites located further towards the interior of the marsh, as evident by EPC results, as well as being affected by algal and plant uptake. The outflow sites, upon re-flooding of drained soil, are a potential source of P to downstream areas. For example, RC1 near the inflow has an EPC approximately $94.5 \mu\text{gL}^{-1}$. Based on water quality data

recorded at the G-410 inflow pumping structure, P will flux from the soil near the inflow sites. In contrast the RC2 site, which is downstream of RC1 and measured an EPC of 18.8 $\mu\text{g/L}$, will potentially sorb P. When allowed to dry out, soil from all sites have the potential to release bioavailable P for seven to ten days, allowing soluble P to travel further downstream and, in the case of RC 4, out of RWMA through the outflow structures into downstream Central Everglades areas. However, over time, if dry soils become continuously flooded, P-flux is reduced and P release shifts from inorganic P to organic forms that are not readily available, and must be mineralized to become bioavailable. Therefore, in a marsh system such as the RWMA, where water inflow and outflow is controlled by pumps and gated weir structures respectively, modifying the operations of the system to retain water for longer periods of time, is a viable option to, minimize drained and oxidizing conditions which would otherwise advance the soluble P front. Finally, there are many important factors such as hydrology, historic P-loading, soil chemistry and a biological component, influencing P-sorption and flux, all of which must be taken into account when applying adaptive management strategies to a natural system. In this study each of these factors, in addition to the data collected from the P-isotherms and P-fluxing experiments, suggests RWMA in its current state of operation has the potential to act as a source of P. Therefore, utilizing the data from this study and the factors outlined above, in conjunction with an adaptive management approach, can allow for flexible operations of the system improving hydrology, providing conditions to inhibit P-fluxing and retain soluble P, thus preventing impacts to downstream areas.

APPENDIX A
P-ADSORPTION RESULTS FROM THE LINEAR, FREUNDLICH AND LANGMUIR
ISOTHERM EQUATIONS AT EACH SITE AND P-CONCENTRATION.

	Linear		Freundlich	Langmuir
	C, $\mu\text{g/L}$	S, $\mu\text{g/g}$	S+So	C/(S+So)
RC1				
0	88.4 \pm 4.7	-0.88	22.3	4.0
10	88.8 \pm 3.5	-0.79	22.4	4.0
30	90.0 \pm 6.3	-0.60	22.6	4.0
50	95.3 \pm 4.8	-0.45	22.7	4.2
100	102.0 \pm 6.9	-0.02	23.2	4.4
500	110.0 \pm 1.0	3.90	27.1	4.1
1000	127.3 \pm 6.7	8.73	31.9	4.0
2000	187 \pm 5.6	18.13	41.3	4.5
5000	333 \pm 3.1	46.67	69.9	4.8
10000	626 \pm 25.0	93.74	116.9	5.4
RC2				
0	18.7 \pm 0.7	-0.19	17.5	1.1
10	20.4 \pm 0.2	-0.10	17.6	1.2
30	18.9 \pm 0.6	0.11	17.8	1.1
50	18.8 \pm 1.9	0.31	18.0	1.0
100	20.5 \pm 1.5	0.79	18.5	1.1
500	21.5 \pm 2.1	4.78	22.5	1.0
1000	29.4 \pm 1.0	9.71	27.4	1.1
2000	36.1 \pm 0.3	19.64	37.3	1.0
5000	80.1 \pm 2.3	49.20	66.9	1.2
10000	182.0 \pm 2.0	98.18	115.9	1.6
RC3				
0	67.6 \pm 1.3	-0.68	13.5	5.0
10	69.3 \pm 0.6	-0.59	13.6	5.1
30	71.7 \pm 1.7	-0.42	13.8	5.2
50	76.2 \pm 3.9	-0.26	13.9	5.5
100	75.1 \pm 1.7	0.25	14.4	5.2
500	94.6 \pm 2.6	4.05	18.3	5.2
1000	118.7 \pm 3.1	8.81	23.0	5.2
2000	197.7 \pm 2.5	18.02	32.2	6.1
5000	421.3 \pm 6.1	45.79	60.0	7.0
10000	1002.7 \pm 4.6	89.97	104.2	9.6

RC4				
0	83.2 ± 4.2	-0.83	8.3	10.0
10	98.1 ± 17.4	-0.88	8.3	11.8
30	77.2 ± 10.2	-0.47	8.7	8.9
50	99.5 ± 30.2	-0.49	8.7	11.5
100	92.4 ± 3.8	0.08	9.2	10.0
500	121.4 ± 30.9	3.79	13.0	9.4
1000	176.3 ± 3.1	8.24	17.4	10.1
2000	258.3 ± 5.5	17.42	26.6	9.7
5000	644.0 ± 9.2	43.56	52.7	12.2
	$1607.7 \pm$			
10000	32.7	83.92	93.1	17.3

APPENDIX B
WATER QUALITY NITROGEN RESULTS FROM INTACT SOIL CORES
SAMPLED FROM THE P-FLUX EXPERIMENT.

TKN, mg/L				
Time, hours	RC1-D	RC2-D	RC3-D	RC4-D
0	2.15 ± 0.08	2.93 ± 0.38	8.34 ± 0.38	4.16 ± 1.8
168	4.18 ± 0.19	3.64 ± 0.32	2.86 ± 0.02	3.05 ± 0.28
380	5.81 ± 0.90	6.07 ± 0.31	5.09 ± 0.31	6.09 ± 1.09
	RC1-F	RC2-F	RC3-F	RC4-F
0	2.94 ± 0.63	3.37 ± 0.32	3.61 ± 0.11	2.48 ± 0.15
168	2.57 ± 0.15	2.78 ± 0.31	2.36 ± 0.03	2.63 ± 0.02
380	$3.2 \pm .014$	3.95 ± 0.53	2.74 ± 0.02	3.03 ± 0.02
TDKN, mg/L				
Time, hours	RC1-D	RC2-D	RC3-D	RC4-D
0	2.07 ± 0.07	2.37 ± 0.20	2.51 ± 0.43	2.32 ± 0.30
168	3.68 ± 0.14	6.78 ± 0.49	5.73 ± 0.11	5.86 ± 0.38
380	4.40 ± 0.25	5.07 ± 0.07	3.26 ± 0.74	4.61 ± 0.24
	RC1-F	RC2-F	RC3-F	RC4-F
0	1.85 ± 0.03	1.81 ± 0.01	1.79 ± 0.003	1.82 ± 0.02
168	2.67 ± 0.15	2.84 ± 0.27	2.47 ± 0.03	2.75 ± 0.01
380	3.17 ± 0.12	3.67 ± 0.29	2.68 ± 0.03	3.07 ± 0.004
NOx, mg/L				
Time, hours	RC1-D	RC2-D	RC3-D	RC4-D
0	1.52 ± 0.4	1.73 ± 0.32	2.40 ± 1.13	2.80 ± 1.60
168	0.04 ± 0.02	0.009 ± 0.02	0.077 ± 0.02	0.018 ± 0.004
380	0.005 ± 0.001	0.008 ± 0.002	0.007 ± 0.005	0.005 ± 0.003
	RC1-F	RC2-F	RC3-F	RC4-F
0	0.02 ± 0.003	0.014 ± 0.002	0.016 ± 0.003	0.076 ± 0.01
168	0.007 ± 0	0.018 ± 0.008	0.014 ± 0.004	0.009 ± 0.001
380	0.004 ± 0	0.005 ± 0.001	0.0007 ± 0.002	0.002 ± 0.001

LITERATURE CITED

- Bostrom, B., J. M. Andersen, S. Fleischer and M. Jansson. 1988. Exchange of phosphorus across the soil-water interface. *Hydrobiologia* 170:229-244.
- Clescerl, L., A. E. Greenberg and A. D. Eaton. 1999. Standard Methods for the Examination of Water and Wastewater. American Public Health Association, 20th edition, pp. 1329, Cincinnati, OH.
- DeBusk, W. F., K. R. Reddy, M. S. Koch and Y. Wang. 1994. Spatial distribution of soil nutrients in a Northern Everglades Marsh: Water Conservation Area 2A. *Soil Science Society American Journal* 58:543-552.
- Eckert, W., A. Nishri and R. Parparova. 1997. Factors regulating the flux of phosphate at the soil-water interface of a subtropical calcareous lake: A simulation study with intact soil cores. *Water, Air and Soil Pollution* 99:401-409.
- Fisher, M. M., and K. R. Reddy. 2001. Phosphorus flux from wetland soils affected by long-term nutrient loading. *Journal of Environmental Quality* 30:261-271.
- Gale, P.M., K.R. Reddy and D.A. Graetz. 1994. Phosphorus retention by wetland soils used for treated wastewater disposal. *Journal of Environmental Quality* 23:370-377.
- Gunnars, A. and S. Blomqvist. 1997. Phosphate exchange across the soil-water interface when shifting from anoxic to oxic conditions – an experimental comparison of freshwater and brackish-marine systems. *Biogeochemistry* 37:203-226.
- Khalid, R.A., W.H. Patrick, Jr. and R.D. DeLaune. 1977. Phosphorus sorption characteristics of flooded soil. *American Journal of the Soil Science Society* 41:305-310.
- Leeds, J.A., P. B. Garrett and J. Majer-Newman. 2005. Assessing impacts of hydropattern restoration in an over-drained wetland on soil nutrients, vegetation and fire. In progress.
- Malecki, L. M., J. R. White and K. R. Reddy. 2004. Nitrogen and phosphorus flux rates from soil in the lower St. Johns River Estuary. *Journal of Environmental Quality* 33:1545-1555.

- Miao, S. L. and F. H. Sklar. 1998. Biomass and nutrient allocation of sawgrass and cattail along a nutrient gradient in the Florida Everglades. *Wetlands Ecology and Management* 5:245-263.
- Moore, P.A. Jr., Reddy, K.R., Graetz, D.A. 1991. Phosphorus geochemistry in the soil-water column of a hypereutrophic lake. *Journal of Environmental Quality* 20:869-875.
- Nair, V. D., D. A. Graetz and K. R. Reddy. 1998. Dairy manure influences on phosphorus retention capacity of spodosols. *Journal of Environmental Quality* 27:522-527.
- Newman, S., K. R. Reddy, W. F. DeBusk, Y. Wang, G. Shih and M. M. Fisher. 1997. Spatial distribution of soil nutrients in a Northern Everglades Marsh: Water Conservation Area 1. *Soil Science Society of America Journal* 61:1275-1283.
- Newman, S., J. Schuette, J. B. Grace, K. Rutchey, T. Fontaine, K. R. Reddy and M. Petrucha. 1998. Factors influencing cattail abundance in the northern Everglades. *Aquatic Botany* 60:265-280.
- Newman, S., P. V. McCormick, S. L. Miao, J. A. Laing, W. C. Kennedy and M. B. O'Dell. 2004. The effect of phosphorus enrichment on the nutrient status of a northern Everglades slough. *Wetlands Ecology and Management* 12:63-79.
- Novak, J. M., K. C. Stone, A. A. Szogi, D. W. Watts and M. H. Johnson. 2004. Dissolved phosphorus retention and release from a coastal plain in-stream wetland. *Journal of Environmental Quality* 33:394-401.
- Olila, O.G., Reddy, K.R., Stites, D.L. 1997. Influence of draining on soil phosphorus forms and distribution in a constructed wetland. *Ecological Engineering* 9:157-169.
- Pant, H. K. and K. R. Reddy. 2001A. Hydrologic influence on stability of organic phosphorus in wetland detritus. *Journal of Environmental Quality* 30:668-674.
- Pant, H. K. and K. R. Reddy. 2001B. Phosphorus sorption characteristics of estuarine soils under different redox conditions. *Journal of Environmental Quality* 30:1474-1480.
- Pant, H. K., K. R. Reddy and E. Lemon. 2001. Phosphorus retention capacity of root bed media of sub-surface flow constructed wetlands. *Ecological Engineering* 17:345-355.
- Pant, H. K., V. D. Nair, K. R. Reddy, D. A. Graetz and R. R. Villapando. 2002. Influence of flooding on phosphorus mobility in manure-impacted soil. *Journal of Environmental Quality* 31:1399-1405.

- Pant, H. K., K. R. Reddy and R. M. Spechler. 2002. Phosphorus retention in soils from a prospective constructed wetland site: Environmental implications. *Soil Science* 167:607-615.
- Pant, H. K. and K. R. Reddy. 2003. Potential internal loading of phosphorus in a wetland constructed in agricultural land. *Water Research* 37:965-972.
- Patrick, W.H., Jr. and R.A. Khalid. 1974. Phosphate release and sorption by soils and soils: Effect of aerobic and anaerobic conditions. *Science (Washington, DC)* 186:53-55
- Raven, K. P. and L. R. Hossner. 1993. Phosphorus desorption quantity-intensity relationships in soils. *Soil Science Society American Journal* 57:1501-1508.
- Reddy, K. R., W. F. DeBusk, Y. Wang, R. DeLaune and M. Koch. 1991. Physico-chemical properties of soils in the Water Conservation Area 2 of the Everglades, Final Report, South Florida Water Management District.
- Reddy, K.R. , M.M. Fisher and D. Ivanoff. 1996. Resuspension and diffusive flux of nitrogen and phosphorus in a hypereutrophic lake. *Journal of Environmental Quality* 25:363-371.
- Reddy, K. R., G. A. O'Conner and P. M. Gale. 1998. Phosphorus desorption capacities of wetland soils and stream soils impacted by dairy effluent. *Journal of Environmental Quality* 27:1-10.
- Reddy, K. R., G. A. O'Conner and P. M. Gale. 1998. Phosphorus sorption capacities of wetland soils and stream soils impacted by dairy effluent. *Journal of Environmental Quality* 27:438-447.
- Reddy, K. R., Y. Wang, W. F. DeBusk, M. M. Fisher and S. Newman. 1998. Forms of Soil phosphorus in selected hydrologic units of the Florida Everglades. *American Journal of the Soil Science Society* 62:1134-1147.
- Richardson, C. J. 1985. Mechanisms controlling phosphorus retention capacity in freshwater wetlands. *Science* 228:1424-1427.
- Richardson, C. J. and P. Vaithyanathan. 1995. Phosphorus sorption characteristics of Everglades soils along a eutrophication gradient. *Soil Science Society American Journal* 59:1782-1788.
- Sallade, Y.E. and J.T. Sims. 1997. Phosphorus transformations in the soils of Delaware's agricultural drainage ways: I. Phosphorus forms and sorption. *J. Environ. Qual.* 26:1571-1579.
- SASJump, version 5. 2002. SAS Institute Inc., Cary, NC, USA.

- Schlichting A. and P. Leinweber. 2002. Effects of pretreatment on sequentially-extracted phosphorus fractions from peat soil. *Commun. Soil Sci. Plant Anal.*, 33:1617-1627.
- Smith, S. M., S. Newman, P. B. Garrett and J. A. Leeds. 2001. Differential effects of surface and peat fire on soil constituents in a degraded wetland of the northern Florida Everglades. *Journal of Environmental Quality* 30:1998-2005.
- South Florida Water Management District. 1992. Surface water improvement and management plan for the Everglades: Supporting information document. SFWMD, West Palm Beach, Fl.
- Wade, D., J. Ewel and R. Hofstetter. 1980. Fire in South Florida Ecosystems. U.S. Department of Agriculture, Forest Service General Technical Report SE-17, p. 125, Southeast Forest Experimental Station Asheville, North Carolina.
- White, J. S., S. E. Bayley and P. J. Curtis. 2000. Soil storage of phosphorus in a northern prairie wetland receiving municipal and agro-industrial wastewater. *Ecological Engineering* 14:127-138.
- Zhou, M., R.D. Rhue and W.G. Harris. 1997. Phosphorus sorption characteristics of Bh and Bt horizons from sandy coastal plain soils. *Soil Sci. Soc. Am. J.* 61:1364-1369.
- Zhou, M. and Y. Li. 2001. Phosphorus-sorption characteristics of calcareous soils and limestone from the Southern Everglades and adjacent farmlands. *Soil Science Society American Journal* 65:1404-1412.

BIOGRAPHICAL SKETCH

I received my B.S. in biology from San Diego State University in June of 1997, where I worked as an undergraduate research assistant in the Pacific Estuarine Research Lab on tidal wetland restoration projects. In July of 1997, I began working at the South Florida Water Management District as an Environmental Scientist on Everglades restoration projects and wetland assessments. I completed the University of Florida's graduate certification in environmental policy and management in spring 2003, and then was accepted into the Soil and Water Science Department's distance education program for a master's in environmental science in which I will graduate spring 2006.